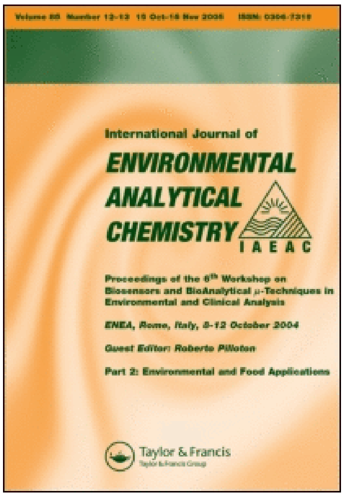


International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Determination of Selected Organic Pollutants in Indoor Air using Permeation Passive Samplers

J. Namieśnik[a]; T. Górecki[a]; B. Kozdroń[a]; L. Torres[b]
[a] Institute of Inorganic Chemistry and Technology, Technical University of Gdańsk, Gdańsk, Poland [b] Ecole Nationale Superieure de Chimie, Toulouse, Cedex, France

To cite this Article Namieśnik, J. , Górecki, T. , Kozdroń, B. and Torres, L.(1989) 'Determination of Selected Organic Pollutants in Indoor Air using Permeation Passive Samplers', International Journal of Environmental Analytical Chemistry, 37: 3, 139 — 147

To link to this Article: DOI: 10.1080/03067318908026894

URL: http://dx.doi.org/10.1080/03067318908026894

Intern. J. Environ. Anal. Chem., Vol. 37, pp. 139–147
Reprints available directly from the publisher
Photocopying permitted by license only

DETERMINATION OF SELECTED ORGANIC POLLUTANTS IN INDOOR AIR USING PERMEATION PASSIVE SAMPLERS*

J. NAMIEŚNIK,† T. GÓRECKI and B. KOZDROŃ

Institute of Inorganic Chemistry and Technology, Technical University of Gdańsk, PL 80-952 Gdańsk, Poland

L. TORRES

Ecole Nationale Superieure de Chimie, 31077 Toulouse Cedex, France

(Received 5 October 1988; in final form 5 November 1988)

KEY WORDS: Organic pollutants, indoor air, permeation passive dossimeter

INTRODUCTION

Man spends ca. 70% of his time in closed areas. Hence, the quality of indoor air is of utmost importance to his health. Extensive use of organic paints, enamels, adhesives, plastics, preservatives, etc., results in deterioration of indoor air quality.[1] Direct determination of organic compounds in indoor air by means of a majority of currently used detectors is impossible due to their usually extremely low concentration. Hence, a preconcentration step is required. Preconcentration is most often accomplished by pumping a certain known volume of the examined air through a suitable adsorbent or absorbent. Charcoal tube (CT) constitutes an example of one of the most commonly employed in such methods sorbent traps.[2, 3] However, dynamic sampling techniques have certain disadvantages. The greatest one is the necessity of using pumps, which require power supply and are quite expensive.

Passive sampling seems to be a promising alternative to dynamic methods. Beginning from 1973, when the first papers have been published on use of passive samplers for quantitative analysis,[4, 5] they are becoming increasingly popular. The scope of their application includes determination of both inorganic and organic

---

*Partly presented at the 18th International Symposium on Environmental Analytical Chemistry and 4th International Congress on Analytical Techniques in Environmental Chemistry, September 5–8, 1988, Barcelona, Spain.

†Author to whom correspondence should be addressed.

