Sensors and Materials, Vol. 17, No. 7 (2005) 355–364
MYU Tokyo

S & M 0613

"Electronic Nose" —A New Monitoring Device for Environmental Applications

Krishna C. Persaud*, Peter Wareham,
Anna Maria Pisanelli and Emmanuel Scorsone

School of Chemical Engineering and Analytical Science, The University of Manchester,
PO Box 88, Sackville Street, Manchester M60 1QD, UK

(Received February 21, 2005; accepted May 9, 2005)

Key words: odour sensing, sensor arrays, environmental monitoring

Environmental applications of odour sensing technology have been limited by problems of achieving stable measurements when confronted with highly variable environmental factors. We present three case studies for odour sensor technology applied to (a) detection of dry rot in buildings using a sampler and preconcentrator based on solid phase microextraction coupled to a metal oxide sensor array; (b) continuous monitoring of the odour of waste water; (c) discrimination of volatiles emitted by fires in the development of a smart fire alarm system. Each of these applications has required understanding of the nature of the volatiles to be detected and discriminated, specific sampling methods and dedicated sensors, electronics and software.

1. Introduction

The remarkable capabilities of biological chemosensory systems in detection, recognition and discrimination of complex mixtures of chemicals have stimulated the imagination and interest of many researchers and commercial organisations for the development of electronic analogues. The responses of individual odour sensors combined into an array, where each sensor possesses slightly different response selectivity and sensitivity towards the sample odours, when combined using suitable mathematical methods, can provide information to discriminate between many sample odours.[1] Arrays of gas and odour

*Corresponding author, e-mail address: krishna.persaud@manchester.ac.uk

sensors, made from different technologies, are finding their way into a variety of specialised applications.[2] Some motives arise from the perceived limitations of traditional analytical chemistry and instrumentation in classification of gas mixtures, or odours; applications where the gestalt of a defined mixture of chemical species may be important in perception, and where it is important to separate subjective and objective assessments; and also the commercial drive to achieve devices capable of operating rapid, on-line process-measurement and control in areas of foods, beverages, chemical industries, and waste management. Such devices have become known as "electronic noses" and consist of three elements: a sensor array which is exposed to the volatiles, a converter of the sensor signals to a readable format, and software analysis of the data to produce characteristic outputs related to the odour encountered. The output from the sensor array correspond to patterns of information that may be interpreted using a variety of methods such as principal component analysis, discriminant function analysis, cluster analysis and pattern recognition algorithms such as artificial neural networks to discriminate among samples.

Sampling methodology, sensors and material science, electronics and software techniques are important aspects of the development of the systems for any practical application. The selection of an effective set of descriptors of the patterns in question is highly important. Where an odour is concerned, the problems to be addressed are which characteristics of the molecules can be measured, and how can the resulting pattern be encoded. The selection of a procedure for processing the parameters chosen to represent the pattern is required to optimise the parameter values. This increases the resolution of the system so that certain representative pattern classes may be differentiated from others. Solving these problems for diverse practical applications can be difficult.

In this paper, we describe three different environmental applications for such technology and illustrate how the problems were resolved. Common aspects of all three applications are the use of chemoresistive gas sensors using either metal oxide sensors or conducting polymer sensors. A microprocessor-based system that measures gas sensor resistance changes was developed. The types of sensor used were different for each application. A micro-controller collected real-time data from resistance interrogation circuitry and controlled a multiplexer, sequentially selecting different sensors from the array. Data are either stored for later download or transferred to a host PC via an RS232 serial communication protocol.

2. Detection of Dry Rot Infections in Buildings

We aimed to develop a portable sensing instrument that can be used by property surveyors in the field to detect of volatiles at very low concentrations that are emitted from fungal infections of *Serpula lacrymans* in buildings. Because of the low concentrations of volatiles, some mode of preconcentration of the volatiles during sampling was essential for the success of the project. In this case we chose solid phase microextraction as an optimal means of preconcentration. Our approach was the analysis of dry rot chemical species and the identification of markers. This involved growth of dry rot in culture medium, innoculation of wood —pine and oak— followed by GC/MS analysis of volatile components, identification of key marker compounds, reconstitution of a dry rot surrogate mixture, and confirmation of findings from field tests.[3]

2.1 *GC-MS Headspace analysis*

In the first instance it was important to determine which key volatile components could be used as markers for the volatiles emitted from the fungal infections. We found three SPME fibre types more applicable for this work. These consist of 100 μm polydimethylsiloxane (red hub), 65 μm polydimethylsiloxane/divinylbenzene (blue hub) and 75 μm carboxen/polydimethylsiloxane (black hub), all available from Supelco (UK). For this study, these three SPME fibres were used to concentrate the head space volatiles from the samples. The analysis was carried out with an HP-GC 5890/MS on a ZB-1701 (14% cyanopropylphenyl, 86% dimethylsiloxane phase) column.

