HEADSPACE ANALYSIS USING CONDUCTING POLYMER SENSOR ARRAYS

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1. Abstract

Research efforts have been under way for over twenty years aimed at investigating and understanding the use of conducting polymers to monitor volatile chemicals. In some cases, this work has led to commercial exploitation. The mechanisms by which interaction between the polymer surface and the volatile chemicals give rise to electrical changes in the polymer are not fully understood and this paper will briefly review this fundamental topic. It will go on to show that major advantages accrue from interrogating conducting polymers using high frequency techniques rather than the dc methods used by most researchers. These advantages will be quantified by reference to simple lumped circuit models that have been built for a sensor configuration in use by the present authors. In addition, comparisons between the dielectric properties of the sensors predicted by the model and from a number of measurements will be used to justify the model structure. The paper will also discuss conducting polymer array technology, methods of interrogating such sensor arrays and their deployment as part of new sampling strategies aimed at eventually achieving ppt levels of detection of contamination in water using headspace analysis.

2. Introduction

Increasingly, stringent regulations are being put in place concerning the trace levels of undesirable and, indeed, dangerous compounds that can exist in potable water. Despite this, water companies frequently experience customer complaints, often concerning off-odours and off-tastes present in water supplies. The problem is particularly difficult to deal with since the human nose is exquisitely sensitive to certain of the potential contaminants of drinking water. A good example of this is geosmin, for which a typical sensitivity for the human nose is below 10 parts per trillion (10 parts in 10^{18} v/v) (ppt). There is no instrumental method of directly measuring geosmin at this concentration, even though in the headspace above water contaminated at 10 ppt we are likely to find much higher concentrations. This is because the geosmin molecule prefers not to be in the presence of compounds such as water. Headspace analysis is, therefore, a potentially good approach for this type of compound and when combined with the appropriate sampling techniques, conducting polymer sensor arrays are able to detect such compounds at ppb levels. Further work is still required to get down to ppt concentrations.

3. Gas, odour and aroma sensing

We can approach the gas sensing problem in two ways: if we know the gas that is to be detected and furthermore, that there is little risk of contamination from other species, then a variety of technologies exist that can be made specific for such an approach. Examples of such technologies are: chemiresistors constructed from metal oxides or phthalocyanines, potentiometric and amperometric sensors employing electrochemical techniques, and optical and infrared absorption sensors. These technologies are capable of dealing with gases such as NO_x, H_2, NH_3, CO, CO_2 and CH_4 [1]. Another technology of use in detecting combustible gases is that based on catalytic gate MOSFETs. There are also examples of the use of pellistors as catalytic metal sensors and these are suitable for detecting a wide range of organics. In the main, these technologies are used in the form of single sensors.

The alternative approach is to use arrays of sensors. The first report of the use of sensor arrays appeared in 1982 [2]. The authors showed that by combining a set of commercially available metal oxide sensors, deliberately selected to have non-specific response to a wide range of gases and odours, the response obtained from such an array had some of the characteristics associated with the mammalian olfactory system. Since the publication of this paper, enormous effort has been directed into understanding the characteristics of sensor arrays constructed from a number of technologies, such as conducting polymers, quartz crystals and surface acoustic wave based devices. Many of these are also now available commercially and there is even the promise of commercially available mixed technology arrays, although to date, there is little evidence that this approach attracts much in the way of advantage.

3. 1. Conducting polymer arrays: construction and characterisation

There has been considerable interest in electrically conducting polymer materials for many years. The first report on the chemical oxidation of pyrrole appeared in 1888 and subsequently reports on the polymerisation in the presence of hydrogen peroxide to yield what was commonly referred to as pyrrole black had to wait until 1916. It was not until 1968 [3] that the first report of electrochemical production of polypyrrole appeared. Since then this material has been intensively studied and there is a considerable body of literature, see for example Skotheim [4]. In the 1970s reports began to appear on the gas detecting properties of certain conducting polymers [5].

We have been involved for some time in studies of the chemistry and applications of organic conducting polymers for sensing of volatile chemicals. The strategy adopted has been to develop sensing systems where individual elements in an array show broad, and overlapping selectivities to various chemical species, each sensor element responding more selectively to certain chemicals. This approach has the advantage that the array can respond to many thousands of chemical species due to the broad selectivity of the adsorbent surfaces. On the other hand, extremely selective information for discrimination between adsorbed chemical species or mixtures can be obtained by analysis of the cross-sensitivities between sensor elements. The relative responses between sensor elements produce patterns that may be unique "fingerprints" and that may be used as odour descriptors.