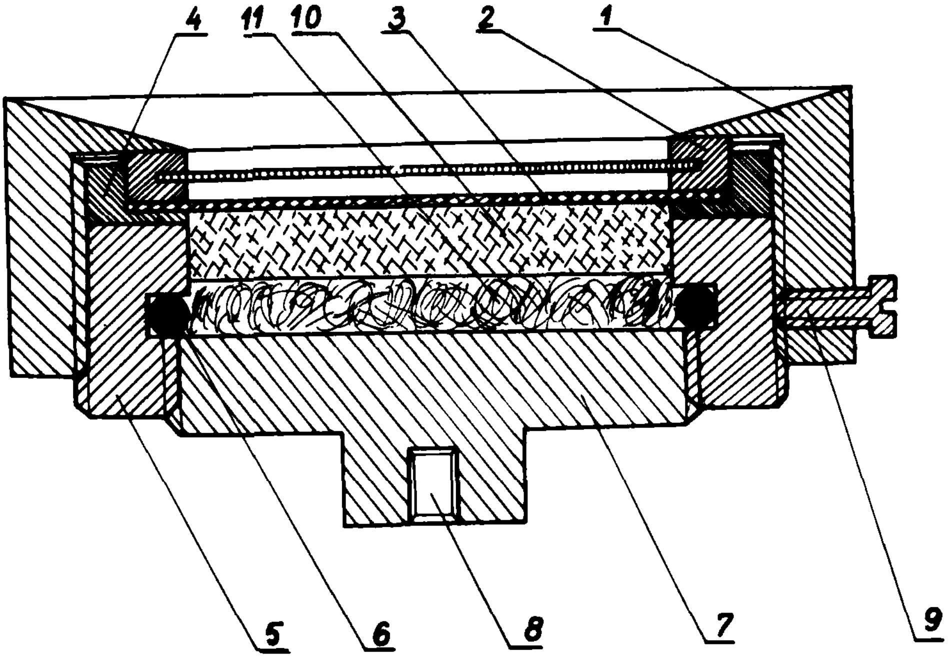


Figure 1 Passive sample design: 1. outer shield; 2. washer with metal gauze; 3. membrane; 4. teflon washer; 5. sampler body; 6. rubber O-ring; 7. back cover; 8. holder socket; 9. fastening screw; 10. active carbon bed; 11. cotton wool.

substances in workplace atmosphere, area monitoring, etc.[6] Two basic types of passive samplers can be distinguished, viz. diffusive and permeation ones. Diffusive samplers are characterized by a simple design and possibility of fully-automated sample recovery. Sampling rate of these samplers can be calculated from the dimensions of a sampler and known value of the diffusion coefficient.[7] However, they can be affected by ambient air velocity, temperature, humidity, etc.

Permeation passive samplers are devoid of majority of these drawbacks. On the other hand, their design is more complicated, and sampling rate must be determined individually for each component (and very often also for each sampler due to non-uniformity of membrane materials).

The presented research aimed at development of a passive sampler capable of determination of trace levels of organic pollutants in indoor air during long-term investigations. Benzene, toluene, m-xylene and butyl acetate were chosen as the determined compounds due to great impact on human health they induce.

EXPERIMENTAL

A permeation type passive sampler developed by the authors[8] was chosen due to a negligible effect exerted by environmental conditions on the results. The design of the sampler is presented in Figure 1. The sampler is made of polyamide. A chamber in the body (5) contains 200 mg of active carbon 40–50 mesh (10) used as a sorbent.

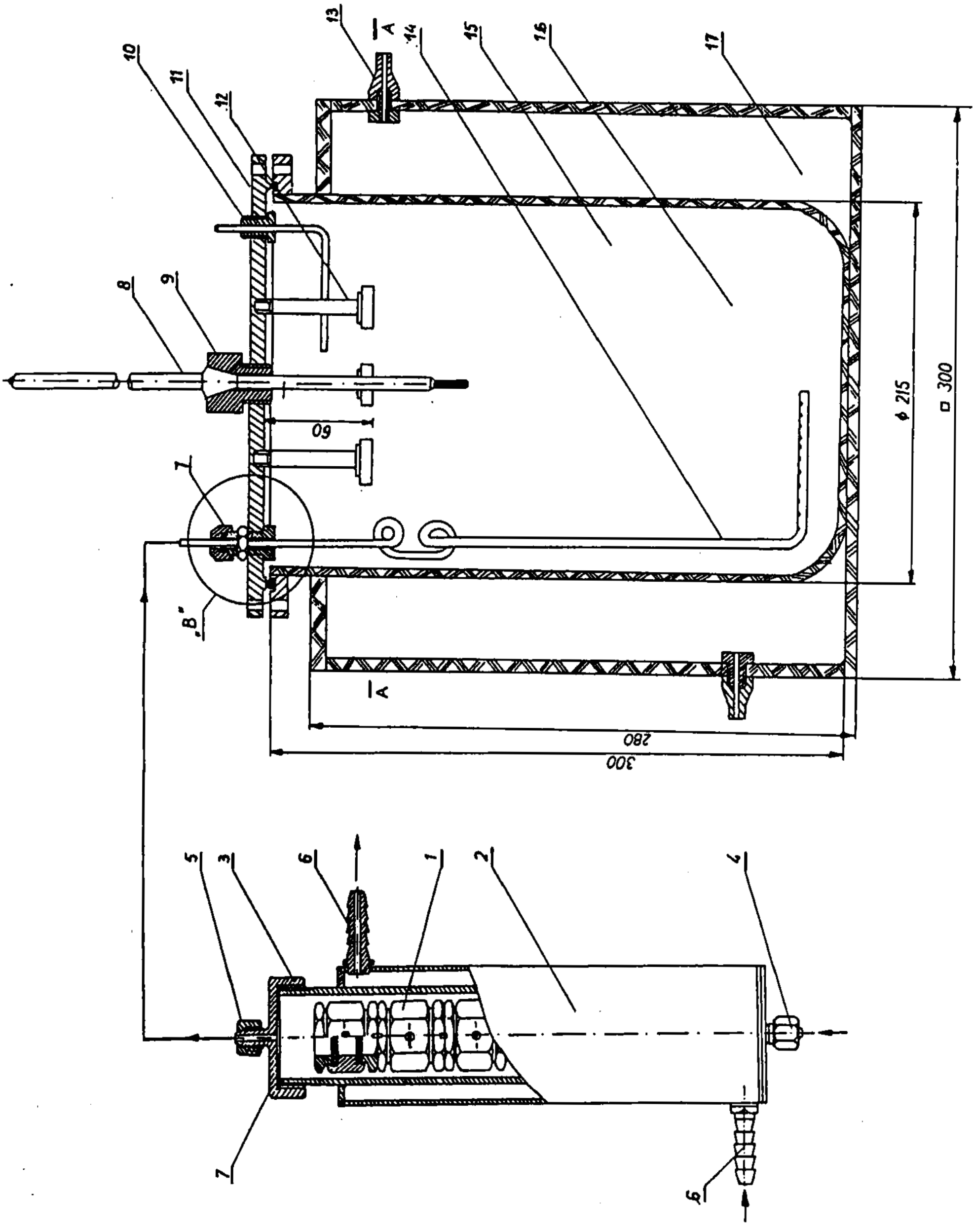
Table 1 Materials used as membranes in permeation type passive samplers

