Supporting Information:

Ferric nitrate concentration

To ascertain the optimum dopant concentration, paper elements were produced from DMAc solutions containing varying amounts of ferric nitrate. Paper elements were then exposed to a set vapour challenge of 10 µL of MeS in a stainless steel chamber. Increasing the dopant levels beyond 130 mg mL^{-1} led to only minimal increases in sensitivity. It was thus decided to use 130 mg mL^{-1} ferric nitrate in DMAc as a standard for the testing phase of the work.

Sensor response to static vapour methyl salicylate (MeS) challenge - Experimental Setup

Experiments were set up in the following manner:

1. Sensors were loaded with battery power source and doped sensor paper.
2. Each sensor was then mounted on a glass vial and placed onto stainless steel testing platform.
3. A 2 cm diameter computer fan was installed at the centre of the stainless steel platform and sensors were arranged in a circle equidistant from the fan
4. The fan was started and sensors were allowed to equilibrate in clean air for a period of 2-3 minutes.
5. A 21.7 L bell jar was then charged with MeS by injecting a liquid sample onto a small piece of filter paper attached to the inner surface of the bell jar using a GC syringe.
6. The large bell jar was finally placed over the top of the stainless steel testing platform. In calculating the concentration of MeS within the large bell jar assumptions were made that all MeS had been vapourised and no MeS had adsorbed to surfaces within the jar.

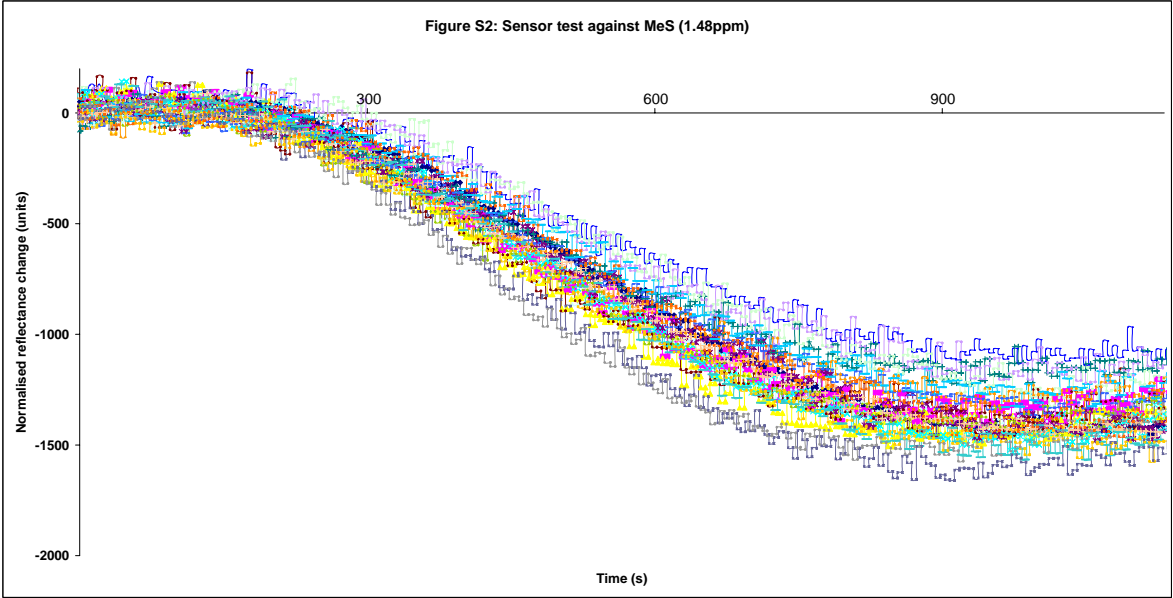Figure S1: Static MeS vapour challenge experimental set-up