Polymers of some heterocyclic materials show reversible changes in electrical conductance with adsorption and subsequent desorption of odour molecules. There is high sensitivity to polar molecules, and although chemical selectivity of individual polymers is broad, arrays of sensors that contain different functional groups on the surface show different but overlapping responses to different chemical families. Functionalisation of conducting polymers and their applications have recently been reviewed [6]. There is a quantitative relationship to odour concentration since the change in conductance measured is directly proportional to the concentration of adsorbed odour molecules and their binding affinity to the conducting polymers [7]. Of advantage in these kinds of sensing materials is the ability to react rapidly and reversibly at ambient temperatures, and that they are more sensitive to polar volatiles than to non-polar volatiles. This correlates well with the range of volatile chemicals to which the human nose is most sensitive, and therefore in many cases the sensor responses can be correlated to human perception.

3. 2. Mechanisms of interaction between polymer surface and volatile chemicals

The molecular recognition capabilities of organic semi-conducting polymers means that they are materials with very powerful sensing properties. Specific stimuli (ie, gaseous environments) are recognised by characteristic changes in resistance or conductivity of the material following adsorption of the vapours at the polymer surface. Conducting polymers have, therefore, been described as "intelligent materials" [8].

A conducting polymer gas sensor may be prepared electrochemically or chemically. However, both methods produce materials that are oxidatively doped, and generate a delocalised positive charge along the polymer backbone (ca. one charge per four monomer units). This positive charge means that an anionic species (counter-ion) must also be present within the polymer matrix to retain electroneutrality and stability within the system (Figure 1). It is the presence of these charges along the polymer backbone that facilitates molecular interaction.

There are a variety of interactions that may occur at the sensor surface between the polymer and the vapour molecules, such as ionic-ionic or ionic-dipole [9]. However, all of these interactions create physical changes in the polymer structure. A water molecule for example may interact with polypyrrole via the lone pair of electrons on the water oxygen atom and the positive charge on the polymer chain (dipole-ionic). The interaction at the positive sites therefore means that the conductivity of the polymer is reduced. Alternatively, interaction with electrophilic gases (where electron density is withdrawn from the polymer) results in an increase of charge carriers and therefore also an increase in conductivity [10]. The chemical interaction that occurs at the polymer surface may also be influenced by choosing the appropriate monomer and counter-ion contribution [8]. By altering the counter-anion within the matrix it is possible to vary the gas sensing capability, since anion-exchange is thought to be a predominant process in oxidised polypyrrole. Different response kinetics may therefore be observed for like polymers with differing anion content.

3. 3. Sensor preparation

As discussed above, conducting polymers can be prepared either chemically or electrochemically. Some while ago the gas sensing research group within the Department of Instrumentation and Analytical Science at UMIST developed a technique based on combining both approaches. Initially, a layer of conducting polymer is chemically deposited between two electrodes spaced some 100 µm apart. Of course, this is far greater than the spacing that would be amenable to electrochemical growth. Following this stage, the two electrodes are connected together and the conducting polymer is then used as one of the electrode systems within an electrochemical cell in order to grow a further layer of alternative conducting polymer upon the original chemically deposited layer. It has been found that these bilayer polymer sensors give rise to much wider choice in terms of the type of odorant molecule to which they are targeted than is possible using either of the alternative approaches on their own. Originally, these sensors were arranged in arrays of 20 elements, each one being a different material. In a commercial instrument now available, a 32-element array is employed [11].

3. 4. Interrogation

All the early work based on characterising conducting polymers employed direct current (dc) interrogation techniques. Each element is interrogated in turn by a stable current source and the voltage across the sensor element used to determine its electrical resistance. Subsequently, any relative change in resistance is recorded once exposure to an odorous compound has been arranged. A block diagram showing this arrangement is given in Figure 2. The form of response that this provides is shown in Figure 3(a). Characteristic patterns of response of this nature are associated with different odorous compounds and it is a relatively simple matter to organise pattern recognition algorithms in order to learn the various sensor responses.

Clearly, these materials also possess dielectric properties and providing the dc resistance is not too low, the dielectric property measurement may yield more information concerning the nature of the interaction between odorant molecules and the sensor material than a simple dc measurement. With this in mind, a programme of research was initiated some years ago concerned with examining the alternating current (ac) characteristics of these polymers. Typical of the form of response that can be obtained is that shown in Figure 3(b) where, for a single sensor element, we can examine its relative change in, say, electrical capacitance for a set of frequencies. Potentially, this means that we can drastically reduce the number of sensor elements and yet retain the high information content associated with large numbers of sensor elements.

3. 5. Sensor modelling

Our initial work using ac interrogation focused on simple sensor structures which were self-resonant, but at frequencies approaching 1 GHz [12]. Later, we moved to new electrode geometries which were designed to reduce the resonant frequency into the region of 63 MHz [12]. More recently, we have adopted a structure that enables us to choose resonant frequencies in the region of 1 MHz which is much more amenable to simple electronic systems for automatically and rapidly interrogating the sensors.