No. of membrane	*Membrane material*	*Thickness (mm)*
1	Polyethylene film I	0.010
2	Polyethylene film II	0.020
3	Polyester film	0.050
4	Nylon gauze covered with POLASTOSIL M-60 silicone rubber	0.200
5	Tissue paper I covered with POLASTOSIL M-60	0.160
6	Tissue paper II covered with POLASTOSIL M-60	0.100
7	Tissue paper III covered with POLASTOSIL M-60	0.090
8	Silicone rubber	0.580
9	Tissue paper I covered with SILAK M-11 silicone rubber	0.040
10	Tissue paper II covered with SILAK M-11	0.035
11	Tissue paper III covered with SILAK M-11	0.045
12	Polyethylene film II covered with SILAK M-11	0.040

Sorbent bed is isolated from the examined atmosphere by a thin membrane (3) made of a suitable material. The membrane is protected by a metal gauze (2). Both the membrane and gauze situated in a PTFE washer (4) are pressed to the body by a threaded cover (1). The chamber in the body is closed by a back cover (7) and sealed by an o-ring (6). The empty space in the chamber is filled with cotton wool (11), immobilizing the sorbent which enables the sampler to be used in an arbitrary position. All the parts of the sampler were precleaned by prolonged washing with n-hexane and methanol, and subsequently by heating in a drier at 80 °C for a few hours.

Proper selection of a membrane material constitutes an important stage in developing an analytical procedure utilizing permeation passive sampling. Membrane material should be hydrophobic, yet permeable to the determined substances to the highest possible extent. It is important that the membrane should be hydrophobic because concentration of water vapour in indoor air is much higher than concentrations of the determined substances, and water permeating through a membrane can deactivate the sorbent, particularly in cases when it has hydrophillic properties (majority of commonly used solid sorbents). A number of commercially available (polyethylene films, polyester films, silicone rubber) and home made materials (base material impregnated with silicone polymers delivered by the Research and Development Division of the Institute of Industrial Chemistry in Nowa Sarzyna, Poland) were examined. The tested membrane materials are listed in Table 1.

