Talanta 99 (2012) 50–54

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

A swelling-based chemiresistor for a biogenic odour

Hadi AlQahtani [a,b,*], Delia Puzzovio [a], Antonis Dragoneas [a], Tim Richardson [a], Martin Grell [a]

[a] Department of Physics and Astronomy, University of Sheffield, Hounsfield Road, Sheffield S3 7RH, UK
[b] Department of Physics, College of Teachers, King Saud University, Riyadh 11451, Saudi Arabia

ARTICLE INFO

Article history:
Received 3 April 2012
Received in revised form
2 May 2012
Accepted 10 May 2012
Available online 17 May 2012

Keywords:
1-Decanol
Odour sensor
Swelling
Chemiresistor
Core–shell nanoparticles
Undecanolthiol
Langmuir–Schäfer
E. coli

ABSTRACT

Escherichia coli bacteria release 1-decanol as a byproduct of their metabolism. We demonstrate the detection of 1-decanol odour at a partial pressure in the order 100 ppb by the resistance change of a swelling-based sensor, consisting of Langmuir–Schäfer deposited Au core/organic ligand shell nanoparticle films. This is an exceptionally low limit of detection for swelling-based sensors, and relies firstly, in the careful matching of the CSNPs ligands to the targeted odour, and secondly, in the very low volatility of this odour. Sensor response can be substantially increased further when films are cooled below the freezing point of 1-decanol. We observe unexpected quantitative behaviour of our sensors: response is only weakly dependent on the odour's partial pressure, and scales differently with temperature than the response of other Au-CSNP odours to more volatile odours. This may be related to their unusually strong thermal resistance drift, the difficulties in delivering very low partial pressure odour atmospheres, and the proximity to the analyte's freezing point.

1. Introduction

'Swelling-based' chemiresistor sensors use composites (typically, thin films) of an electrically insulating matrix, filled with conductive particles. Sensitivity and selectivity to analytes result from the selective swelling of the matrix in some analyte odours, a consequential increase in the separation of conductive particles, and a resulting increase of electrical resistance, R (or, decrease of conductance, G), which is monitored readily. The classic examples of swelling-based sensors are insulating polymers filled with carbon black (CB) particles, e.g. [1]. The same concept has been downscaled to the nanoscale, using films of core–shell nanoparticles (CSNPs), typically with Au cores decorated with thiol-coupled, insulating organic ligand shells [2–8]. Typically, Au CSNP sensors have been used to detect odours of solvents or fuels. The relevant concentration benchmark for flammable odours is the 'lower explosive limit' (LEL), which typically is a few 1000 or 10,000 ppm of atmospheric pressure [9] (we understand 'ppm' as partial atmospheric pressure throughout this contribution). For example, the LEL of iso-octane, the main component of petrol, is 7900 ppm. Biologically relevant odours often occur at much lower concentrations e.g. [10], and their sensing traditionally relies in specific chemical 'lock/key' recognition, which often is inspired by their biological functioning rather than the more generic swelling.

However, recent progress in the understanding of swelling-based Au CSNP sensors [8,11] has encouraged us to attempt the sensing of a biologically relevant odour at sub-ppm concentration by swelling, without specific molecular recognition. Assuming suitable ligands are chosen (e.g., alkanethiol ligands for alkane or aromatic odours), Lewis et al. [8] have shown that the sensitivity, s_R, of Au CSNP sensors is only weakly dependent on the length of ligands, and the identity of the odour, if s_R is defined as the slope of the sensors' relative resistance change, $\Delta R/R$, plotted against the vapour's partial pressure expressed as a fraction of the same odour's saturated vapour pressure, p/p_{sat}. Under this unusual pressure normalisation convention, s_R for a variety of ligands, and hydrocarbon vapours, fall into a small range (0.8–2). s_R somewhat increases for longer ligands, and for odours chemically similar to the ligands, but it remains confined to this rather narrow interval. This implies that odours with low volatility, i.e. low p_{sat}, can be detected at much lower partial pressures (vapour pressure expressed as fraction of atmospheric pressure, p/p_{atm}) than highly volatile odours. We have since directly confirmed the link between volatility and sensitivity by showing that sensitivity of swelling-based Au CSNP sensors increases manifold when sensors are cooled with respect to ambient temperature, thus reducing the volatility of the odour in the swollen matrix [11].