A lumped circuit model of such a sensor is given in Figure 4 and the model response is compared with measured data for a sensor subjected to a clean dry air stream in Figure 5. As can be seen, the model and the measured data are very closely matched and both responses exhibit characteristic resonance behaviour (where the reactance crosses the zero axis) at around 840 and 1,040 kHz. The manner in which these data were obtained experimentally is illustrated in Figure 6 which shows the automated vapour sampling system employed in conjunction with a commercially available impedance analyser (Hewlett Packard 4192A).

We have found that monitoring the change in resonant frequency is a simple and effective way of differentiating between different headspaces. For example, if we arrange to calculate the dissipation factor which is defined as the resistance of the sensor divided by its reactance, then clearly at resonance where the reactance tends to zero, the dissipation factor will rise to large values. Provided the sensor and its electrodes plus any additional electronic circuitry give rise to large electrical quality factor (Q), then these peak values of dissipation factor can be easily tracked to indicate changes in the headspace above the sensor. A simple illustration of this is shown in Figure 7 which illustrates the results of an experiment in which the odour of fresh milk was sampled at various stages over 25 hours at normal room temperature. As can be seen, a significant trend in dissipation factor emerges from this and there is clear discrimination between fresh milk and milk only three hours old. A sensory panel could not detect any difference between fresh and three-hour old milk.

Another experiment was conducted using a similar approach, but now aimed at differentiating between different types of beer. The results for this experiment are shown in Figure 8, where there is quite clear discrimination between the various beers examined. Of significance is the degree to which such measurements can be repeated and in Figure 9 we show a series of six measurements of beer samples of the same brand conducted over a period of several days which indicate that the repeatability of these measurements is extremely good.

4. Applications in the water industry

As discussed in the introduction, if gas sensors are to be useful in alerting water treatment works of potential problems in the output of potable water, we require detection limits approaching tens of ppt. No simple instrumentation method is able to achieve such a limit. To date, the best performance known to the authors results in detection limits of hundreds of ppb. However, if such an instrument is preceded by a sampling system that promotes species such as geosmin into the headspace, then this can be considerably improved. One method of achieving this is to employ an ultrasonic nebuliser which breaks up the geosmin molecular clusters in the water and promotes them into the headspace. Of course, a nebuliser also pushes a lot of water molecules into the headspace and a system such as this requires a method for removing the water molecules and leaving the geosmin behind. A technique that has proved successful is to use a Peltier based condenser above the sample and prior to the sensor array (see Figure 10)

[13]. This work, which arises out of collaboration between AromaScan plc and Mitsubishi Electric Corporation, is still in its preliminary stages and a commercial instrument will be forthcoming in the near future.

5. Conclusions

The detection of certain species which lead to unpleasant odours and tastes in water is probably best done by headspace analysis. Unfortunately, without specialised sampling procedures the detection limits required are beyond the reach of existing instrumental devices. Sampling systems capable of dealing with the problem are in the process of development and should become commercial realities in the near future. In parallel with this, there are many benefits obtained from ac interrogation of conducting polymer based sensors , not the least of which is an increase in the sensitivity of such a sensor under ac interrogation conditions. The combination of these two approaches is likely to lead to successful monitoring for species such as geosmin in water at the levels typical of the performance of the human nose.

6. Acknowledgements

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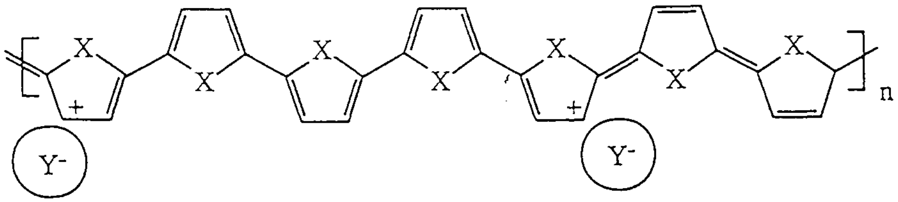
Figure 1 : Structure of conducting polymer



X = heteroatom (e.g. S, NH)

Y^- = counter-ion (e.g. BF_4^-, *p*-toluenesulphonate)