Figure S4: Sensor test against static MeS vapour challenge of 1.5 ppm
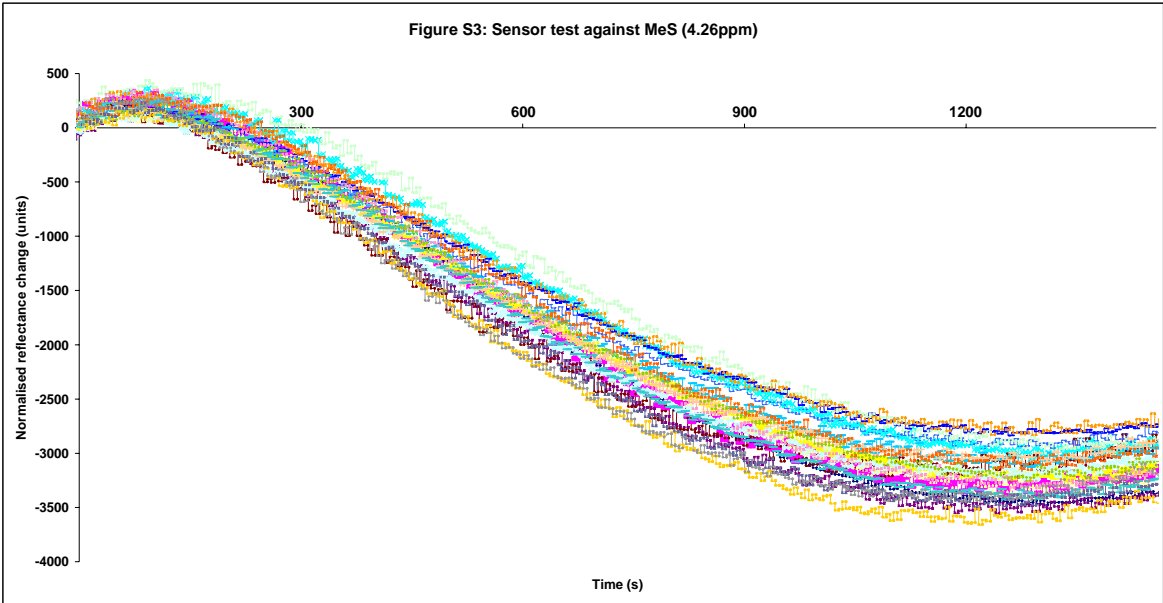

Figure S3: Sensor test against static MeS vapour challenge of 4.3 ppm
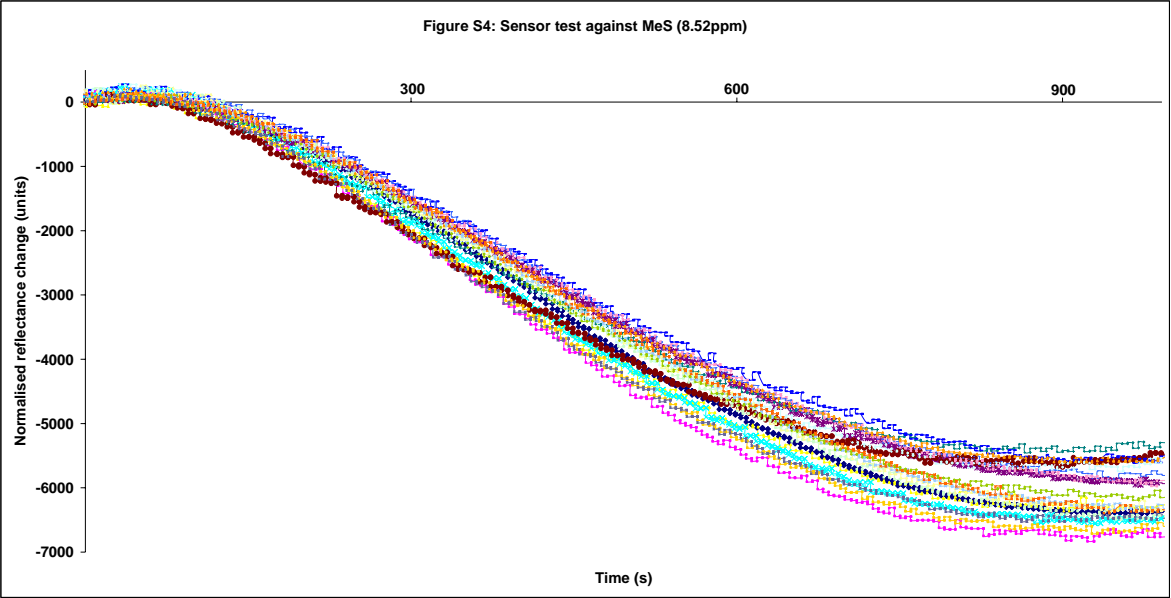
Figure S4: Sensor test against static MeS vapour challenge of 8.6 ppm
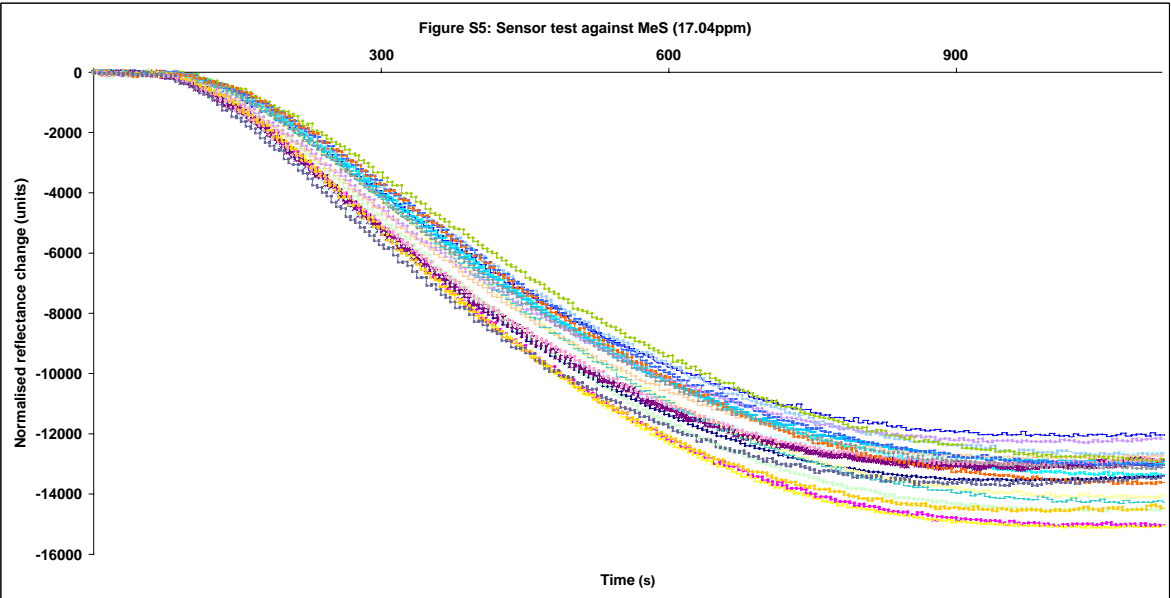