However, this does not imply that there is a sensitivity advantage for the detection of low-volatility odours with swelling-based sensors, when the source of the odour is e.g. an accidental spillage, as it would be likely for explosive or

* Corresponding author. Tel.: 1142223508.
E-mail address: php08hra@sheffield.ac.uk (H. AlQahtani).

0039-9140/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2012.05.019

poisonous odours: volatility controls both, the build-up of vapour atmosphere from the spillage, and the degree of swelling of the sensor matrix. Hence, there is no overall advantage (nor disadvantage) for sensing low volatility odours. The situation is different when instead the odour is biogenic, i.e. its source are living organisms. Life forms are not in thermodynamic equilibrium, therefore vapour build-up is controlled by the organism's rate of metabolism, rather than the vapour's volatility. Matrix swelling, on the other hand, still is controlled by volatility. We therefore expect a sensitivity advantage for 'heavy' (low volatility) biogenic odours, because vapour build-up is no longer limited by low volatility, but low volatility still enhances swelling.

Here, we report on the sensing of 1-decanol, a biogenic odour with low saturated vapour pressure, by its swelling of an Au-CSNP at less than 1 ppm odour concentration. 1-Decanol is released by strains of *Escherichia coli* (*E. coli*) [12]. Since some serotypes of *E. coli* are associated with serious food- and water-borne infections [13–16], the sensing of 1-decanol is relevant for food health and safety monitoring. Previous attempts at sensing 1-decanol released by *E. coli* involved the pumping of headspace air above an *E. coli* culture through a filter, subsequent extraction of the 1-decanol from the filter by a solvent, and chromatographic determination of the concentration of 1-decanol in the extraction solvent. Results ranged from 23.6 ng/mL to 148 ng/mL [12], however, concentration in ng of 1-decanol per mL extraction solvent does not allow a direct conclusion on the 1-decanol partial pressure in the original atmosphere. Hence, currently, neither convenient 1-decanol sensors nor typical partial pressures of 1-decanol from biological sources are available.

Interestingly, 1-decanol freezes at 6.4 °C, which we can easily access with a Peltier cooler [11]. This allows us to investigate the behaviour of a swelling-based sensor when temperature drops below the analyte's freezing point.

2. Experimental

2.1. Materials

As the material for our swelling-based sensors, we used monodisperse Au CSNPs with self-assembled 11-mercapto-1-undecanol ('undecanolthiol') ligands, sourced from PlasmaChem [17]. Ligands were selected for their similarity to the target analyte.

2.2. Sample preparation

Nanoparticles were dissolved in methanol (1 mg/mL), rather than in chloroform as used for alkanethiol CSNPs [7,11], because a good dispersion could not be achieved in chloroform even after sonication. 400 µL of such solutions were spread on a Nima Langmuir trough and compressed to 11 mN/m, a Langmuir isotherm is shown in Fig. 1. We used the Langmuir–Schäfer (LS) technique for 5 deposition cycles on glass substrates, previously cleaned and silanised with hexamethyldisilazane (HMDS). For a control experiment, Au-dodecanethiol CSNP films were prepared similarly, as reported previously [7].