A basic criterion of evaluation of a membrane material is a sampling rate of a given substance. Small sampling rates result in poor sensitivity and necessity of application of prolonged exposure times. Sampling rate must be determined individually for each substance and each sampler. Exposition of samplers to known concentrations of the determined compounds for a known time constitutes the most commonly applied method of sampling rate determination, although other methods are also used.[9] The design of an exposure chamber for calibration of membrane materials is presented in Figure 2. The chamber consists of a 10 l


1
2
3
4
5
6
6
7
7
8
9
10
11
12
13
14
15
16
17
„B"
A
A
60
ϕ 215
□ 300
280
300

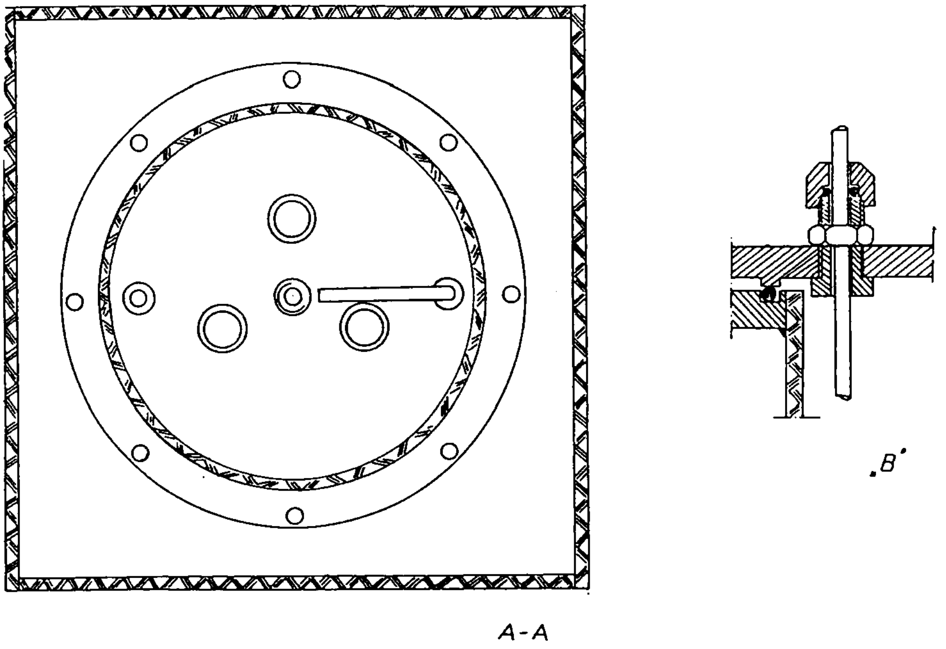


Figure 2 Exposure chamber for calibration of passive samplers: 1. permeation vessel; 2. standard gaseous mixtures generator; generator cover; 4. diluting gas inlet; 5. standard mixture outlet; 6. connections with thermostat; 7. standard mixture inlet; thermometer; 9. thermometer socket; 10. outlet; 11. chamber cover; 12. sampler; 13. connections with thermostat; 14. perforated tu supplying standard mixture to the bottom of the chamber; 15. exposure chamber body; 16. water jacket.

glass beaker (15) sealed in a thermostated water jacket (17). A stream of air (from which organic compounds were removed by oxidation on heated Körbl catalyst) flows through a standard gaseous mixtures generator (2) and is directed to the bottom of the chamber through a perforated tube (14). The components of a standard mixture are trapped by passive samplers (12) with a rate proportional to their concentration and dependent on the membrane material. Dynamic generation of a standard multicomponent mixture by means of permeation sources was selected as optimal, since it assures good accuracy and stability of concentration in the chamber.[10] The volume of air passing through the chamber was controlled by precision needle valves and additionally determined with a gas meter connected to the outlet of the chamber.

Membrane materials were preliminary examined in a single exposure run. Six samplers were exposed simultaneously. Sampling rates determined during such exposures constituted a criterion for selection of materials for further, more detailed investigations. The selected materials were subjected to 7 exposures. The amount of trapped substances was determined chromatographically after desorption by means of carbon disulphide. A Hewlett-Packard HP 5830A gas chromatograph equipped with a 18830A GC terminal and a 2 m × 2 mm i.d. column packed with 10% of Carbowax 20 M on Chromosorb W-AW-DMCS was used. One microliter aliquots were analysed. Temperature of the column was equal to 100 °C.

After such an examination some of the samplers were utilized for the determination of the level of benzene, toluene and m-xylene in six flats. The results were calculated from the known values of mass of trapped compound (M), exposure time (t) and calibration constant (k):

$$c=\frac{Mk}{t} \tag{1}$$

where c—unknown concentration.

RESULTS AND DISCUSSION

Table 2 presents the results of calibration of some of the samplers equipped with home made membranes, while Table 3—of samplers equipped with membranes made of commercially available polyethylene film of 10 μm thickness. The values of a and b correspond to intercept and slope of calibration curves, respectively, r is the linear correlation coefficient, and k is the calibration constant. The conditions of exposition are listed under the tables.