2.2 *Procedure*

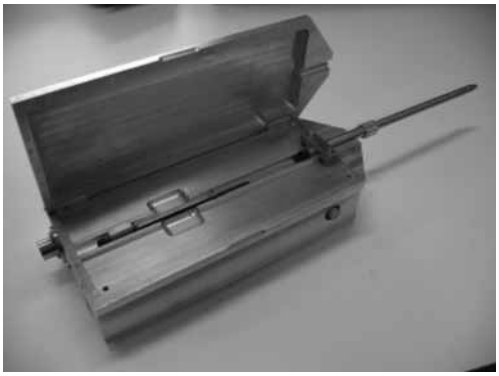
Samples were placed in a 20 ml headspace vial. In the case of cultured samples, samples were placed in a larger wide-mouthed container, with the headspace extracted via a pre-drilled septum. The Teflon-lined septum covering the vial was pierced and the fibre was exposed to the sample headspace for 30 min. The fibre was then retracted into the needle and immediately transferred to the gas chromatograph and desorbed for 5 min in the GC injection port. Compounds were resolved on a ZB-1701 column (30 m × 0.25 mm × 0.25 μm) under the following conditions: injection port temperature 250°C; helium flow 2.5 ml/min; oven temperature program 40°C (4 min hold) then 4°C/min to 220°C.

2.3 *Results*

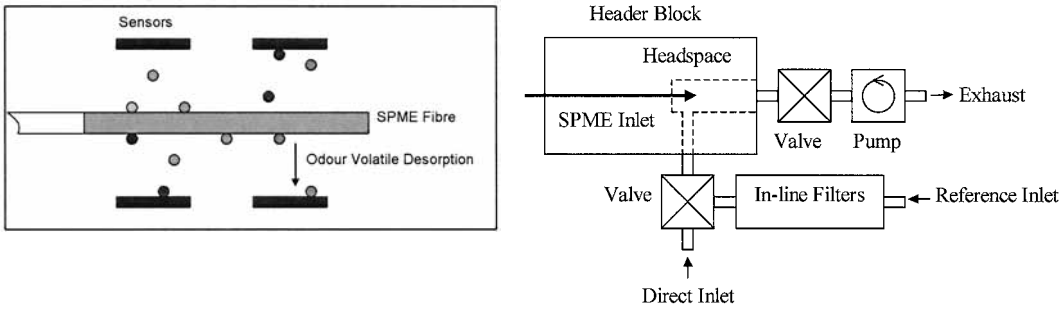
Results from GC-MS analysis indicated that the presence of 1-octen-3-ol (mushroom odour) and 3-octanone (resinous odour) appear to be common to all samples of dry rot, whether cultured, recovered or distilled, and to a slightly lesser extent, 3-octanol was also identified. Where dry rot fungus is present on pine wood substrate, additional compounds also appear in the headspace including α-pinene (pine odour), hexanal (cut grass odour) and carene (lemon odour), likely originating from the wood itself.

For a practical device that could be used in the field, we developed an automated system for sampling and preconcentration of these volatiles that was incorporated into a probe that could be inserted into crevices or cracks and be used to probe wall cavities or spaces under floors. This was based on the solid phase microextraction fibres that were encapsulated into a probe (Fig. 1(a)) that allowed rapid sampling of odour at very low concentrations from previously inaccessible locations.