2.3. Resistance measurements

The electric resistance of resulting films was measured with an AlphaLab Teraohm meter (HR2 Model). The baseline resistance prior to exposure was averaged over 3 min. Although we kept film deposition procedure as constant as we possibly could, we observed baseline resistances for different Au-undecanolthiol samples ranged from ~250 MΩ to 1 GΩ prior to any vapour exposure. We believe this variation results from the difficulty in ensuring that Au-undecanolthiol Langmuir films are strictly monolayers. Unlike the Langmuir isotherms for alkanethiol CSNPs [7,11], the isotherm in Fig. 1 shows no defined monolayer collapse. The differences between alkane- and alkanol-ligand Au CSNPs with regards to both, suitable dispersion solvent and isotherms, probably result from the hydrophilic terminal hydroxyl groups present in the alkanol ligands.

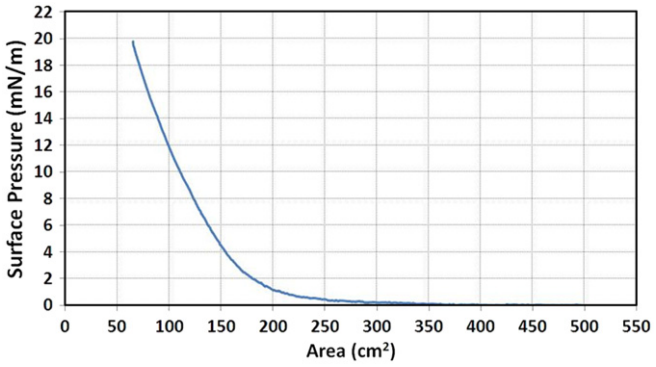

Fig. 1. Langmuir isotherm of Au-undecanolthiol CSNP film spread on water from methanol dispersion. LS deposition was at 11 mN/m.

2.4. Odour exposure

For odour sensing tests, we sourced 1-decanol from Aldrich and generated saturated 1-decanol odour by bubbling inert carrier gas (N_2) through a sparger in a phial that was held at 25 °C in a thermostatted water bath. Saturated odour was then diluted by mixing with carrier gas as required, e.g. down to 1% or 10% p_{sat}. The saturated vapour pressure of 1-decanol is quoted as 11.2 ppm at 25 °C [18,19]. When we quote 1-decanol vapour pressures as 112 ppb or 1.1 ppm, these are to be understood as 1% or 10% p_{sat} of 1-decanol at 25 °C. 1-decanol odour was fed into a Teflon-lined exposure chamber where samples were located. Samples could be cooled with a Peltier element, which was heat-sinked into an ice bath. The exposure set-up is sketched in Fig. 2.

3. Results and discussion

Fig. 2 shows the response of a Au-undecanolthiol CSNP sensor film under exposure/recovery cycles to 112 ppb 1-decanol odours. We find a small, but clearly observable resistance increase $\Delta R/R$ of approximately 0.4% under exposure, which is more than 10 times larger than the noise in $\Delta R/R$. Under purge, the resistance recovers fully to its previous value. We thus observe a response at a partial pressure that is remarkably low for a swelling-based sensor, e.g., Lewis et al. exposed Au CSNP sensors to various analytes (e.g., alkanes, alcohols, toluene) at odour concentrations in the order 100–1000 ppm for a resistance change in the order 2% [8]. However, all their analytes were significantly more volatile than 1-decanol. This confirms our premise that swelling-based sensors can detect 'heavy' (i.e., low volatility) odours at remarkably low partial pressure.

For comparison, we also exposed a Au-dodecanethiol CSNP film to 1-decanol up to 10% p_{sat}=1.1 ppm. We have used such films in previous work, and found good sensitivity to aromatic and alkane odours, e.g. toluene and decane [7]. However, even at 10% p_{sat} 1-decanol, there was no measurable resistance change, while the same Au-dodecanethiol film did clearly respond e.g. to toluene, when a soaked cotton bud was placed nearby. Lewis et al. [8] have

