

CHROM. 20 840

APPLICATION OF HEADSPACE GAS CHROMATOGRAPHY TO THE MEASUREMENT OF ORGANIC EMISSIONS

A.M. CANELA* and H. MUEHLEISEN

Sandoz Ltd., Building 360/503, P.O. Box, 4002 Basle (Switzerland)

SUMMARY

A method is presented for the determination of volatile organic compounds in industrial air emissions, based on sampling by means of either active or passive adsorption on active charcoal and silica gel, followed by headspace gas chromatographic analysis. An improvement in the identification and determination of priority pollutants is achieved by coupling the headspace gas chromatograph with a mass spectrometer (ion-trap detector). The detection limits conform to current legal requirements. The method can easily be used for similar applications in other industries.

INTRODUCTION

Most industrial processes generate some waste, both organic and inorganic, often in the form of atmospheric gas emissions. These can include dust and aerosols, gases and vapours. The principal origins of the organic compounds are internal combustion engines and industrial processes. In order to arrive at the ambient air quality defined by the Swiss Ordinance for the Maintenance of Clean Air, both the concentration and the total emission discharge must be within set limits¹. Control of such limits implies efficient and easily automated analytical methods. Although continuously recorded on-line measurements² would bring advantages, the current state of the art is not yet developed and today's sensors, IR and mass spectrometric (MS) monitors do not reflect all the practical needs.

The application of headspace gas chromatography (GC) offers a cost-efficient off-line analysis³ of volatile organic compounds (VOCs) such as those listed in Table I. A method for the sampling and determination of VOCs in air emissions is described. The method is based on taking samples by means of adsorption samplers, followed by headspace GC coupled with MS for identification.

EXPERIMENTAL

Instrumentation

A Perkin-Elmer Model HS-100 headspace sampler coupled with a Sigma 2000 gas chromatograph and equipped with instruments for flame ionization, electron-

TABLE I
VOLATILE ORGANIC COMPOUNDS SUITABLE FOR HEADSPACE GC DETERMINATION

<i>Compound</i>	<i>Boiling point (°C)</i>	<i>Compound</i>	<i>Boiling point °C</i>
Ethylene oxide	11.5	Isopropanol	82.4
Diethyl ether	34.6	<i>n</i> -Propanol	97.4
Dichloromethane	40.0	Benzene	110.0
Acetone	56.2	Toluene	111.0
Chloroform	61.7	2-Pentanone	116.0
Methanol	64.9	<i>n</i> -Butanol	117.0
Tetrahydrofuran	67.0	Tetrachloroethylene	121.0
Hexanes	70.0	<i>n</i> -Butyl acetate	127.0
Ethyl acetate	77.0	Chlorobenzene	132.0
Acrylonitrile	77.0	Xylenes	144.4
Ethanol	78.5	<i>o</i> -Dichlorobenzene	180.5
2-Butanone	80.0	White spirit	190.0

capture and nitrogen-phosphorus detection was used. A duplicate system was coupled with a heated interface to a mass spectrometer (Finnigan ion-trap detector). The connection was made via a splitter at the end of the chromatographic column.

A J&W Scientific fused-silica capillary column (30 m × 0.32 mm I.D.) with a 1- μ m DB-1701 chemically bonded phase was used. After a 6-min isothermal period at 45°C, the temperature was increased from 45 to 120°C at 20°C/min, followed by a holding time of 15 min at 120°C. The detector temperature was 250°C. The carrier gas was helium at a flow-rate of 1 ml/min.

Mass spectra were acquired in the full-scan mode, in the range 25–260 a.m.u., at a scan rate of 1 scan/s. The multiplier voltage was set to 1450 V and the transfer line temperature was 250°C.

PROCEDURES

Charcoal and silica gel samples were loaded into 20-ml headspace vials and, after addition of 1 ml of benzyl alcohol (pro analysi; Merck) and 1 ml of doubly distilled water, respectively, were sealed with caps having aluminium-coated silicone septa. After a thermostating time of 20 min at 80°C for charcoal samples and 70°C for silica gel samples, an aliquot of the gas phase was injected into the chromatographic column (injection time 0.08 min). Blanks of active charcoal and benzyl alcohol and also of silica gel and doubly distilled water were run together with each sample series. Quantitation was effected using an external standard method.