Figure 2 : Direct current interrogation method

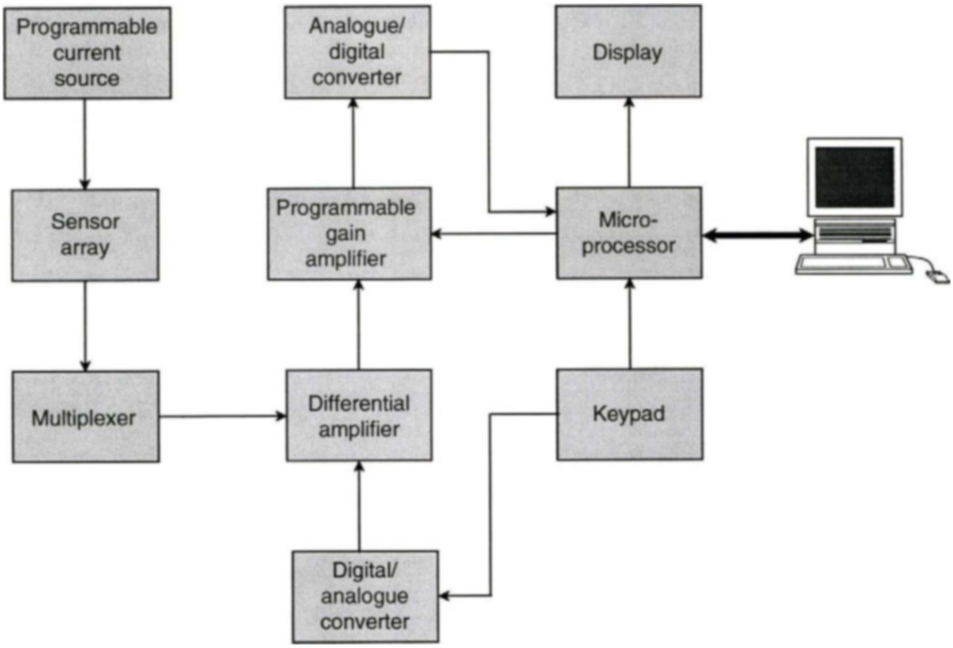
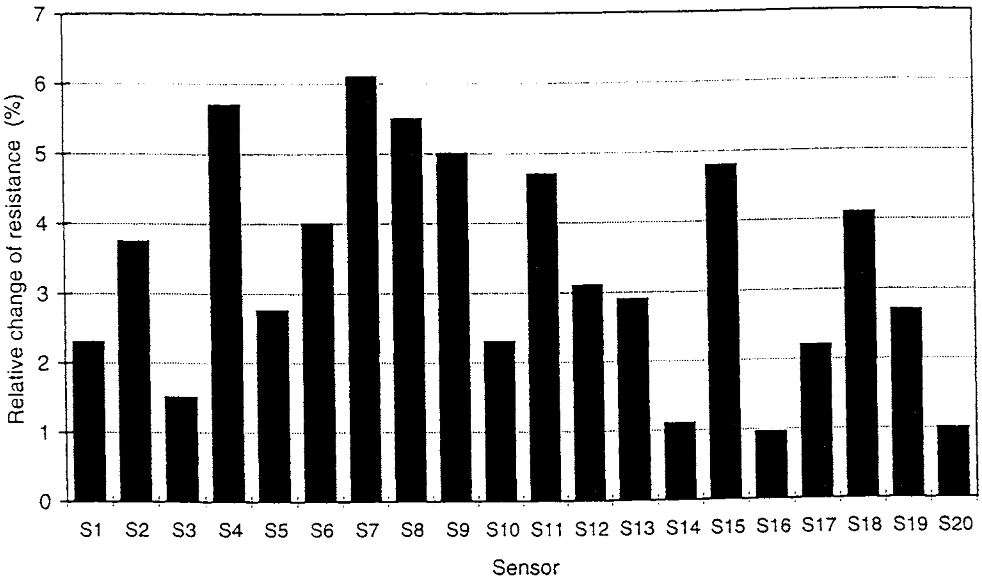