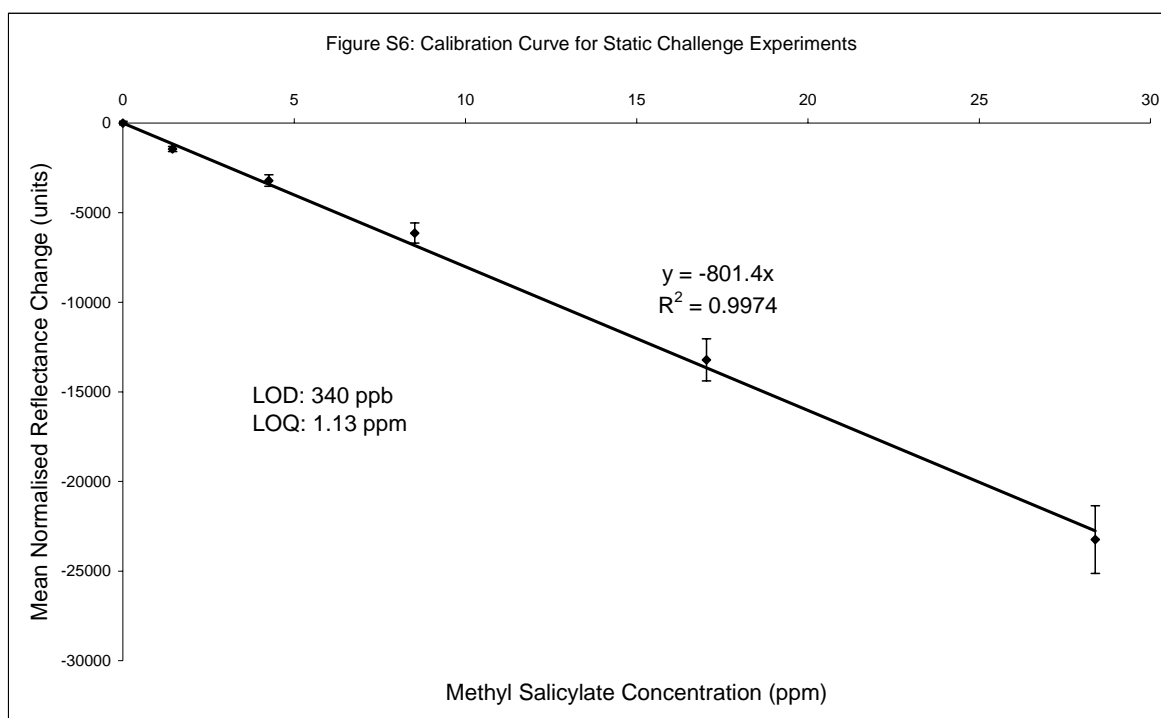Figure S5: Sensor test against static MeS vapour challenge of 17 ppm