For the calibration, linearity and sensitivity experiments, two standard solutions of mixtures of up to ten components in benzyl alcohol prepared volumetrically in headspace vials, which were filled to the top in order to avoid the presence of any gas phase: in the first solution, each component was present at a concentration of about 80 μ g/ μ l, depending on the density; in the second, the concentration was about 4 μ g/ μ l. A series of dilutions were prepared taking samples of 0.5–10 μ l of the standard solutions by means of a Hamilton syringe and injecting them into sealed vials containing the appropriate adsorbent and the corresponding elution solvent. To

avoid flashing in the gas phase, the standard solution was injected directly into the adsorbent–eluent phase. The adsorbent was 150 mg of an active charcoal (NIOSH approved; SKC) or 225 mg of a silica gel (SKC). A minimum of four vials were analysed for each concentration value.

RESULTS AND DISCUSSION

Sampling

Air monitoring involves air sampling and sample preparation followed by the measurement of pollutants. A basic characteristic of most air sampling methods is that a representative portion of the volumetric flow is taken from flue gas and the sample is concentrated outside the stack. Fundamental for the reliability and accuracy of any method are correct sampling and sample-preparation techniques. For our purposes both must be simple, reproducible and precisely defined. The most commonly chosen technique is pollutant enrichment^{4,5}, either actively or passively, on an adsorbent.

In active adsorption a representative sample is drawn from the chimney flue through an adsorbent tube at a constant rate by means of a pump (Fig. 1). The flow-rate is usually between 0.5 and 10 l/h; normally National Institute for Occupational Safety and Health (NIOSH, Cincinnati, OH, U.S.A.) approved tubes⁶ filled with active charcoal, silica gel, Tenax or certain Chromosorbs are used. Using this technique, the individual breakthrough volume^{4,7–9} is determined in our laboratory by varying the amount of adsorbent (100–1000 mg) and the exposure time (30 min to 24 h). Additionally for on-site sampling, the eventual breakthrough is checked by connecting two tubes in series. Active adsorption has proved to be especially suitable for short-term measurements.

Passive adsorption samples are taken by means of “diffusion samplers” developed at Sandoz (Fig. 2). They consist of adsorbent-filled glass tubes with a precisely defined diffusion path where gases and vapours are adsorbed solely by free diffusion^{4,10}. They are mounted directly to the chimney flue as illustrated in Fig. 2. The sampler design and the type and amount of adsorbent are varied according to the particular needs of the measurements. Two diffusion sampler tubes were tested: 11 cm × 0.7 cm and 5 cm × 0.7 cm I.D. The sampling time was varied between 4 h and 1 week; the best results were obtained with the 11 cm × 0.7 cm I.D. tubes.

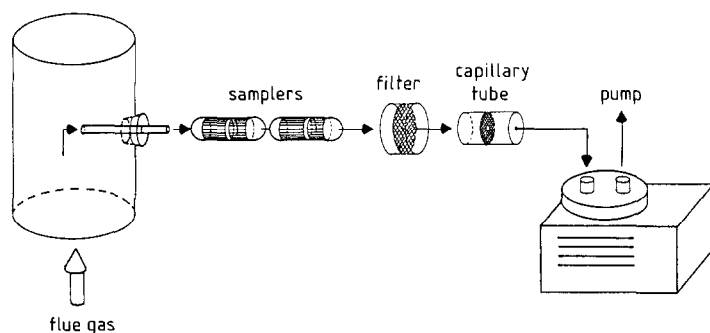


Fig. 1. Active sampling.

