The determination of gaseous molecular density using a hybrid vapour sensor

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The simultaneous responses from a conductance sensor and a gravimetric quartz crystal sensor can be combined as a hybrid measurement which yields the analyte vapour's molecular density.

The measurement of odours is of importance in the monitoring of industrial, bio-agricultural and environment processes. Traditionally analytical methods, including gas chromatographic mass spectrometry[1] or optical measurements,[2] have made use of inherent physical characteristics of the vapour. In other gas sensing systems, such as electronic noses,[3–5] where the instrumentation and methodology may be more simple, there is often a lack of detailed mechanistic knowledge as to what determines the sensor response. As a consequence, one of the greatest challenges in artificial olfaction is the development of a convenient sensor technology where the analytical response results from an intrinsic molecular signature or property of the gas. Here, we show how a hybrid device, comprising a conductimetric and gravimetric sensor pair, can, through the simple ratioing of their responses, determine the molecular density of one or more vapour(s). The method that we propose has an advantage over existing olfactory techniques in that it generates quantitative physical information describing the gas composition (analogous to, for example, an IR stretch).

Much work on the development of electronic noses[3–9] has focused on two distinct sensing methods, namely, conductivity measurements based on chemoresistors[3–5] and the (mass sensitive) quartz crystal microbalance (QCM).[6–9] In both technologies, a transducing element is coated with a membrane, which may be either an organic polymer, an inorganic oxide, or simply a functionalised self assembled monolayer.[3–9] Responses are measured, either by an increase in mass (as is the case for a QCM), or by a change in electrical resistance (exemplified by the chemoresistor) due to the interaction of the gas with the overlayer. A notable difference, however, between the two systems is the common use of non-conducting overlayers in QCM sensors, and of conducting polymers or metal oxides in the chemoresistor systems.

Both the QCM[9–11] and conductimetric techniques[3–5] have been expanded to utilise arrays of different sensors. Consequently, commercial instruments have exploited signal processing as a means of producing an olfactory image and hence identifying the composition of an unknown vapour stream.[12]

A recent innovation has resulted in the manufacture of conductimetric sensors, fabricated using a dispersion of carbon-black[13] or any other finely divided conducting material[14] in a non-conducting polymer (so forming a conducting membrane). Sorbtion of a vapour into such a composite matrix causes a change in the electrical resistance by influencing the length of percolation paths between conducting particles within the polymer film. A consequence of this methodology for sensor fabrication has been to greatly extend the variety of polymers and deposition methods which can be used in these sensor systems. Additionally, by using these composites, interpretation of the measured resistance changes becomes simplified through the finding that changes in conductivity are linear with the (single component) vapour phase concentration[13] (below the percolation threshold). Importantly, it has been proposed[13,14] that the resistance change is proportional to the change in polymer-composite's volume, due to swelling.

In producing our sensors, we have exploited the possibility of measuring resistance changes in thin films of carbon black composite materials at a conductimetric sensor, on exposure to a range of vapours (due to changes in the polymer-volume) whilst simultaneously determining increases in mass at a similarly coated QCM (due to vapour sorbtion). Thus, we have developed a device which is capable of determining the molecular density of an odour (as a vapour's mass divided by its volume). This measurement, which can be determined by ratioing the voltage outputs from the QCM and the conductimetric sensor pair using a simple potential divider, provides a straightforward method to obtain an intrinsic physical signature of a gaseous species.

In the series of experiments described below, conductimetric sensors (Fig. 1, left) were fabricated as interdigitated electrodes with gap sizes of either 20 or 40 μm and an effective length of 10 cm. These electrodes have the advantage that they can be functionalised by spin coating (2000 rpm) or by an ink jet printer, from a solution containing both dissolved polymer and a carbon-black dispersion. The gravimetric (QCM) sensors (Fig. 1, right) were 10 MHz AT cut quartz crystals (ICM Co., Oklahoma, USA) and were spin coated using a solution of the polymer alone. Typical coating solutions contained 200 mg poly(ethylene oxide) (Aldrich) with/or without 50 mg carbon black (Cabot Co., Bilerica, USA), in 10 g of chloroform.