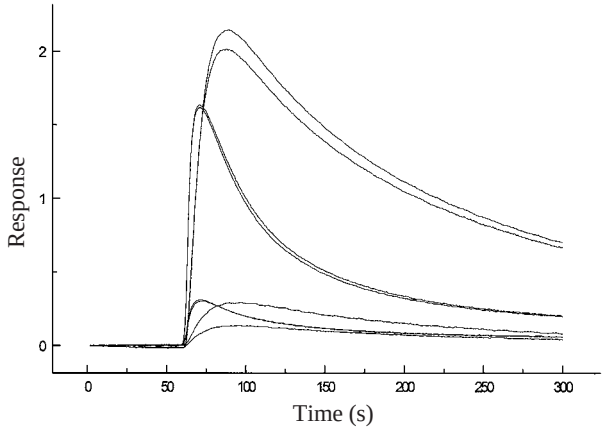
For this application —because of the requirements that volatiles be thermally desorbed from the SPME fibres— we chose commercially available metal oxide sensors such as Taguchi gas sensors (TGS) (Figaro Inc., Japan) or Capteur sensors (now City Technology, Ltd.) as the core sensing element for an array of odour detectors. These devices consist of an electrically heated ceramic pellet onto which a thin porous film of SnO_2 doped with various precious metals has been deposited. The doped SnO_2 behaves as an n-type semiconductor and the chemisorption of oxygen at the surface results in the removal of electrons from the conduction band. Gases interact with the surface adsorbed oxygen and thereby affect the conductivity of the SnO_2 film. The devices are run at elevated temperatures (typically 300–400°C) to achieve rapid response/recovery times and to avoid interference from water. This results in relatively high power consumption. The response



(a)



(b)



(c)

Fig. 1. (a) Portable field sampler based on a solid phase microextraction. (b) Design of the measurement system (inset -SPME fibre). The sensors are mounted in a symmetrical 3-dimensional array within a stainless-steel header block. The array encloses a small headspace volume that is rapidly heated to elevated temperatures by the sensors themselves. The header block allows the introduction of the SPME fibre. The sample volatiles are thus desorbed directly into the enclosed region between the sensors as shown. (c) The desorbed volatiles are sensed and the resulting response profile depends on the selectivity and sensitivity of the sensors to the mixture of volatiles.

characteristics can be tailored by varying the operating temperature and the doping agent.

The final measurement system was based on an array of metal oxide sensors (Capteur, UK), incorporated into a suitable header (Fig. 1(b)) so that when a SPME fibre was inserted, thermal desorption of trapped volatiles occurred and dynamic responses of the sensors could be recorded (Fig. 1(c)). A neural network based on radial basis function architecture was utilised to give real-time classification of the incoming volatiles and signal the presence of dry rot.[5]

Two hand-held prototype devices were built and tested in the field and gave similar results. Greater than 70% positive detection of dry rot was achieved in the field since Feb. 2003. The automated sampler device developed was tested in the field with excellent results.

3. Monitoring Waste Water Volatiles

The abatement of odour nuisance and increased efficiency within a plant is now seen as a major issue for water companies. The development of green field sites for sewage treatment or the major refurbishment of existing treatment plants requires that the company considers the problem at the planning stage and shows that the "best available technology" is being used.

Spot measurements of a single compound, hydrogen sulphide, previously used, were recognised as not effectively describing the multi-component sludge and sewage odours. In recent years chemical analysis has been supplemented with dynamic dilution olfactometric measurements of odour concentration of the emissions.[6] This method is time consuming and costly and provides only a snap-shot of the emission. Continuous monitoring by any of these techniques is not representative or feasible.

To meet the needs of water companies, monitoring equipment is required that is both reliable and robust and that can objectively and continuously monitor odours. If the technology could be applied using distributed systems, this would enable individual processes to be monitored, optimised and controlled. The system may have wider application where volatile compounds are indicators of process variations and, being non-invasive, should have a high reliability.

We have been developing instrumentation that is capable of sensing and recording in real time changes in "odour" correlated to concentrations of volatile organic chemicals emitted at a sewage site. This technology is of interest because it does not only use hydrogen sulphide monitoring as a surrogate for odour emission, but it is able to sense a broad spectrum of organic chemicals that are emitted.

The equipment has been tested for monitoring the inlet stream of a sewage plant. It is capable of transmission of data in real time to a computer screen in a control room. The software produces a strip chart display of odour changes with time, and set points and alarms can be programmed remotely (Fig. 2). This can be used to trigger collection of a sample via an autosampler, to control a valve for chemical release, or to control diversion of a stream to a holding tank.

