Sensors and Actuators B 69 (2000) 214–218
www.elsevier.nl/locate/sensorb

Electronic nose: a useful tool for monitoring environmental contamination

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Received 27 September 1999; accepted 28 February 2000

Abstract

The advances in the technology of multisensor arrays and neural computation have allowed the development of "electronic noses", which has enabled the discrimination of compounds by their odours and consequently, has played a fundamental role in the environmental monitoring. An electronic nose MOSES II (MOdular SEnsor System) with two arrays of eight (tin oxide and quartz microblance) sensors, each one manufactured by Lennartz Electronic/MoTech, was employed in this work. The aim of this research was to discriminate the following factors by odours: (a) small concentrations (ppm) of lindane and nitrobenzene in water, (b) dry solid insecticides (synthetic pyrethroids) such as permethrin, deltamethrin and cypermethrin, (c) mixtures of different quantities of cypermethrin in an inert substance, and (d) solutions of these pyrethroids in an appropriate organic solvent.

Contaminating residues of insecticides (lindane and syntethic pyrethroids) and products from the leather manufacture (phenols, nitrobenzene, anilines) are often offloaded into streams or rivers — despite the prohibition regulations — in heedless disregard of the danger they present to the health of the population and the survival of fish and flora.

Keywords: Electronic nose; Water contamination; Nitrobenzene; Lindane; Synthetic pyrethroids

1. Introduction

Few studies on water contamination were performed with electronic noses in comparison with the assessment of food quality, most of them devoted to monitoring changes in the organic contents of waste water [1–3], sewage treatment works [4,5] and water contamination with petroleum hydrocarbons [6].

Projects dealing with environmental monitoring consider water contamination with industrial effluents — e.g., nitrobenzene, mainly coming from the leather industry and lindane from the insecticide manufacturing sector. Lindane is toxic for human beings (ADI: 0.008 mg/kg). When it comes into contact with the skin, it penetrates this natural barrier (percutaneous absorption), acting on the nervous system and produces respiratory and digestive symptoms. Its toxicity in fish is produced at concentrations of 0.16–0.3 mg/l in water [7]. Nitrobenzene ($C_6H_5NO_2$) exhibits high oral and dermic toxicity, particularly among women, at concentrations of 200 mg/kg, causing acute blood tissue damage. When inhaled, it causes cyanosis due to the formation of methemoglobin leading to asphyxia severe enough to injure the cells of the central nervous system [8]. Prolonged exposure can lead to cancer. Moreover, it is a common air contaminant.

Mixtures of permethrin, deltamethrin and cypermethrin (synthetic pyrethroids) are used worldwide as insecticides for cotton, tobacco, fruit and vegetable crops. They are also employed on cereals, corn and soybean and on various other crops. The three compounds are active and odourless, particularly deltamethrin, which is used in forestry, protection of public health (e.g., Chagas disease control in South America, malaria control in Central America and Africa, against cattle infestation, lice, ants and cockroaches) and most commonly used to protect stored commodities (cereals, grains, coffee beans, dry beans). As might be expected for compounds that are fairly stable on leaf surfaces, the amount of residues found on the different parts of crops depends largely on direct exposure at the time of application. Further, wheat grains revealed residues of these insecticides even after milling and backing pro-

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0925-4005/00/$ - see front matter
PII: S0925-4005(00)00491-3

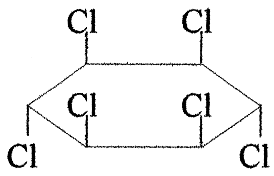

Fig. 1. Molecular structure of lindane.

cesses though in very low quantities. Even lactating cows, after a high dietary level of permethrin, revealed residues in their milk. However, all these insecticides (even the most active, deltamethrin) are not deemed as seriously toxic for human beings or hot-blooded animals (third class for the World Health Organization) but are toxic (mainly deltamethrin) for aquatic organisms: fish and crustacea as well as useful insects like honeybees [9–11]. These popular compounds are generally dissolved in organic solvents to fabricate commercial insecticides. As the solutions are sprayed or fumigated, organic solvents are easily volatilized leaving solid, highly water insoluble residues. By subsequent cleaning of fumigated places, residues are drawn to flowing waters, leading to the contamination of fauna.