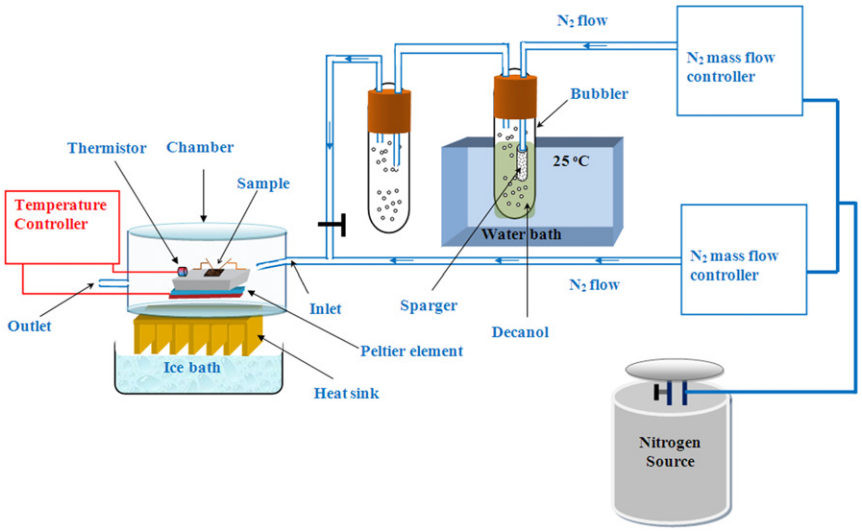

Fig. 2. Schematic showing the temperature controlled sensing and gas delivery set-up. The chamber is coated from inside with Teflon and electrically shielded with grounded Al foil. The Peltier element is in contact with the heat sink which in turn is in contact with an ice bath.

shown previously that swelling-based sensors are somewhat more sensitive to analytes that are chemically similar to the nanoparticle's ligand. We conclude that the choice of ligand is particularly important when working with 'heavy' odours at low partial pressure odours: here, 1-decanol swells the undecanolthiol ligand that carries a terminal –OH group, but not the dodecanethiol ligand that lacks such a group.

Following our recent demonstration of enhanced sensitivity when swelling-based sensors are cooled [11], we have studied the temperature-dependent sensing behaviour of Au-undecanolthiol CSNP films. To establish baseline temperature dependency, we first measured the variation of resistance of Au-undecanolthiol films with temperature in the range 8–22°C. Resistance displayed a relatively strong, approximately linear, decrease with increasing temperature of (1 to 1.3)%/K (1% for a 1 GΩ sample, 1.3% for a 500 MΩ sample). This compares to a much smaller resistance decrease with increasing temperature of 0.1%/K for Au-hexanethiol CSNP films [11], which also displayed a much smaller resistance overall, and 0.3%/K for Au-dodecanethiol CSNP films [7]. Resistivity, ρ, of CSNP films is generally described by Eq. (1), which accounts for both, carrier tunnelling, and thermally assisted hopping:

$$\rho \sim \exp(2\beta d + E_c/kT) \quad (1)$$

where d is the distance between adjacent cores, β is a tunnelling factor, k is Boltzmann's constant, T is the temperature, and E_c is an activation energy [3,21]. The increase of d with swelling in odour qualifies such films as sensors, but d also slightly increases with T due to thermal expansion, which should lead to a small increase of R with T. However, the thermally activated second term in the exponent in Eq. (1) predicts a decrease of resistance with increasing T, $(1/\rho)(d\rho/dT) = -E_c/kT^2$, if thermal expansion is ignored. The observed decrease of R with increasing T in Au CSNP films not exposed to any odours shows that $R(T)$ is dominated by thermal activation. From the observed 1.3%/K resistance drift at ambient temperature we estimate $E_c \sim 0.1$ eV. The relatively high activation energy observed for undecanolthiol ligands may be related to its terminal –OH group.