Odours from sewage treatment plants arise principally from the biological degradation of the constituents of domestic sewage and are particularly associated with anaerobic

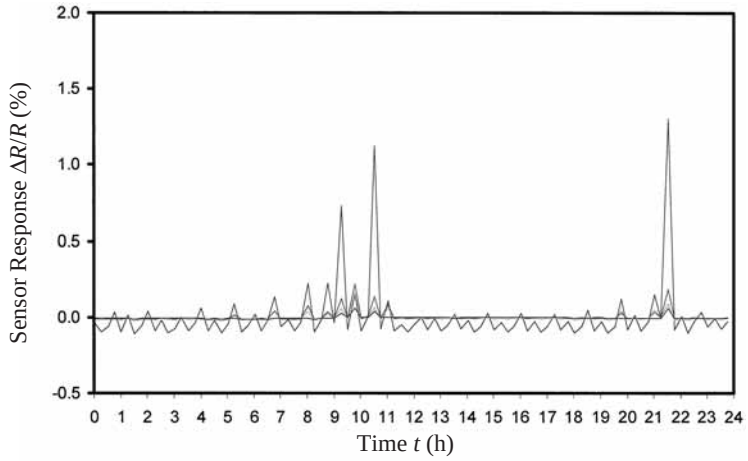


Fig. 2. Continuous monitoring of odour at the inlet of a sewage plant. The trace shows a 24 h recording using an array of four sensors sensitive to sulphurous odours. Odour events are recorded in real time; peaks are observed between between 0800–1100 and 2100–2200 h in this trace.

microbial activity. Additional odours may arise directly or indirectly from industrial wastewater or other discharges to sewers. Odorous components such as solvents, petroleum derivatives and other volatile organic compounds contribute directly to an odour problem, whereas indirect odour formation can be caused by highly degradable or warm effluents, or effluents with high sulphur content. In this case we had to choose a sensor system capable of measuring volatile organic chemicals, but which would not be degraded by the high sulphur content of the environment.

The requirements were for a device to monitor the odour of waste water at the inlet of a sewage plant, where continuous measurement of the organic load can be measured. The requirements are stringent —the device has to operate continuously in real-time transmitting odour concentration data so that abnormal organic or industrial loads are detected in time. Because this device needed to be operated in a very harsh outdoor environment, the packaging requirements were also stringent.

For this application —because of the constraints implied in using systems in an outdoor environment where temperature and humidity would vary greatly— we have chosen commercially available metal oxide sensors such as Taguchi gas sensors (TGS) (Figaro Inc., Japan) or Capteur sensors (now City Technology Ltd) as the core sensing element for an array of odour detectors.

We constructed microprocessor based electronics to measure the percentage change in resistance of the sensor array in response to volatile organic chemicals in the environment and incorporated automated sampling and filter systems to optimise the performance of the instrument in a harsh environment. These have proven to be robust in monitoring changes in odour level over time (see Fig. 2).

4. Smart Fire Detection Systems

Fire detectors such as discrete heat, ionisation or optical fire detectors are widely used in industrial premises. These detectors use a single sensor and generally are not able to discriminate between real fires and nuisance alarms. Fire brigades deplore a large number of false alarms that can be costly in both financial and human terms. Sensor combinations including gas sensors and specific signal processing algorithms have been used to address this problem. For instance, carbon monoxide sensors have been added to standard fire detectors since CO is generated in most fires.[7] However, all other sources of CO such as cigarette smoke or diesel engines potentially cause false alarms. Only the combination with another sensor type may avoid a false alarm. Another approach is to measure volatile organic compounds (VOCs) in smoke as they are produced in large numbers during combustion and can constitute "fingerprints" of fires.[8] This could be achieved at low cost using an e-nose with a dedicated sensor array for smoke detection. In this paper, we report the development of an e-nose for fire detection based on an array of eight sensors. One requirement of such a device is low power consumption, as it should run continuously and remotely from power mains or with a battery backup. Sensors made of conducting polymers (CP) based on aromatic or heteroaromatic compounds are therefore potentially suitable, as they can operate at room temperature. A big problem in fire detection is that of false alarms, and many optical detectors do not discriminate between different types of smoke. GC/MS analysis indicates that the odorous volatile profiles emitted from different type of standard fires can be characterised. We have developed a conducting polymer sensor array that allows discrimination of these profiles (Fig. 3).