Figure S6: Calibration curve for static vapour challenge tests. Plotted points are the average response of 20 sensors at a given concentration of MeS

Although an LOD and LOQ for static challenge experiments could be determined from the calibration curve shown in Figure S6, it did not give a true reflection of the sensitivity of the sensor. When calculating the challenge concentrations within the chamber it was assumed that all MeS had vapourised and no MeS was lost from the chamber or adsorbed onto the inner surfaces of the chamber set-up. It is unlikely that these assumptions are completely correct leading to an under estimation of sensor sensitivity. In fact the very nature of the sensor, being an accumulator, does not lend itself easily to determinations of LOD and LOQ using vapour challenges. It was for this reason that direct dosing of liquid challenges was used to determine the absolute LOD for the sensor. Thus it was possible to specify an amount of MeS to which the sensor will respond rather than a vapour concentration.

Constant flow experiments
Using an Owlstone® (OVG-4) vapour generator constant flow experiments could be performed by passing controlled challenge air over the sensor. The sensor responds rapidly to an MeS challenge of 50 ppb within seconds. However, as stated above the sensor is an accumulator thus under a constant flow of challenge air it will continue to respond until saturation. This is problematic for determining sensitivity so liquid direct dosing was employed for determination of absolute LOD as discussed below.

Limits of detection/quantification

To determine the absolute LOD, experiments were undertaken where sensor paper elements were dosed directly with a dilute solution of MeS. These experiments were set up as follows:

1. Solutions containing low concentrations of MeS were made up in n-hexane (n-hexane was chosen as a solvent because it does not dissolve the ferric nitrate dopant and also evaporates rapidly).
2. Sensor platforms were loaded with sensor paper and then dosed with 2 µL of diluted MeS solution through the ventilation holes of the sensor cap using a syringe.
3. After each experiment sensors were allowed to off-gas for 30-40 minutes after which they were charged with a new sensor paper element for the next test
4. The concentration of MeS solutions was lowered incrementally until a mean normalised reflectance change (for all sensors tested) of less than $3 \times SD$ noise (the LOD) was observed.

A graphical representation of a typical direct dosing experiment in n-hexane is shown in Figure S7. When the dilute MeS solution is dosed onto the paper element an initial steep drop in reflectance is observed, associated with a colour change caused by wetting of the sensor paper. As the n-hexane evaporates the reflectance steadily increases before levelling off once again. The difference between the initial and final base line reflectance is thus caused by the reaction of MeS with the ferric nitrate doped paper. As a control, tests with pure n-hexane were also undertaken. In these experiments it was found that after the evaporation of the n-hexane there was no discernable difference between the initial and final baseline reflectance even upon repeated dosing (Figure S7).
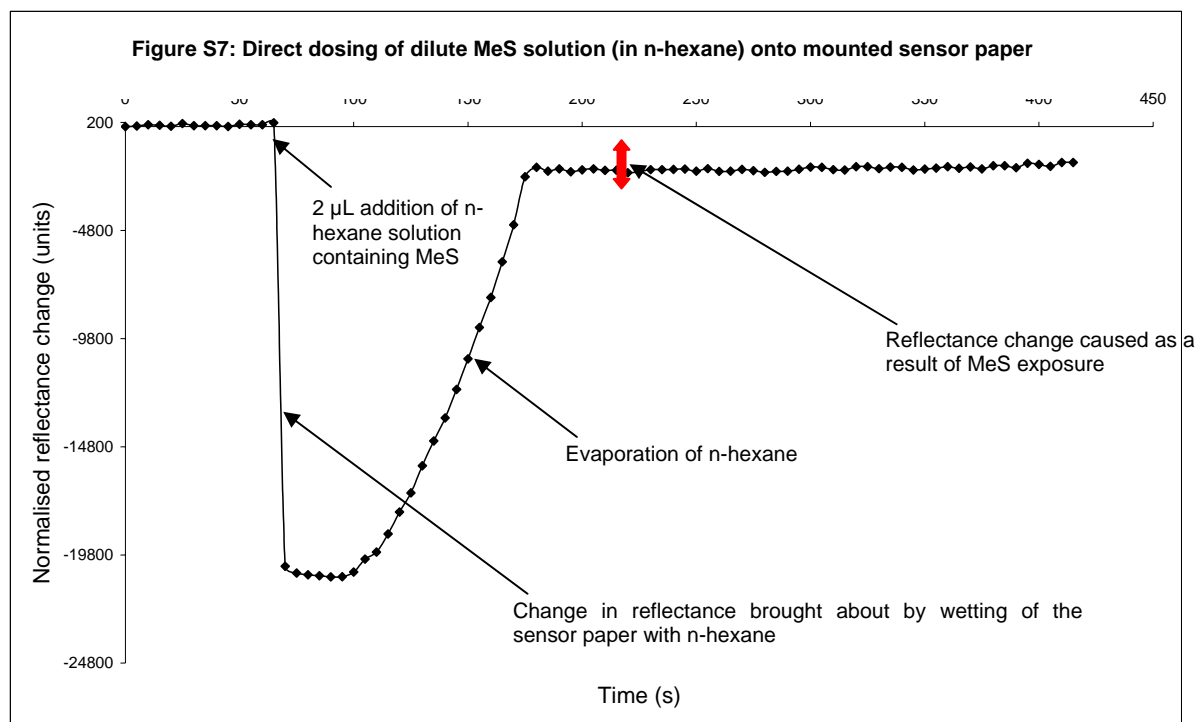