We then studied the temperature-dependency of Au-undecanolthiol CSNP film resistance under both 112 ppb and 1.1 ppm 1-decanol exposure/recovery cycles. This was motivated by our recent observation of sensitivity enhancement of swelling-based sensors when these were cooled [11]. Results are shown in

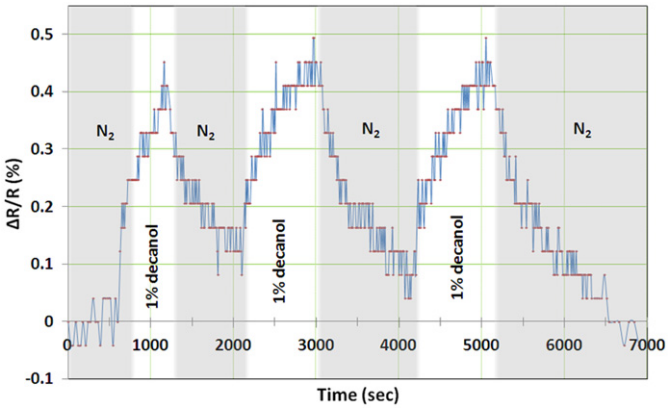

Fig. 3. Resistance of Au-undecanolthiol CSNP film under repeated exposure/recovery cycles to 1% p_{sat} (112 ppb) decanol odour. We observe a reversible resistance change of about 0.4%, with an initial resistance of 242 MΩ. Measurement at ambient temperature (20 °C).

Fig. 4(a) (112 ppb) and (b) (1.1 ppm). Relative resistance change $\Delta R/R$ was defined at each temperature as $(R_{ex}(T) - R_o(T))/R_o(T)$, where $R_{ex}(T)$ is the recorded resistance at any exposure/recovery time at a specific temperature T, while $R_o(T)$ is the average of the initial resistances taken under N_2 purge before the exposure at the same temperature T, i.e. the underlying temperature drift of R is accounted for, and the shown $\Delta R/R$ reflects changes due to 1-decanol exposure only. Although the sample used for Fig. 4 differed from the sample used for Fig. 3 in its initial resistance (1 GΩ vs 250 MΩ), Fig. 4 shows a similar relative resistance change of 0.4% under 112 ppb 1-decanol at ambient temperature (18 °C). However, $\Delta R/R$ at ambient temperature is very similar for 1.1 ppm and 112 ppb. We believe this may be caused by the condensation of some 1-decanol at the inner surfaces of the exposure chamber and its inlet valve, the more so for higher odour concentration as the entire chamber is in thermal contact with the heat sink. It is therefore not sensible to calculate sensitivity, s_R, at such low odour concentrations, as this calculation relies in a linear relation of response $\Delta R/R$ with odour concentration. With falling temperature, response somewhat