Figure 3 : Comparaison of measurements based on ac and dc interrogation

(a) Typical dc response of a 20-element sensor array



(b) Typical ac response of a single sensor

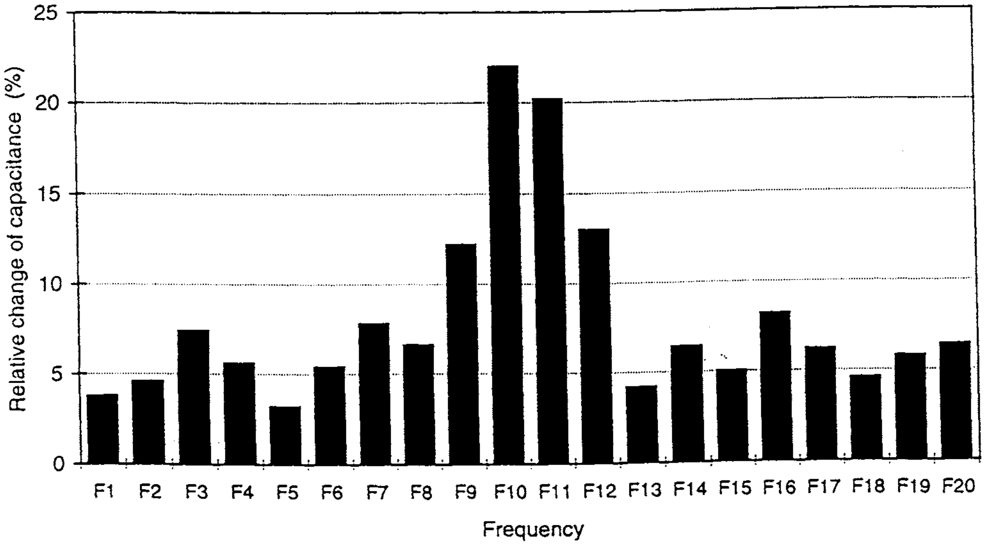


Figure 4 : Equivalent circuit for sensor showing typicaly lumped circuit values obtainde by measurements at 1 MHz