It follows from Tables 2 and 3 that linearity of calibration curves measured by the value of linear correlation coefficient is quite satisfactory in all the cases. Home made membrane materials are characterized by higher sampling rates (smaller values of calibration constant) compared to polyethylene membranes, despite much smaller thickness of the latter. The phenomenon agrees with expectations, since silicone rubber is characterized by large values of permeation constants of

Table 2 Statistical parameters of calibration curves and calculated values of calibration constants (k) of selected passive samplers[a]

Sampler no.	*Membr. no. see Table* 1	*Compound*	a [*mg*]	$b \times 10^{-6}$	r	$k \times 10^{6}$ [$min\ m^{-3}$]
12	4	benzene	−0.250	334.3	0.990	0.27
		toluene	−0.019	40.0	0.981	0.25
		m-xylene	0.045	72.4	0.984	0.28
		b. acet.	−0.004	3.7	0.992	0.16
13		benzene	−0.299	329.0	0.988	0.28
		toluene	−0.038	41.5	0.989	0.25
		m-xylene	−0.053	75.8	0.988	0.29
		b. acet.	−0.005	3.6	0.986	0.17
14	6	benzene	−0.125	86.7	0.979	1.08
		toluene	−0.024	16.5	0.978	0.65
		m-xylene	−0.067	54.2	0.978	0.57
		b. acet.	−0.001	1.6	0.975	0.37
15		benzene	−0.122	91.7	0.984	1.02
		toluene	−0.021	17.0	0.987	0.62
		m-xylene	−0.043	43.8	0.992	0.51
		b. acet.	−0.002	1.6	0.993	0.38
16	5	benzene	−0.066	46.4	0.982	2.02
		toluene	−0.014	9.8	0.981	1.08
		m-xylene	−0.378	29.4	0.983	2.51
		b. acet.	−0.002	1.0	0.986	0.64
17		benzene	−0.064	52.5	0.983	1.76
		toluene	−0.012	10.6	0.984	0.99
		m-xylene	−0.022	29.8	0.987	0.74
		b. acet.	−0.001	1.0	0.992	0.60

[a] *Calibration conditions.* Concentration of compounds: benzene 86.40 mg/m^3; toluene—9.80 mg/m^3; m-xylene 21.06 mg/m^3; butyl acetate—0.57 mg/m^3; Exposure times: 1000÷28000 min; Number of exposures 7; Std. mixture flow rate: 30 ml/min.

Table 3 Statistical parameters of calibration curves and calculated values of calibration constants (k) of selected passive samplers[a]

Sampler no.	*Membrane type*	*Compound*	a [*mg*]	$b \times 10^{-6}$	r	$k \times 10^{6}$ [$min\ m^{-3}$]
3	POLYETHYLENE 0.010mm	benzene	−0.034	29.5	0.994	2.24
		toluene	−0.016	8.4	0.980	0.90
		m-xylene	−0.064	28.3	0.975	0.58
4		benzene	−0.006	23.4	0.997	2.69
		toluene	−0.006	6.5	0.990	1.10
		m-xylene	−0.027	22.6	0.989	0.68
5		benzene	−0.010	23.9	0.994	2.66
		toluene	−0.007	6.9	0.984	1.04
		m-xylene	−0.030	24.0	0.988	0.64
6		benzene	−0.012	25.8	0.983	2.47
		toluene	0.003	6.2	0.961	1.06
		m-xylene	0.085	21.4	0.969	0.55
10		benzene	−0.048	39.2	0.995	1.70
		toluene	−0.014	9.2	0.987	0.80
		m-xylene	−0.040	27.3	0.992	0.57
11		benzene	−0.034	34.2	0.996	1.92
		toluene	−0.075	7.9	0.989	0.82
		m-xylene	−0.023	24.7	0.992	0.61

[a] *Calibration conditions.* Concentration of compounds: benzene—61.98 mg/m^3; toluene—6.78 mg/m^3; m-xylene—14.33 mg/m^3; Exposure times: 5700÷43260 min; Number of exposures 7; Std. mixture flow rate: 30 ml/min.