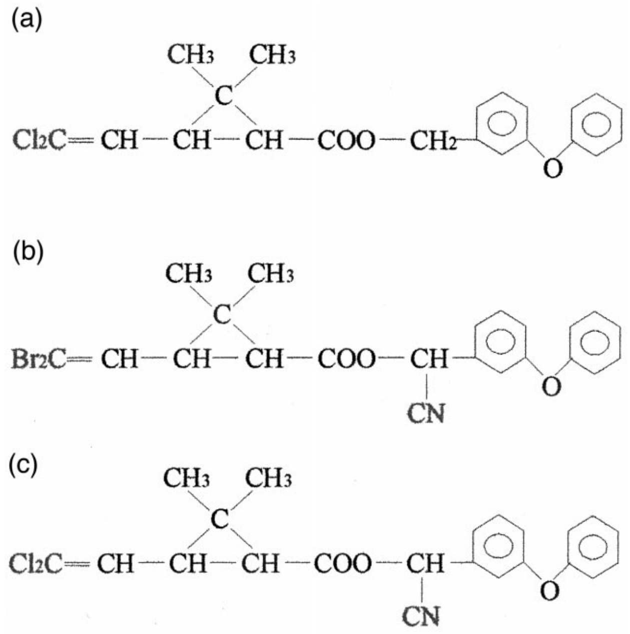

Fig. 3. (a) Molecular structure of permethrin. (b) Molecular structure of deltamethrin. (c) Molecular structure of cypermethrin.

2. Experimental procedure

Lindane, $C_6H_6Cl_6$ (Fig. 1) or 1α,2α,3β,4α,5α,6β-hexachlorocyclohexane (IUPAC) is an insecticide that is soluble water: 7.3 mg/l at 25°C. It is extremely stable when exposed to light, air and acids, and at temperatures of up to 180°C. In alkalis, it undergoes dehydrochlorination [7].

To prepare the specimens, solutions of lindane in water were obtained from an initial solution of 3.8 mg/l (∼4 ppm). The employed solutions had the following concentrations: 4, 2 and 1 ppm.

Nitrobenzene, $C_6H_5NO_2$ (Fig. 2) exhibits a low solubility in water: 0.019 mg/l at 20°C [12]. Water solutions were prepared from a saturated 2000-ppm solution. The final solutions had the following concentrations: 1000 and 500 ppm, respectively. These solutions, as well as pure nitrobenzene and distilled water specimens, were measured.

The permethrin molecular formula is $C_{21}H_{20}Cl_2O_3$ (Fig. 3a) exhibiting four isomers (two *cis* and two *trans*). The *cis* form is the most active as an insecticide. It shows low solubility in water (0.2 mg/l at 30°C) and a considerable solubility in organic solvents (acetone, xylene, hexane, methanol, ethanol, etc.) [9].

Deltamethrin has the following molecular formula: $C_{21}H_{19}Br_2O_3CN$ (Fig. 3b) and it is the first pyrethroid composed of a single isomer of eight stereoisomers. It is stable when exposed to heat (6 months at 40°C), light and air but unstable in an alkaline media. It is practically insoluble in water (0.002 mg/l at 20°C) but soluble in organic solvents (acetone, ethanol, cyclohexane, dioxane, xylene, etc.) [10].

Cypermethrin, whose molecular formula is $C_{21}H_{19}O_3$-Cl_2CN (Fig. 3c), exhibits three asymmetric centres giving rise to eight isomers. It is virtually insoluble in water (0.009 mg/l at 20°C) but it is considerably soluble in organic compounds (acetone, cyclohexanona, ethanol, chloroform, etc.). It decomposes at 220°C [11].

The synthetic pyrethroids (samples I) consisted of equal weight (∼65 mg) of pure solid permethrin (P), deltamethrin (D), cypermethrin (C) and an isolated permethrin *cis*-isomer (CP), which were placed in closed vials. Synthetic air containing vials were intercalated between

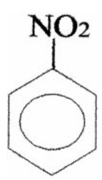

Fig. 2. Molecular structure of nitrobenzene.