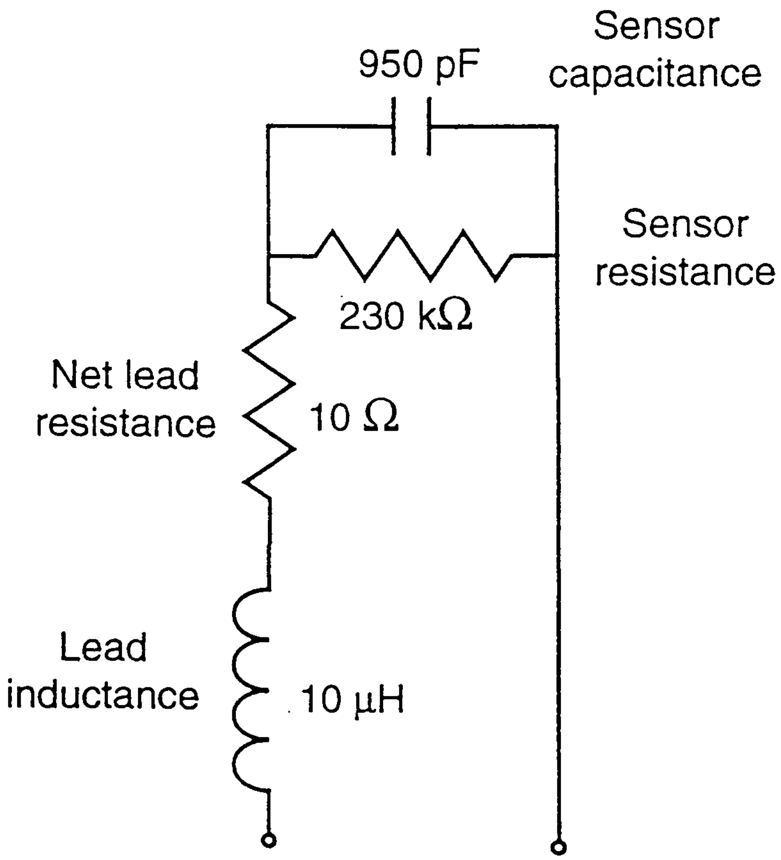


Figure 5 : Measured and calculated data

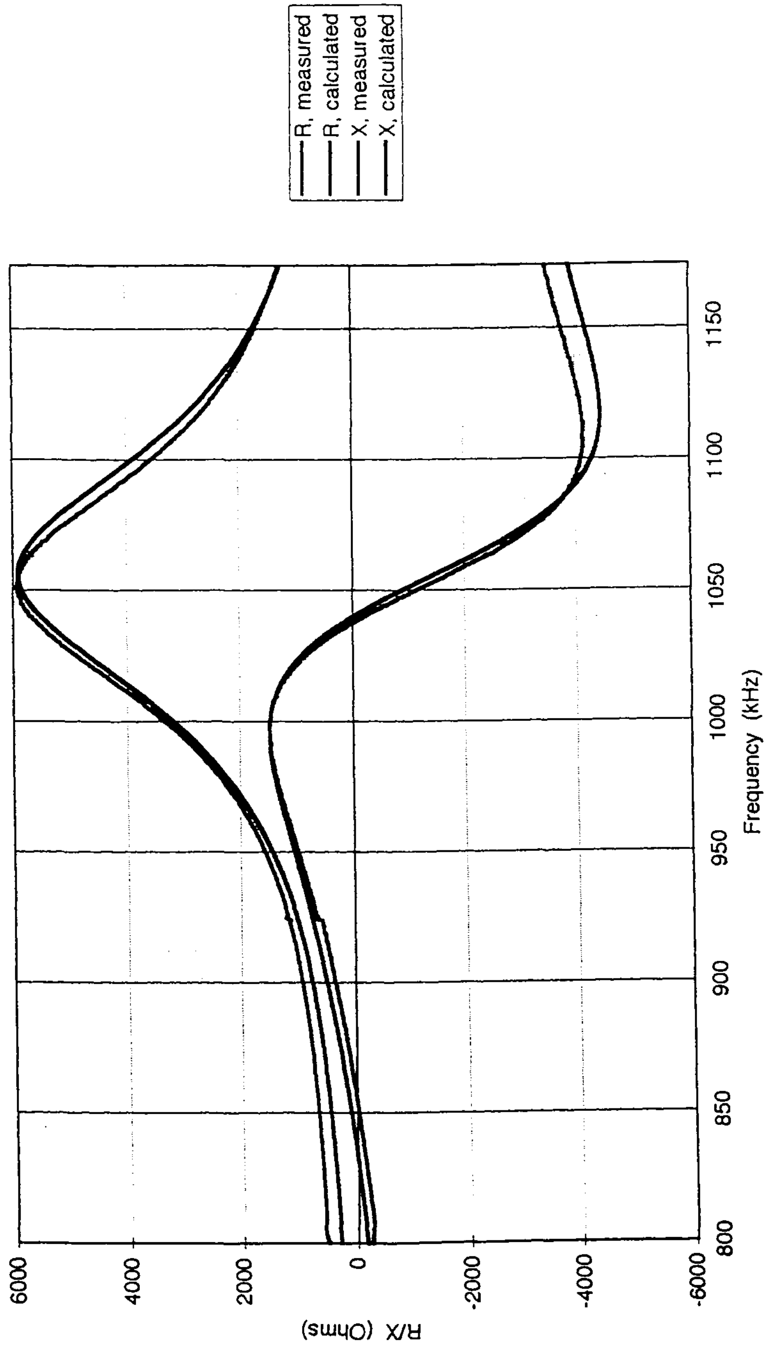


Figure 6 : Automated vapour sampling system

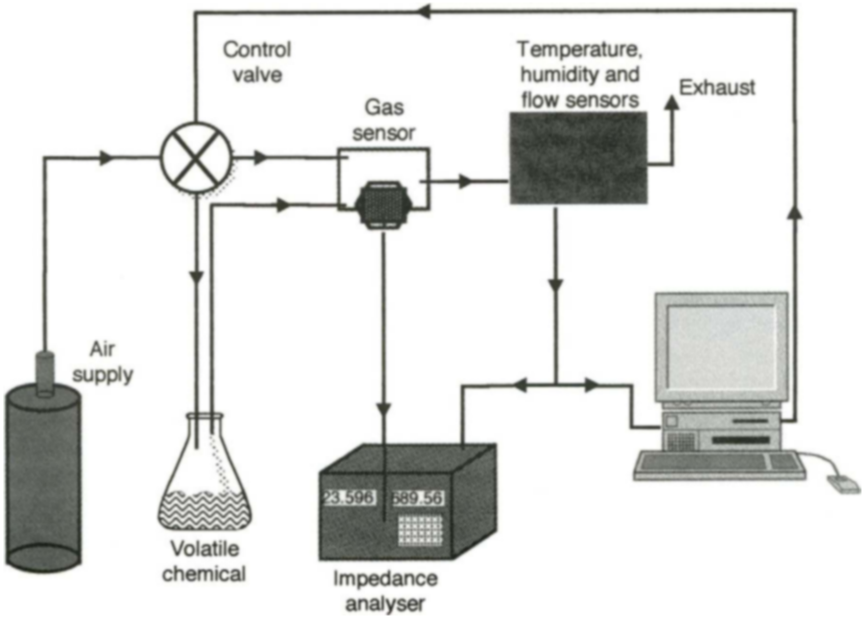


Figure 7 : Dissipation factor versus frequency for a conducting polymer gas sensor exposed to milk odour (measured over a 25 hour period at room temperature)