4.1 *Analysis of smoke and identification of possible markers*

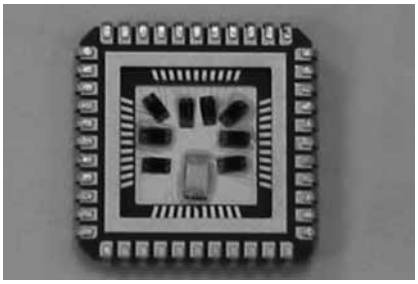
Four common fires (wood, paper, cotton, polyurethane) and a common source of nuisance (cigarette smoke) were generated in a purpose-built fire cabinet. Smoke was analysed using a portable Fourier transform ispectrometer GASMET DX-4000 (Ansyco, Germany) and a model Saturn 2200 gas chromatograph—mass spectrometer (Varian) equipped with a splitless injector, 30 m ZB1701 capillary column (Phenomenex) and a flame ionisation detector. Samples for GC-MS analysis were collected using solid phase micro-extraction (SPME) fibres. SPME fibres were obtained from Supelco (UK) and have a stationary phase 75 μm thick made of carboxen™/polydimethylsiloxane.

4.1.1 *Instrumentation*

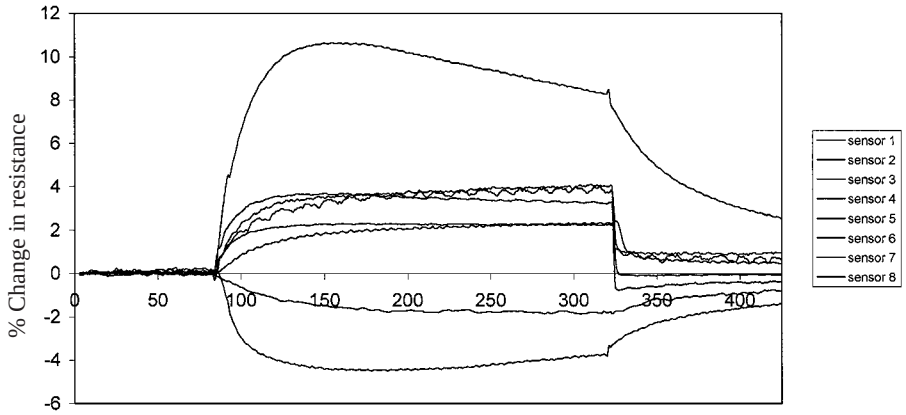
The prototype system incorporated a microprocessor-based system that measures sensor resistance changes, as described earlier. A dedicated sampling system has been built that includes a small pump and filters that protect the pump and the sensors from particulate materials in smoke.

4.2 *Results*

A number of markers have been identified for the five fire or nuisance events investigated and they are listed in Table 1. The sensors were interrogated with 10 ppm of a marker from each test fire. Fig. 3(b) shows the sensor array response of the system to hexanoic



(a)



(b)

Fig. 3. (a) Conducting polymer sensor array developed for fire detection. (b) Response of the array to a pulse of 10 ppm hexanoic acid, a marker for smouldering wood.

Table 1
Markers identified in smoke from four test fires and cigarette smoke using GC-MS/FTIR analysis.

Test fires	Markers
Smouldering cotton	furfural, 2-(3H) furanone
Smouldering wood	hexanoic acid, guaiacol and heptanoic acid
Smouldering paper	acetohydroxamic acid, hydrochloric acid
Cigarette smoke	pyridine, limonene, nicotine, isoprene,ammonia
Flaming polyurethane	benzonitrile, NO, NO_2, N_2O, HCN

acid, a marker for smouldering wood. Different response patterns were obtained for each marker tested. The responses of an in-line FTIR spectrometer and optical particulate detector sensors (Fig. 4 (top) are compared to the conducting polymer array (Fig. 4 (bottom)) for volatiles emitted from smouldering wood. A time course from the start of combustion is shown in the figure. The data indicate that the conducting polymer array may be just as sensitive as the conventional detectors of particulates but may also provide further discriminatory information.