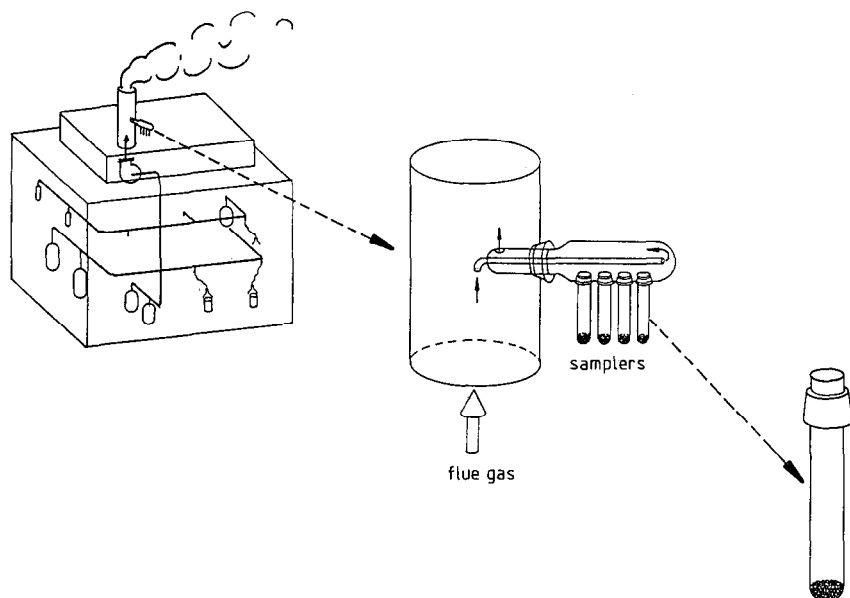


Fig. 2. Passive sampling.

Both active and passive adsorption tests were carried out with dynamic gas mixtures, or with dosing from solution via a syringe. For each compound, concentrations from 4 to 290 mg/m^3 were dosed at 25°C and a relative humidity of 80% and 40%, respectively.

It is virtually impossible to adsorb completely a series of compounds having widely differing physico-chemical properties^{4,11} on a single adsorbent, and normally tubes containing active charcoal and tubes containing silica gel are used simultane-

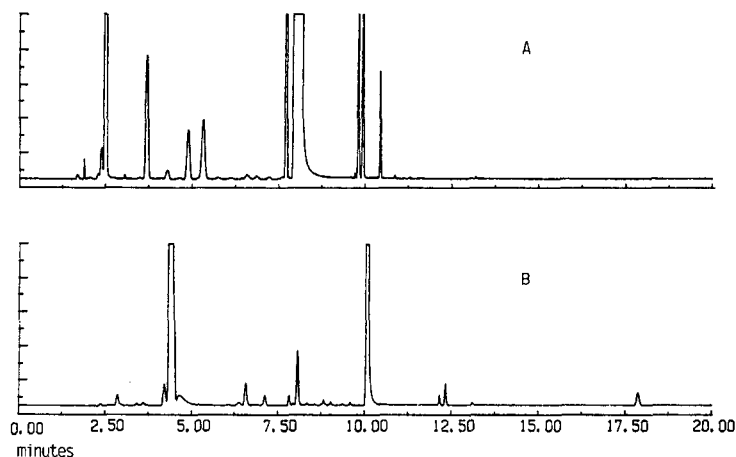


Fig. 3. Headspace gas chromatograms of the same sample showing the differences between (A) silica gel and (B) active charcoal.

ously. Active charcoal has a high affinity for non-polar and silica gel for polar compounds. Both adsorbents have a high adsorption capacity, which is an essential characteristic for sampling where concentrations are relatively high. The striking differences between the adsorption characteristics of charcoal and silica gel for a specific emission are shown in Fig. 3. For headspace elution benzyl alcohol is used for charcoal^{3,12} and doubly distilled water for silica gel. Careful prior testing of adsorbents and eluents is necessary.

Headspace gas chromatography

The sample preparation is independent of the adsorption procedure and can be carried out in three ways: solvent elution, thermal desorption or by the headspace technique. The separation and determination of the individual components are performed by chromatography (Fig. 4). Most in the emissions in the chemical industry consist of volatile organic compounds. This is one of the reasons which makes the use of headspace GC attractive, as none or little of the less volatile components reaches the separation column.