Table 4 Results of determination of aromatic hydrocarbons in indoor air of selected flats using permeation type passive samplers

Examined area	*Exposure time [min]*	*No. of sampler*	*Time-weighted average concentration [mg/m^3]*		
			benzene	*toluene*	*m-xylene*
Flat no. 1	39035	13	<0.004	<0.004	0.379
Living room		15	0.023	<0.009	0.390
		17	<0.027	<0.015	0.398
Flat no. 2	52948	13	0.063	0.072	0.018
Living room		15	0.088	0.084	<0.006
		17	0.109	0.180	<0.008
Flat no. 3	27360	12	0.133	0.105	0.044
Living room		14	0.498	0.254	0.026
		16	0.392	0.343	0.055
Flat no. 4	38970	13	0.173	1.310	0.240
Kitchen		15	0.201	0.922	0.282
		17	0.278	1.354	0.415
Flat no. 5	43200	12	0.145	0.200	0.133
Living room		14	0.358	0.302	0.143
		16	0.517	0.268	0.395
Flat no. 6	50320	13	0.082	0.156	0.079
Living room		15	0.256	0.276	0.122
		17	0.426	0.327	0.150

organic compounds. Moreover, it is well known that permeability of silicone rubber to water is also much smaller than that of polyethylene. Hence, silicone rubber based membrane materials are more suitable for application in passive samplers assigned for sampling organic compounds.

From the group of home made membranes, the membranes made of nylon gauze impregnated with Polastosil M-60 silicone rubber (room temperature vulcanizing polymer based on methylpolysiloxanes with free silanol groups) were characterized by the highest sampling rates. On the other hand, their mechanical properties were quite poor. Tissue paper based membranes had smaller sampling rates, yet they were more robust, hence more appropriate for routine use. The differences in sampling rates of particular samplers equipped with same-type membranes were smaller than 25%, which indicates the possibility of calibration of only the membrane material, and not individual samplers. However, such a conclusion can be drawn only provided the number of examined individual samplers is much greater.

Some of the samplers equipped with silicone rubber based membranes were put to a preliminary test under field conditions. For this purpose, they were exposed in six flats for prolonged periods. Such an approach to examination of indoor air quality seems reasonable, since it enables evaluation of real long-term time-weighted average concentration of pollutants the inhabitants are subjected to, i.e. it takes into account the conditions of ventilation under normal exploitation of flats. The results of the tests are listed in Table 4. It follows from this table that the samplers are capable of determination of low levels of the examined organic substances. The differences between the individual samplers are due to random factors, e.g. localization of a sampler in a room. It should be mentioned that nearly in all the examined flats the levels of the determined compounds were higher than maximum allowable concentration, which is equal in Poland to 0.07, 0.2 and 0.1 mg/m^3 for benzene, toluene and xylene, respectively.[11] Generally, the levels of organic pollutants in indoor air were higher in new flats and in flats with new furniture.

CONCLUSIONS

From the examined membrane materials home-made membranes based on silicone polymers occurred to be the most suitable. Their sampling rate determining the sensitivity of the method can be further increased by application of thinner, yet robust base materials, because sampling rate depends on diffusional resistance, which is directly proportional to membrane thickness. Linearity of calibration curves measured by the value of linear correlation coefficient is quite satisfactory. Further experiments are required in order to establish whether the prepared membranes are uniform enough so that only the membrane material can be calibrated, and not individual samplers. Suitability of the developed samplers for the control of indoor air quality has been preliminary confirmed in field tests.

References

1. A. Niesłochowski, *Ochrona Powietrza* **6**, 130 (1984).
2. B. E. Saltzmann, *J. Assoc. of Anal. Chem.* **62**, 214 (1978).
3. J. Namieśnik, *Talanta* **35**, 567 (1988).
4. E. D. Palmes and A. F. Gunnison, *Am. Ind. Hyg. Assoc. J.* **34**, 78 (1973).
5. K. D. Reiszner and P. W. West, *Environ. Sci. Technol.* **7**, 526 (1973).
6. J. Namieśnik, T. Górecki, E. Kozłowski, L. Torres and J. Mathieu, *Sci. Total Environ.* **38**, 225 (1984).
7. N. Van Den Hoed and M. T. Halmans, *Am. Ind. Hyg. Assoc. J.* **48**, 364 (1987).
8. J. Namieśnik, T. Gorecki and E. Kozlowski, *EUROANALYSISVI*, Paris, Sept. 1987, Abstracts, p. 361.
9. S. Zaromb and T. M. Beasley, *J. Chromatogr.*, in print.
10. J. Namieśnik, *J. Chromatogr.* **300**, 79 (1984).
11. Decree of the Ministry of Health of Poland from 25th January 1986 on maximum allowable concentrations of selected substances in inhabited closed areas.