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# A novel piezo-optical styrene sensor incorporating polymer-supported tribromide ion

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**Encapsulation of Amberlyst® A-26 supported tribromide in a 10,000 MW polyethylene glycol matrix gives a robust colour-sensitive reagent matrix which can be deposited on indium–tin oxide coated polyvinylidene fluoride (PVDF) piezoelectric film for the detection of styrene (and other alkene) vapours.**

Occupational exposure to styrene monomer is widespread. It is used in the preparation of rubber tyres, glass-reinforced plastics, carpet coatings and packaging materials. Styrene causes irritation of the eyes and mucous membranes at 50–100 ppm.[1] It is a central nervous system depressant and may cause dermatitis after repeated exposures. At high levels (10,000 ppm), rats and guinea pigs became comatose after several minutes and die after 30 to 60 minutes of exposure.

Current monitoring methods fall into two main categories. Dräger-style pumped detector tubes rely on the polymerisation of styrene in the presence of sulfuric acid to generate a yellow colour. However, these can only give an instant 'grab' readout, suffer from inaccuracy and are cumbersome to use. Personal monitoring is carried out using pumped or diffusive sampler tubes, usually filled with charcoal sorbent. Analysis of these tubes by desorption and gas chromatography is used to give an accurate measurement of an individual's exposure, however, analysis of these tubes is costly and time consuming.

We have previously described a piezo-optical chemical monitoring system, which gives an immediate readout of exposure to harmful gases using disposable badges and a dedicated reader.[2] This system relies upon imperceptible colour changes to gas-sensitive reagent spots deposited on the surface of a piezoelectric polymer film. These colour changes affect the heat generated by non-radiative decay when the spots are illuminated, and consequently vary the stress on the supporting piezoelectric polyvinylidene fluoride (PVDF) film. The resulting changes in surface electrostatic charge are measured following exposure of the badge, using a sensitive amplifier locked to the LED flashing frequency. An expanded view of our sensor system is shown in Fig. 1. We now describe a robust and reliable novel reagent system for monitoring styrene vapours with this system.

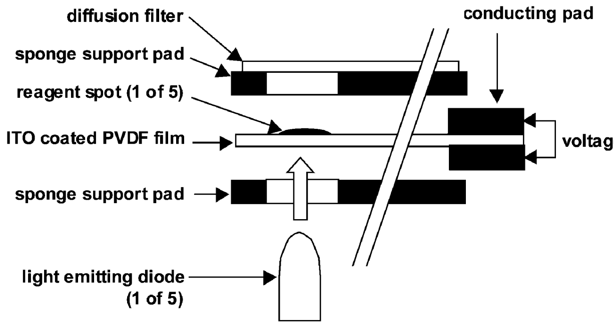

**Fig. 1** Construction of the dosimeter badge (each badge normally holds five reagent spots; for clarity only one is shown).

Decolorisation of bromine water is the classical spot test for alkenes. Initial attempts to develop a styrene-sensitive reagent using bromine trapped in either a molecular sieve or a sol–gel were unsuccessful. We then turned to polymer supported tribromide reagents, which were originally developed as convenient solid-phase bromination agents.[3] Polyvinylpyridinium tribromide and Amberlyst® supported tribromide showed only a small response in a saturated atmosphere of styrene. A systematic study of encapsulating matrices (soluble polymers), co-reagents, humectants and solvents was undertaken to enhance the reactivity of the bromide reagent. The highest response was obtained using a 10,000 MW polyethylene glycol matrix, containing 4% water, deposited from an ethanol solution.† This allowed stabilisation of the tribromide reagent in an entrapped aqueous phase which was still permeable to the styrene vapour. Deposition of the spots from either dioxane or acetonitrile gave markedly smaller responses, suggesting that crystallisation of the PEG matrix has an important effect on the reactivity The decolorisation was monitored using blue LEDs ($\lambda_{max}$ 470 nm).

Fig. 2 shows the response curve for the calibration of the 15 minute styrene dosimeter sensor in a controlled atmosphere at 298 K and 50% relative humidity.‡ The sensor response is measured on an arbitrary scale of $1 \times 10^6$ counts, calibrated against a dark ink which is screenprinted onto an indium–tin oxide coated PVDF polymer.

The sensor exhibits a good response over the 0–70 ppm range, which is ideal for occupational monitoring. In the United States, the occupational maximum exposure limits for styrene vapour are 20 ppm as an 8 hour time weighted average (TWA), or 40 ppm as a 15 minute short term exposure limit (STEL). The corresponding values in the United Kingdom are 100 ppm (TWA) and 250 ppm (STEL).[4] The response of this dosimeter could readily be modified for UK levels by incorporation of a diffusion filter into the device.