Table 1
Samples corresponding to mixture of cypermethrin and alumina

Samples III	% w Cypermethrin/w alumina
A	0
B	4.125
C	8.250
D	12.375
E	100

Table 2
Samples corresponding to mixtures of cypermethrin and distilled water

Samples IV	% w Cypermethrin / w water
A′	0
B′	0.7
C′	1.4
D′	1.4

subsequent measurements to assure the complete elimination of gases coming from the former measurement. Samples II consisted of equal volumes of acetone solutions of each insecticide (0.16% w/w) placed in each vial. Samples III were intimate mixtures of powdered cypermethrin with an inert solid compound (pure and fine particles Al_2O_3 powder) (Table 1) while samples IV were suspensions of solid cypermethrin in distilled water (in which the pyrethroid is practically insoluble) (Table 2). Both types of mixtures were used for determining the nose detection ranges in monitoring insecticide residues that contaminate the environmental atmosphere or even foods.

Samples were taken by the Dani HSS 86.50 headspace sampler and thermostated at 75°C, employing synthetic air as carrier. The principal component analysis (PCA) was the statistical method employed to analyse the results.

3. Results and discussion

Fig. 4 is the plot of the PCA data for different concentrations of lindane aqueous solutions. An easy discrimination of the analysed solutions was possible because they were specimen data clustered in four different regions. A minimal detection level of the electronic nose of 1 ppm was established in the case of lindane solutions. Most of the information (99.8%) is provided by PC1 + PC2 (Fig. 4) — implying that the remaining components contribute only to 0.2% of the information. The proximity of points in each enclosure demonstrated that the results of successive measurements were in agreement (corresponding each point to a vial) while the separation among clusters clearly pointed out the discrimination of different concentration of solutions.

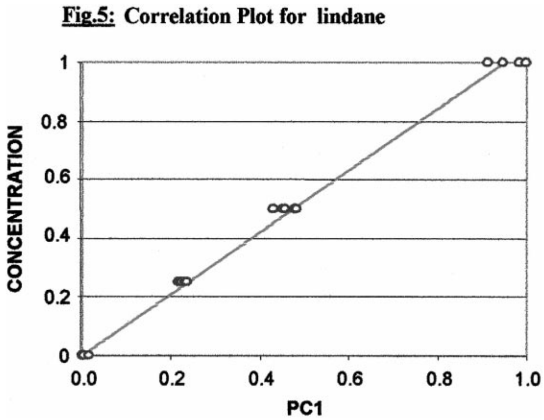

Fig. 5. Correlation plot for lindane.

Fig. 5 is the linear correlation between the instrumental measurements (PC1: *x*-axis) and the concentration of employed solutions (*y*-axis) with a correlation factor of 0.988.

Fig. 6 is the plot of the PCA data of specimens of pure nitrobenzene, their aqueous solutions and pure water, where the more weakly concentrated solutions do not exhibit adequate separation among them since sensors signals from aqueous solutions resulted quite differently from that of pure nitrobenzene.

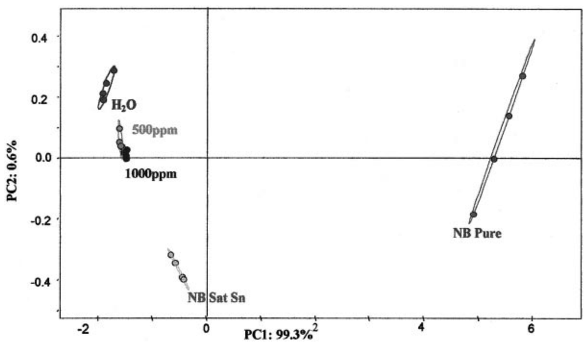

Fig. 6. PCA plot for nitrobenzene specimens.

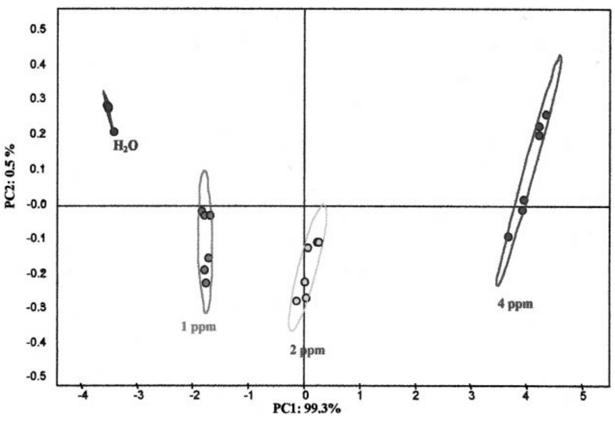

Fig. 4. PCA plot for lindane aqueous solutions.