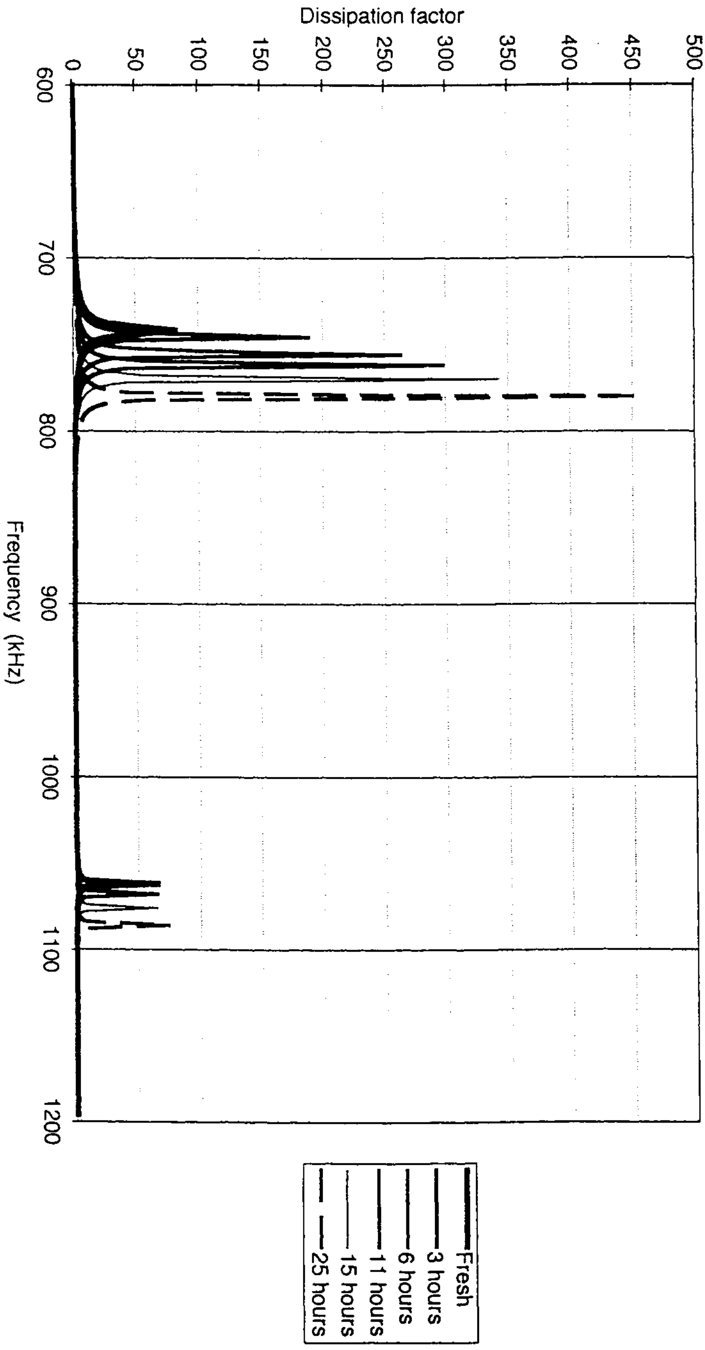


Figure 8 : Dissipation factor versus frequency for a gas sensor exposed to five brands of beer (measured at room temperature)