Vapours were passed over the sensor pair using a regulated flow system enabling the simultaneous measurement of QCM and conductimetric responses. Fig. 2 shows the changes in frequency and resistance of the QCM and interdigitated sensors

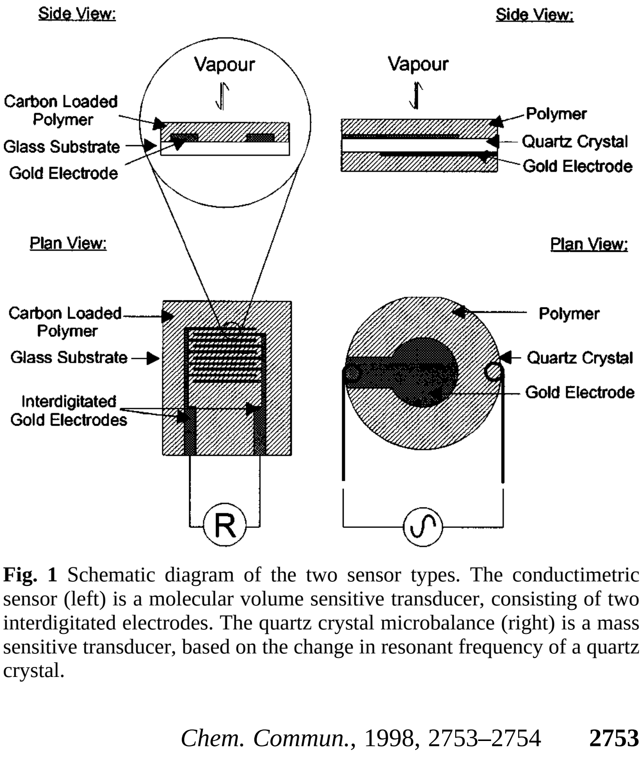

Fig. 1 Schematic diagram of the two sensor types. The conductimetric sensor (left) is a molecular volume sensitive transducer, consisting of two interdigitated electrodes. The quartz crystal microbalance (right) is a mass sensitive transducer, based on the change in resonant frequency of a quartz crystal.

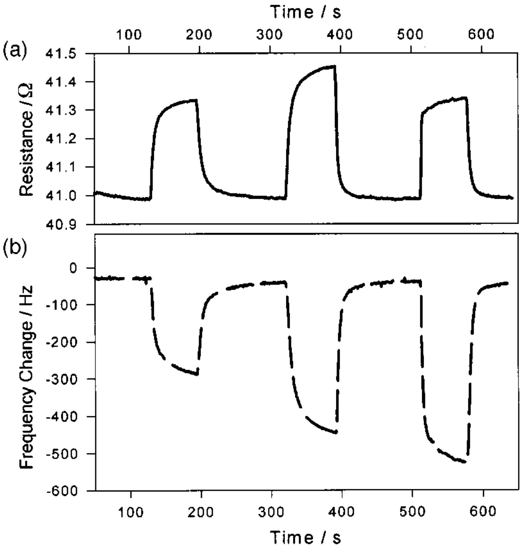

Fig. 2 Response of poly(ethylene oxide) coated (a) conductimetric and (b) QCM sensors to *n*-hexane (13 mmHg), water (9 mmHg) and chloroform (6 mmHg) in nitrogen as a function of time. Between exposure to vapour samples, the sensors were purged with dry nitrogen.