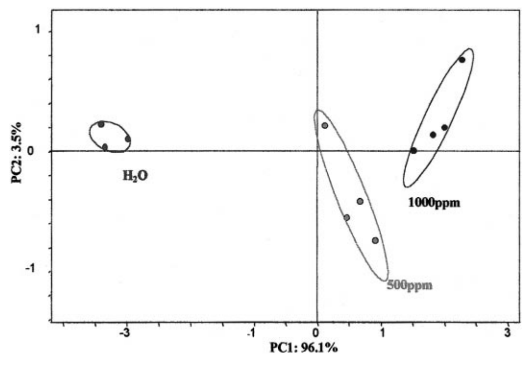

Fig. 7. PCA plot for nitrobenzene dilutions.

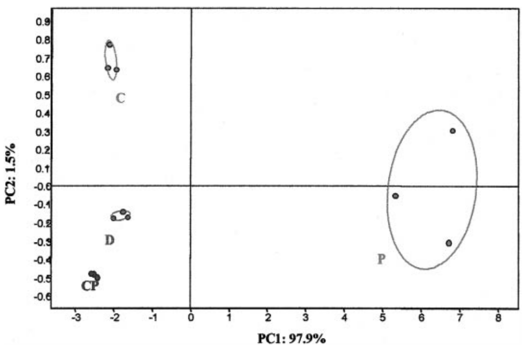

Fig. 8. PCA plot corresponding to dry solid synthetic pyrethroids.

The discrimination of the diluted solutions was performed when pure nitrobenzene and saturated solutions of plot of Fig. 6 were not taken into account (Fig. 7).

A minimal detection level of nitrobenzene contaminant in water of ~ 500 ppm was determined in this work; PC1 + PC2 contributed to 99.6% of the information while all the remaining components have given only 0.4%. Dots inside the enclosures have the same meaning as that in Fig. 4.

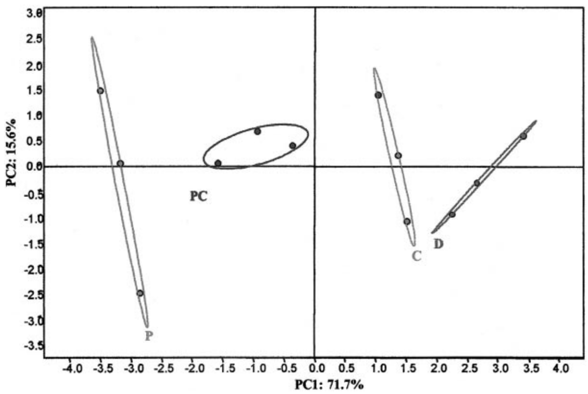

Fig. 9. PCA plot corresponding to the solutions in acetone of the insecticides.

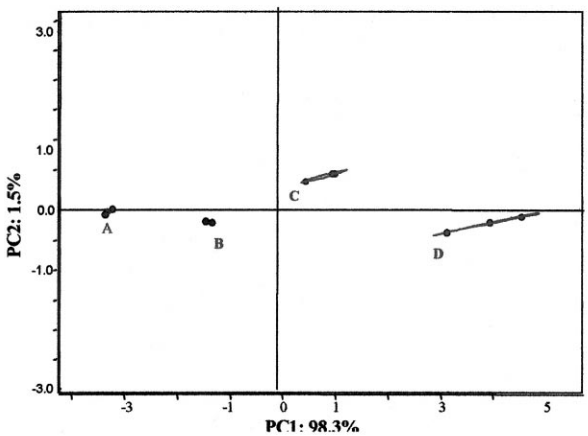

Fig. 10. Different quantities of powder cypermethrin in alumina.

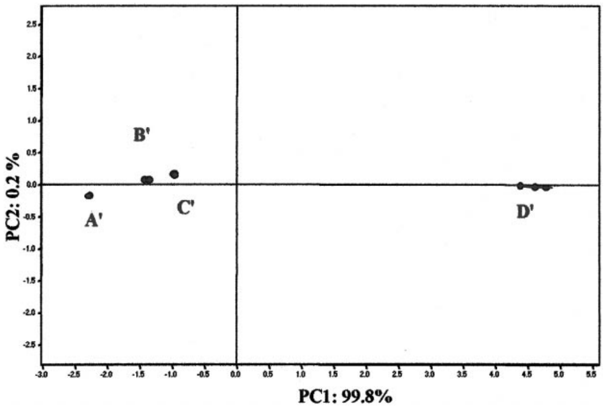

Fig. 11. Different quantities of powder cypermethrin in water.