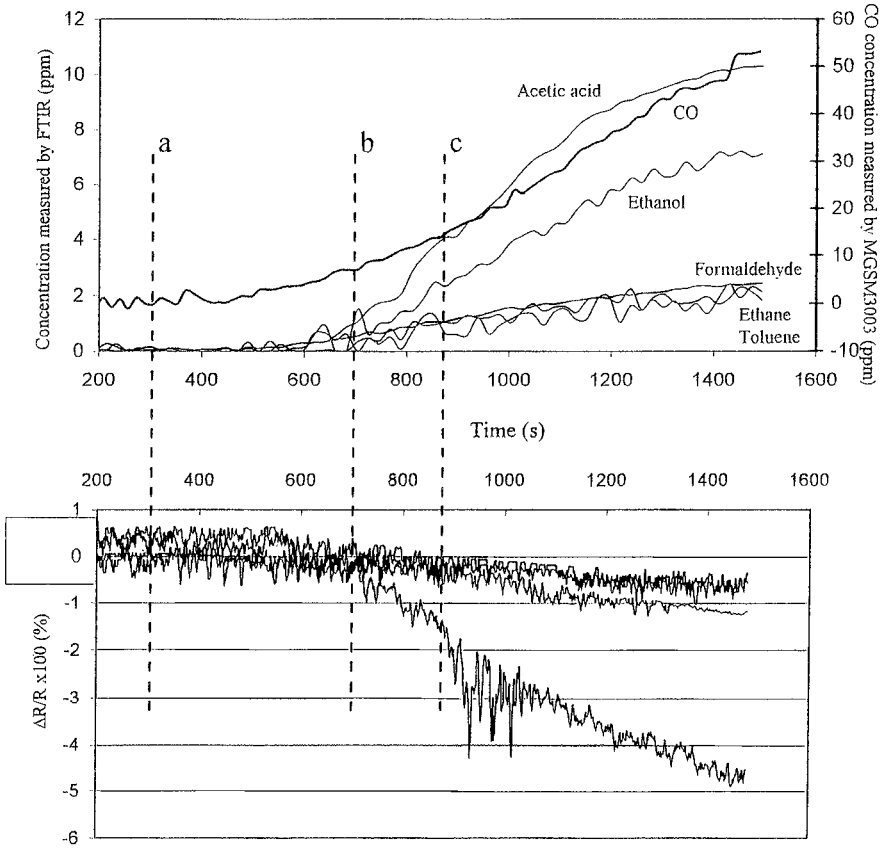


Fig. 4. Example of gas sensing using a conducting polymer array (bottom), VOC measurements using an FTIR (top), and optical particulate detector (Wagner GmBH) (top—bold trace), obtained for smouldering wood (a: fire starts, b: detection limit of optical detector, c: "fire alarm" according to particulate detector).

5. Conclusions

We show that odour sensor array-based technology can be applied to a variety of environmental applications providing the problems to be solved are well understood. When coupled to suitable sampling systems and pattern recognition software, odour sensor array technology can be used to produce instruments that fulfil a variety of sensing needs where a change of condition needs to be monitored.

Acknowledgements

This work was supported through a DTI Link project and EPSRC UK, in collaboration with: ECOLAB (Terminix), Stockport, UK, Yorkshire Water plc, and IST-2001-38404 project IMOS, through the European Commission, Brussels. This work was presented as an oral communication at ISOT 2004, Kyoto, Japan, July 2004.

References

1 T. C. Pearce, S. S. Schiffman, H. T. Nagle and J. W. Gardner eds.: Handbook of Machine Olfaction: Electronic Nose Technology (Wiley-VCH, Weinheim, 2002).
2 K. C. Persaud: Olfactory System Cybernetics: Artificial Noses, Handbook of Olfaction and Gustation, 2nd Edition, ed. R. L. Doty (Marcel Dekker, New York, 2001) p. 295.
3 A. Korpi, A. L. Pasanen and H. Viitanen: Building and Environment **34** (1999) 205.
4 K. C. Persaud, P. W. Wareham and A. M. Pisanelli: Solid Phase Microextraction for Field Sampling, Electronic Noses and Sensors for the Detection of Explosives, NATO ASI Series (Kluwer Academic Publishers, 2004) Chap. 17, p. 267.
5 H. G. Byun, N. Y. Kim, K. C. Persaud, J. S. Huh and D. D. Lee: Application of Adaptive RBF Networks to Odour Classification Using Conducting Polymer Sensor Array, Electronic Noses and Olfaction (IOP Press, Bristol, 2000) p. 121.
6 R. M. Stuetz, G. Engin and R. A. Fenner: Water Sci. Technol. **38** (1998) 331.
7 B. Peat: Physics World **6** (1993) 23.
8 G. A. Eiceman, A. Tarassov, P. A. Funk, S. E. Hughs, E. G. Nazarov and R. A. Miller: Journal of Separation Science **26** (2003) 585.