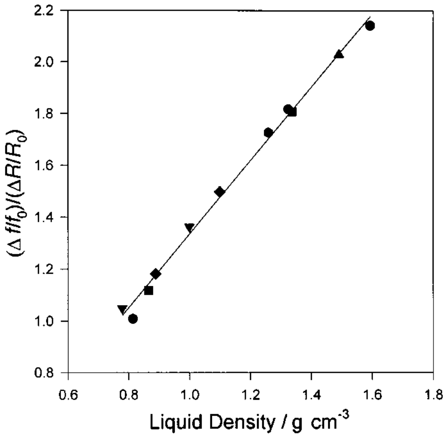

Fig. 3 A plot of $[(\Delta f/\Delta f_0)/(\Delta R/R_0)]$ *vs.* the vapour's liquid density for a range of different solvents, where f_0 is the film's dry mass, and R_0 is its initial resistance. The solvents were cyclohexane (ρ = 0.779 g cm^{-3}), hexanol (0.814), toluene (0.865), THF (0.889), water (1.00), deuterium oxide (1.10), dichloroethanene (1.26), dichloromethane (1.33), trichloroethane (1.338), chloroform (1.49) and carbon tetrachloride (1.59). The straight line is a linear regression fit to the data, (r^2 = 0.99).

on exposure to vapours of *n*-hexane, water and chloroform (at different selected, partial pressures). As can be seen, chloroform gives the largest frequency (mass) change for the given resistance change, and hexane the smallest. Although the rate of change of the response of the sensors is different for each vapour, the time dependent responses of a conductimetric and QCM sensor pair follow each other closely. Indeed, division of the temporal responses from each of the sensors in the pair is linear for a given gas, indicating that the output of the hybrid device is constant for different amounts of sorbed vapour (the actual amount of sorbed vapour can still be determined from the individual conductimetric, or gravimetric responses).

Confirmation that the sorbtion of gas does lead to a volume change in the sensing layer, as proposed by others,[13,14] has been investigated by simple neutron and X-ray reflectivity experiments (not detailed here) showing that thin films of polymers swell to as much as 150% of their original thickness on exposure to suitable vapours.

To demonstrate the independence of the ratio of conductimetric to gravimetric responses, with amount of sorbed vapour, we measured the percentage frequency change and percentage resistance change for different vapour pressures of dichloromethane (9.2 mm–138 mm Hg). The relationship is linear over the concentration range studied, although the non-zero intercept obtained from an unconstrained best fit line may reflect the influence of the bath gas (N_2) on polymer swelling.

To examine the hypothesis that the sorbed species' molecular density can be calculated from a simultaneous measurement dependent on the volume change in the conductance sensor and a corresponding gravimetric measurement, we investigated a hybrid device's response to a variety of vapours generated from volatile liquids. Fig. 3 illustrates the ratio of gravimetric change to the polymer volume increase by showing the ratio of QCM frequency change to interdigitated electrode resistance change as a function of the density of the sorbed vapour. To demonstrate that the hybrid sensor response was independent of vapour–polymer interactions, the odours were chosen in order to be representative of hydrophobic, hydrophilic, polar, non-polar, and isotopically substituted molecules. The wide range of liquid densities covered by these species (0.78–1.59 g cm^{-3}) further emphasises the versatile nature of the methodology in monitoring different vapours, including light hydrocarbon gases and heavier halogenated species. Ultimately, these techniques may be extended to (volatile) metal complexes (*e.g.* UF_6).

In conclusion, we have shown that by combining carbon-black loaded polymer conductimetric and QCM sensors, we can greatly augment the information obtained when compared with the use of either one sensor material, or one measurement system alone. This simplicity of signal processing is not found in current array based conductimetric electronic noses, owing to the numerous factors influencing conductivity mechanisms in, for example, the family of poly(pyrroles).[12] Although QCM and chemoresistance measurements have previously been made simultaneously,[15,16] giving responses which are linear with respect to the amount of (single component) vapour species adsorbed, the magnitude and sign of their proportionality coefficients are not readily related to the molecular species involved. This clearly contrasts with the novel sensor configuration that we have demonstrated here.

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