In this case, only tin oxide sensors were used for PCA plots. The response of these sensors is due to the changes of surface resistivity in relation to the oxidating or reducing properties of gas analytes.

Fig. 8 is the PCA plot corresponding to the three pure, dry, powdered synthetic pyrethroids (samples I), where C is cypermethrin, D is deltamethrin, P is permethrin and CP is *cis*-permethrin. It is easy to observe a very good discrimination of the four compounds considering the fact that all of them are odourless to the human nose.

The eight tin oxide sensors and seven quartz microbalance sensors were used for the PCA plot in this case.

Fig. 9 is the PCA plot corresponding to the solutions in acetone of the three insecticides (samples II) in which an excellent discrimination was also observed.

Fig. 10 is the plot of the mixture of different quantities of solid cypermethrin with alumina (inert powder), as reported in Table 1. It is possible to observe that the enclosures corresponding to the decreasing quantities of cypermethrin approaches that of the pure alumina enclosure.

Fig. 11 is the PCA plot of cypermethrin suspensions in distilled water (Table 2) showing similar results to those of Fig. 10. In these cases, only tin oxides were used.

4. Conclusions

The MOdular SEnsor System (MOSES) II electronic nose with sensors has proven to be a useful tool for the discrimination of two water contaminants, lindane and nitrobenzene, in very low concentrations (1 and 500 ppm, respectively) through a fast, simple and reproducible analysis of their odours.

MOSES II also enabled the satisfactory discrimination of odourless insecticides (synthetic pyrethroids) in very small quantities as $\sim 6 \times 10^{-2}$ g for pure solid residues, as $\sim 4\%$ w/w for homogenous mixtures of powdered pyrethroids in alumina and 0.7% w/w of cypermethrin suspensions in distilled water.

It has been important to evaluate the low olfaction range of MOSES II for solid pyrethroid residues. Usually, insecticides are obtained by dissolving the solid pyrethroids in organic solvents, which are easily evaporated during fumigation, leaving solid residues that for long time if wet cleaning is not performed. In any case, the pyrethroids discrimination in humid media performed in this work was also important since, by subsequent cleaning, solid residues eventually reach streams and rivers — consequently damaging of their fauna and flora.

Another interesting result of this work was accomplished through the detection of low quantities of pure powdered pyrethroids through MOSES II. The requirement of solid residues detection has arisen from professionals belonging to a neighbouring enthomotoxicology research group at CITEFA (CIPEIN–CONICET), who are developing a shampoo to combat lice in human beings and who needed to reckon with a fast and simple discrimination method for solid pyrethroids residues

Acknowledgements

The authors are indebted to the German government through the donation of the MOSES II electronic nose to the PRINSO–CONICET–CITEFA within the auspices of the scientific cooperation between the IPCT–Tübingen University and the PRINSO.

Thanks are given to CIPEIN–CONICET–CITEFA for providing the pyrethroids used in this work.

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Biographies

Rosa E. Baby received her Chemistry Licentiate Degree in 1985 from the University of Buenos Aires. She has been a member of the Technical Career of CONICET (National Council for Scientific and Technological Research) since 1992. She joined the National Technological University (UTN) in 1990 as Chemistry Assistant Professor. She is now performing research at the PRINSO (Program of Solid State Research)–CONICET at CITEFA (Armed Forces Institute for Scientific and Technological Research) in the Gas Sensors Area.

Marcelo Cabezas received his System Programmer Degree in 1997 and has been a member of the Technical Career of CONICET since 1989. In 1988, he joined PRINSO (Program of Solid State Research)–CONICET at CITEFA in the Gas Sensors Area, where he is currently performing research work.

Elisabeth N. Walsöe de Reca received her PhD in Chemistry from the University of Buenos Aires (UBA) on 1966. In the same year, she joined CONICET in the Scientific Researchers Career and CITEFA, where she has been performing research in Materials Science up to the present. She has headed the PRINSO since 1980 and for 16 years, she was a Solid State Physics Professor at the UTN (National Technological University). She is presently a Post-Degree Professor at the Faculty of Engineering — UBA and the UNSAM (National University of San Martin). Dr. Walsöe de Reca has directed numerous doctoral theses (Physics, Chemistry and Engineering). She has authored more than 200 papers, reviews and books on functional materials, gas sensors and infrared detectors.