One important commercial factor in the development of dosimeters of this type is the shelf-life of the final product.

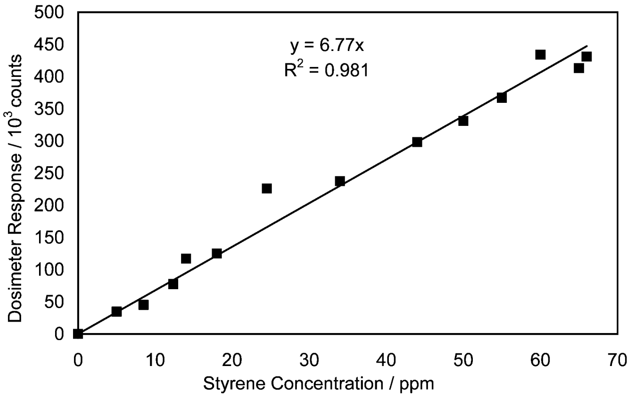

**Fig. 2** Calibration curve for styrene dosimeter badge. Each point is an average of at least three readings. 1 ppm gives 6770 counts, $R^2 = 0.98$.

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Certain dosimeter badges require storage at lowered temperatures in order to achieve the necessary stability. Fig. 3 shows the variation in the initial counts of the styrene dosimeters upon storage at room temperature (298 K), in a fridge (278 K) and in a freezer (258 K). The arbitrary cut-off point at which a styrene dosimeter is deemed unusable is when the initial count falls below 400,000. Thus, the styrene sensor has an effective shelf-life of 30 days at room temperature and predicted shelf-lives of 60 days and 180 days at 278 K and 258 K respectively. Evaporative loss of bromine from the sensor spots is therefore minimised in the polyethylene glycol matrix which is used to encapsulate the tribromide reagent.

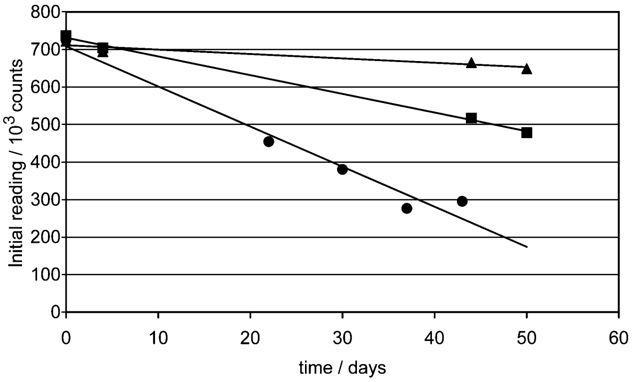

**Fig. 3** Variation in initial sensor reading upon storage at 298 K (●), 278 K (■) and 258 K (▲).

The reactivity of this reagent makes it an ideal sensor for alkenes in general. In particular, we have already shown that the dosimeter can be used in environments which may contain methyl methacrylate (used in plastics production and bone cement), ethyl cyanoacrylate (used in 'superglue' fuming to visualise latent fingerprints) and vinylchloride monomer (PVC production). Lack of specificity between different alkenes is not problematic, since monitoring of alkene mixtures is rarely carried out.

In summary, we have shown that the combination of polymer-supported tribromide ion in an appropriate matrix makes a very effective sensor for personal monitoring of exposure to styrene and other alkene vapours. Studies are underway to characterise further the factors which mediate sensor response.

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## Notes and references

† Experimental: Granular Amberlyst® A-26 tribromide (Aldrich cat. No. 33,809-5, a Rohm and Haas product) was ground at 30 Hz for 15 min on a Retsch MM200 grinder, then 50 mg of this powder was suspended in 0.5 mL of 5% polyethylene glycol (10,000 MW) in ethanol containing 4% water. This was stirred for 20 min then 5 μL drops were pipetted onto the indium–tin oxide surface and left to dry at room temperature for 15 min.

‡ The styrene atmosphere was generated using a permeation vial in an evaporative standards generator, with an overall airflow rate of 900 mL min$^{-1}$. The exposure chamber had a total volume of 2500 mL and was maintained at a constant temperature (298 ± 0.2 K) and humidity (50 ± 0.2 %). The exhaust gases were collected in ethanol and the concentration was monitored by spectrophotometry at 290 nm.[5] The recovery rate for styrene was between 95 and 99% of the calculated value from the evaporator. Three dosimeter badges, each with two spots interrogated by blue LEDs, were exposed for 15 min at each styrene concentration and the average of the three readings was taken. Counts are expressed as the overall difference in signal from the initial (high) reading to the final (low) reading. The numerical value of the initial reading does not affect the overall counts change.

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