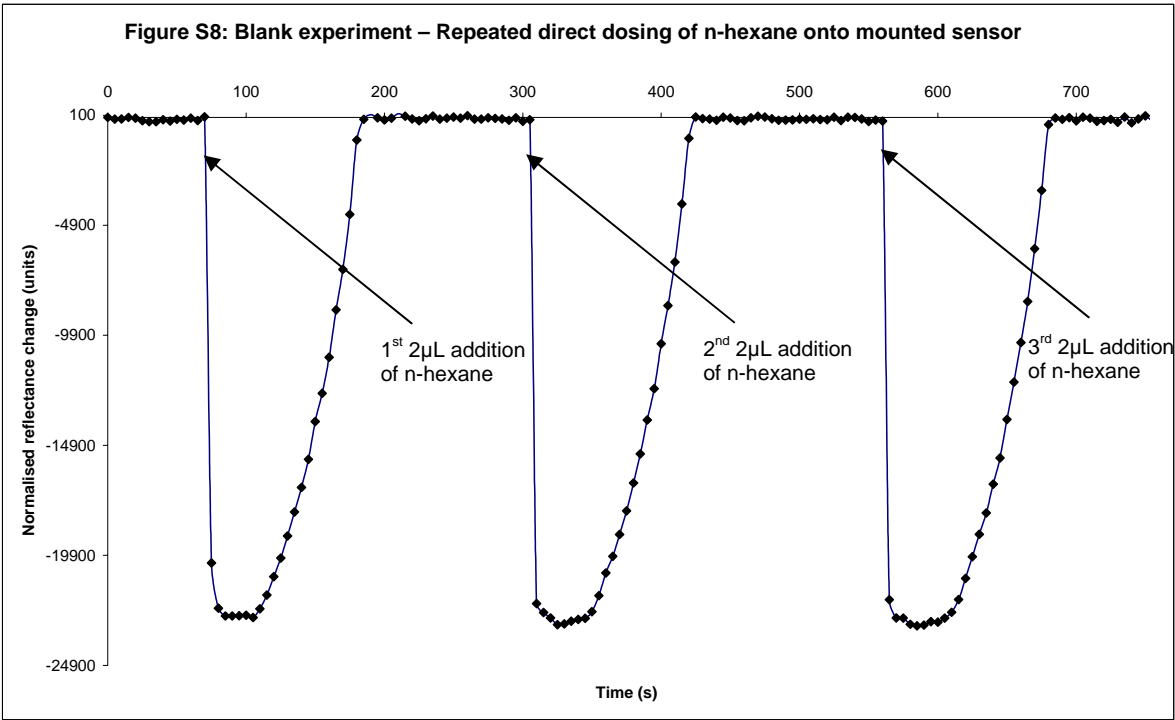Figure S7: Sensor trace from a direct dosing experiment

Figure S8: Sensor trace showing the repeated dosing of n-hexane onto mounted filter paper