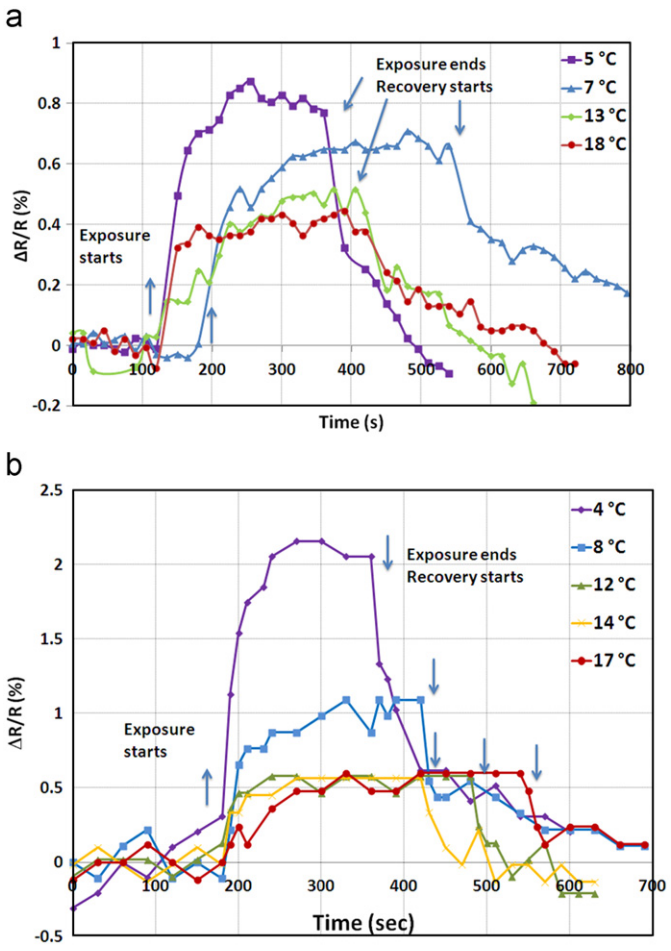

Fig. 4. Resistance of Au-undecanolthiol CSNP films under exposure/recovery cycle to 1% p_{sat} (112 ppb) 1-decanol (a) and 10% p_{sat} (1.1 ppm) 1-decanol (b), when the films were held at different temperatures.

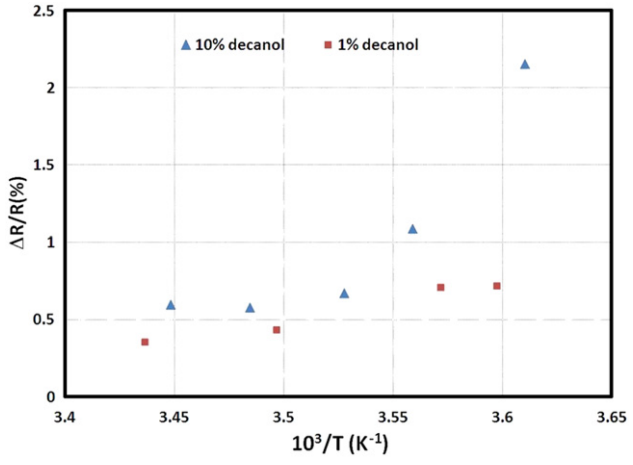

Fig. 5. Arrhenius-like plot of sensor response at different temperatures for 1% p_{sat} (squares) and 10% p_{sat} (triangles) 1-decanol exposure.

increases, more so for 1.1 ppm 1-decanol exposure. Also, for 1.1 ppm, a substantial increase in $\Delta R/R$ is observed when T approaches, and then drops below, the freezing point of 1-decanol, 6.4 °C. This is explained qualitatively by a large drop in 1-decanol volatility on freezing. Quantitatively, however, when temperature dependency is presented in an Arrhenius-like plot, $\ln[R_{max}(T)/R_o(T)]$ vs. $1/T$ (Fig. 5), we do not observe the expected straight-line behaviour above the freezing point, as in our previous work on more volatile odours [11]. We believe the low dependency of our sensors' response on odour concentration, and the anomalous scaling of response with temperature, are related to the unusual properties of our sensors, and circumstances of their use: compared to previous work on Au alkananethiol CSNP sensors, Au-undecanethiol CSNPs show very high resistance, high thermal drift of resistance, and the analyte is at extremely low partial pressure, and close to its freezing point. The high resistances make measurements more difficult; the already very low analyte vapour pressure may be reduced by condensation inside the exposure chamber, in particular when it is cooled; and close to the freezing point, enthalpy of vaporisation often becomes temperature-dependent.