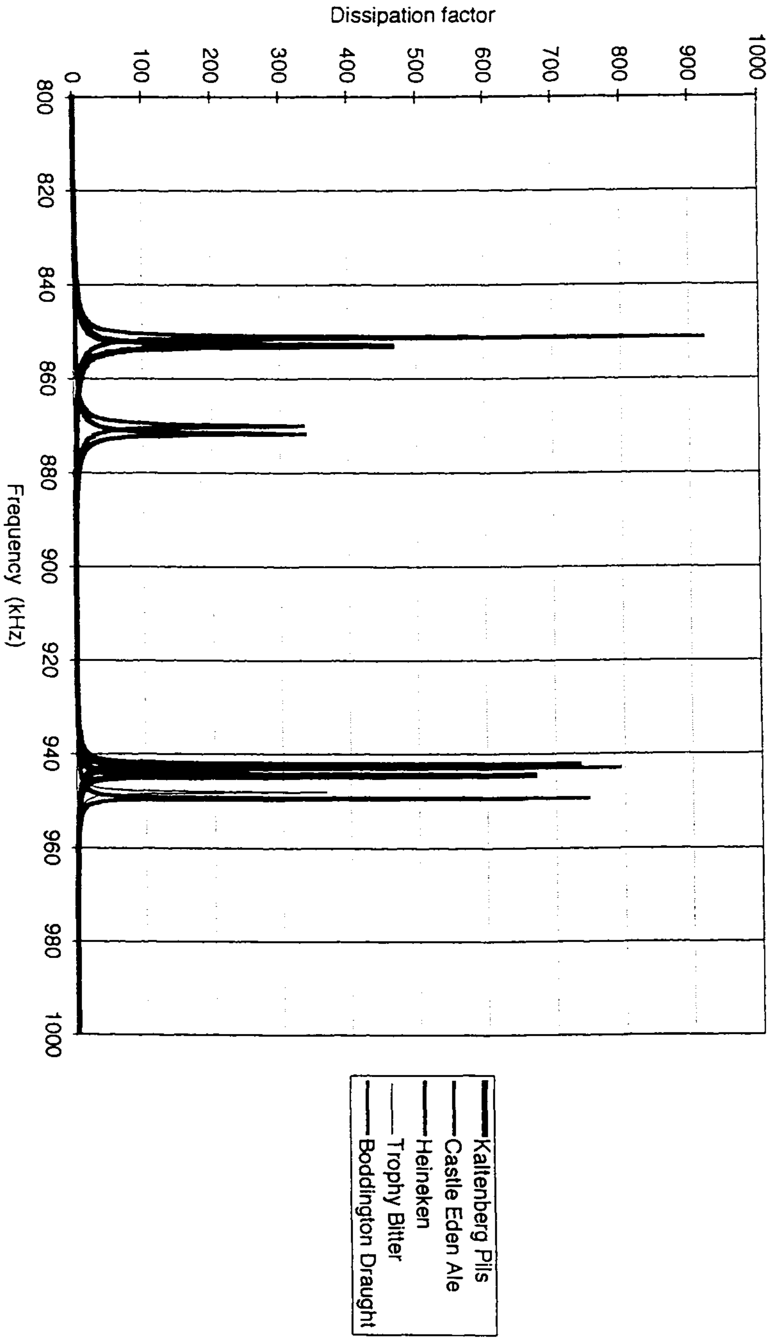


Figure 9 : Dissipation factor versus frequency for a gas sensor exposed to six differerent samples of Boddington's beer measured at room temperature over several days

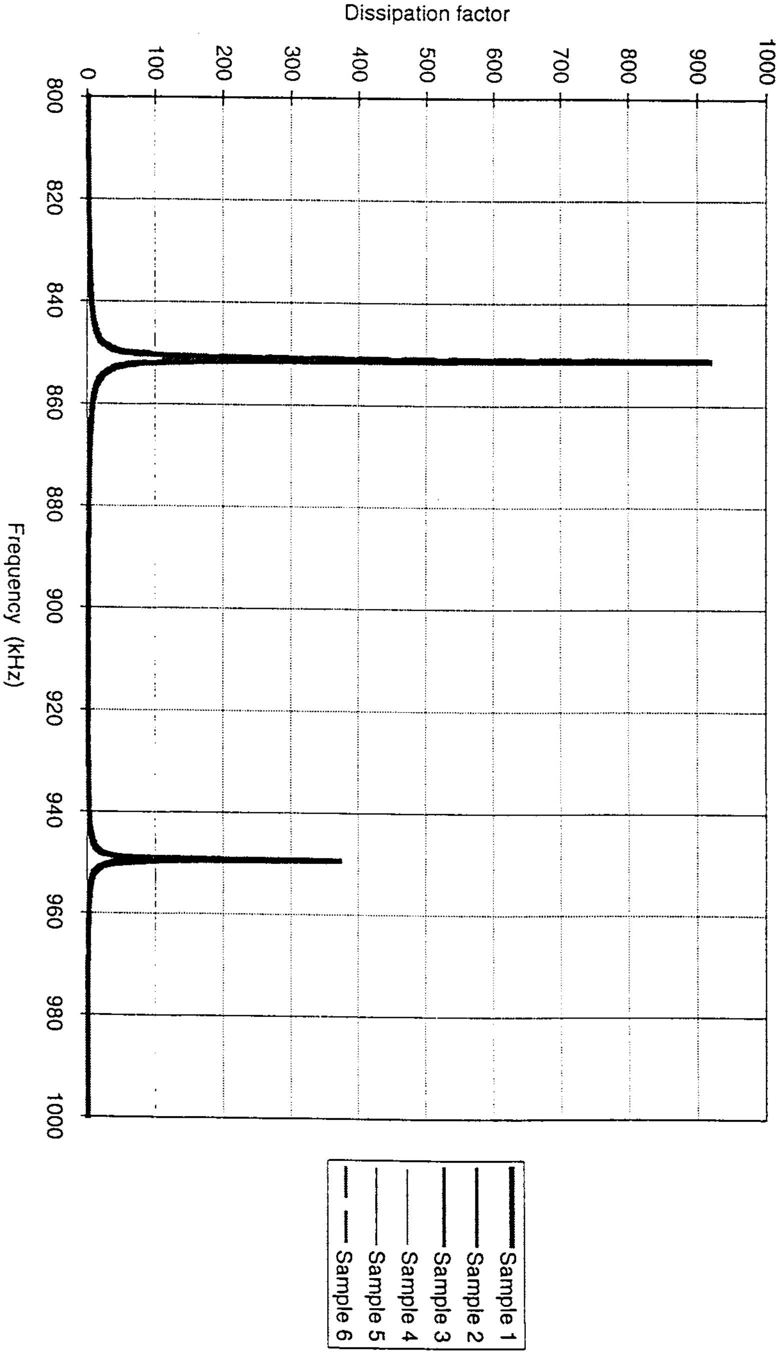


Figure 10 : Arangement for promoting a volatile chemical in a water sample to the sensor array