4. Conclusions

We can detect a resistance change due to swelling in Au core/organic ligand shell nanoparticle films under a biologically relevant odour, 1-decanol, at a partial pressure in the order 100 ppb. 1-Decanol is a metabolite of *E. coli* [12], and as such can serve as an indicator for the presence of bacteria that may cause food spoilage. This is an exceptionally low detection limit for swelling-based sensors, and relies firstly, in the careful matching of the CSNPs ligands to the targeted odour, and secondly, in the very low volatility of this odour. Sensor response can be increased further when films are cooled below the freezing point of 1-decanol. Since there currently are no convenient sensors for 1-decanol [19,20], we consider our work as an important contribution to the sensing of biologically relevant odours. We observe unexpected quantitative behaviour of our sensors: response is only weakly dependent on the odour's partial pressure, and scales differently with temperature than the response of other Au-CSNP odours to more volatile odours. This may be related to their unusually strong thermal resistance drift, the difficulties in delivering very low partial pressure odour atmospheres and the proximity to the analyte's freezing point.

Acknowledgements

Hadi AlQahtani thanks King Saud University, Riyadh, Saudi Arabia, for the provision of a doctoral fellowship. Delia Puzzovio and Antonis Dragoneas thank the European Commission for the provision of an 'Experienced Researcher' (DP) and 'Early Stage Researcher' (AD) fellowship within the 'FlexSmell' ITN.

References

[1] M.C. Lonergan, E.J. Severin, B.J. Doleman, S.A. Beaber, R.H. Grubbs, N.S. Lewis, Chem. Mater. 8 (1996) 2298.
[2] H. Wohltjen, A. Snow, Anal. Chem. 70 (1998) 2856–2859.
[3] S.D. Evans, S.R. Johnson, Y.L. Cheng, T. Shen, J. Mater. Chem. 10 (2000) 183–188.
[4] H. Ahn, A. Chandekar, B. Kang, C. Sung, J.E. Whitten, Chem. Mater. 16 (2004) 3274–3278.
[5] S.Y. Heriot, H.L. Zhang, S.D. Evans, T.H. Richardson, Colloids Surf. A: Physiochem.Aspects 278 (2006) 98–105.
[6] M.D. Hanwell, S.Y. Heriot, T.H. Richardson, N. Cowlam, I.M. Ross, Colloids Surf. A: Physiochem.Aspects 284 (2006) 379–383.
[7] H. AlQahtani, M. Sugden, D. Puzzovio, L. Hague, N. Mullin, T. Richardson, M. Grell, Sensors Actuators B: Chem. 160 (2011) 399–404.
[8] E. Garcia-Berrios, T. Gao, M. Woodka, S. Maldonado, B. Brunschwig, M. Ellsworth, N. Lewis, J. Phys. Chem. C 114 (2010) 21914–21920.
[9] 〈http://www.engineeringtoolbox.com/explosive-concentration-limits-d_423.html〉.
[10] G.A. Sotzing, J.N. Phend, R.H. Grubbs, N.S. Lewis, Chem. Mater. 12 (2000) 593.
[11] H. AlQahtani, M. Alduraibi, T. Richardson, M. Grell, Phys. Chem. Chem. Phys. 14 (2012) 5558–5560.

[12] T. Hamilton-Kemp, M. Newman, R. Collins, H. Elgaali, K. Yu, D. Archbold, Curr. Micobiol. 51 (2005) 82–86.
[13] Medical Microbiology, 4th ed., University of Texas, Medical Branch at Galveston, 2007.
[14] J.P. Nataro, J.B. Kaper, Clin. Microbiol Rev. 11 (1998) 142–201.
[15] R.L. Vogt, L. Dippold, Public Health Rep. 120 (2005) 174–178.
[16] S. Ishii, M.J. Sadowsky, Microbes Environ. 23 (2008) 101–108.
[17] 〈http://www.plasmachem.com/〉.
[18] 〈http://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+1072〉.
[19] 〈http://www.hc-sc.gc.ca/cps-spc/pest/part/consultations/_prvd2009-03/aliphat_alc-eng.php〉.
[20] N.K. Chaki, T.G. Gopakumar, T. Maddanimath, M. Aslam, J. Appl. Phys. 94 (2003) 3663.
[21] W.H. Steinecker, M.P. Rowe, E.T. Zellers, Anal. Chem. 79 (2007) 4977–4986.