In headspace GC the gas phase, ideally in equilibrium with the liquid phase, is analysed. This equilibrium is a function of the matrix, among other factors. If a multiple headspace technique is not applied³, the influence of the adsorbent, as a major component of the matrix, must also be taken into account. For most substances active charcoal did not influence the GC "response factors"¹², with a few exceptions, *e.g.*, butyl acetate and *o*-dichlorobenzene (Fig. 5). In comparison, the influence of silica gel on the response factors is much more marked. The influence of the adsorbent must also be taken into account for the calibration. Two methods are commonly used: determination of the matrix effect by pre-testing or calibration in the presence of each individual adsorbent; we prefer the latter method.

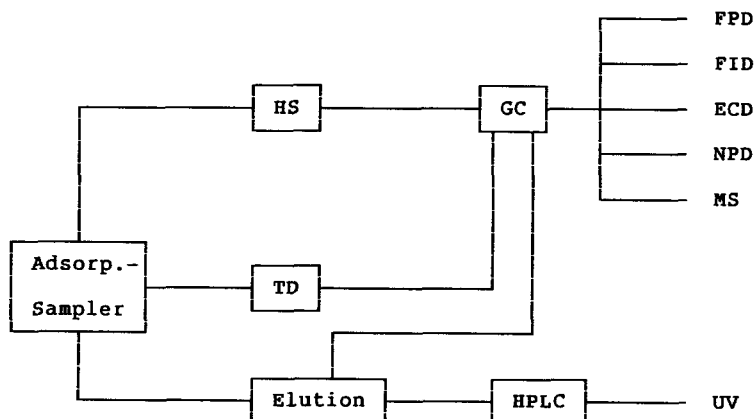


Fig. 4. Analytical methods for an enriched air emission sample. Abbreviations: Adsorp. = adsorption; ECD = electron-capture detection; FID = flame ionization detection; FPD = flame photometric detection; GC = gas chromatography; HPLC = high-performance liquid chromatography; HS = headspace; MS = mass spectrometry; NPD = nitrogen-phosphorus detection; TD = thermal desorption; UV = ultraviolet absorbance detection.

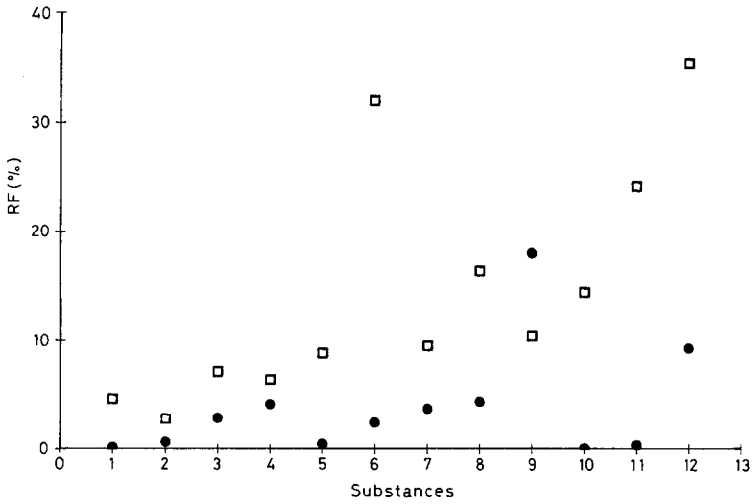


Fig. 5. Influence of the matrix on response factors. Relative difference, $RF(\%) = (RF'' - RF') 100/RF'$, where $RF'' = RF$ in an adsorbent-eluent matrix and $RF' = RF$ in eluent. \square , Silica gel-water; \circ , active charcoal-benzyl alcohol. Substances: 1 = methanol; 2 = ethanol; 3 = isopropanol; 4 = *n*-butanol; 5 = acetone; 6 = tetrahydrofuran; 7 = dichloromethane; 8 = tetrachlorethylene; 9 = butyl acetate; 10 = toluene; 11 = xylene; 12 = *o*-dichlorobenzene.

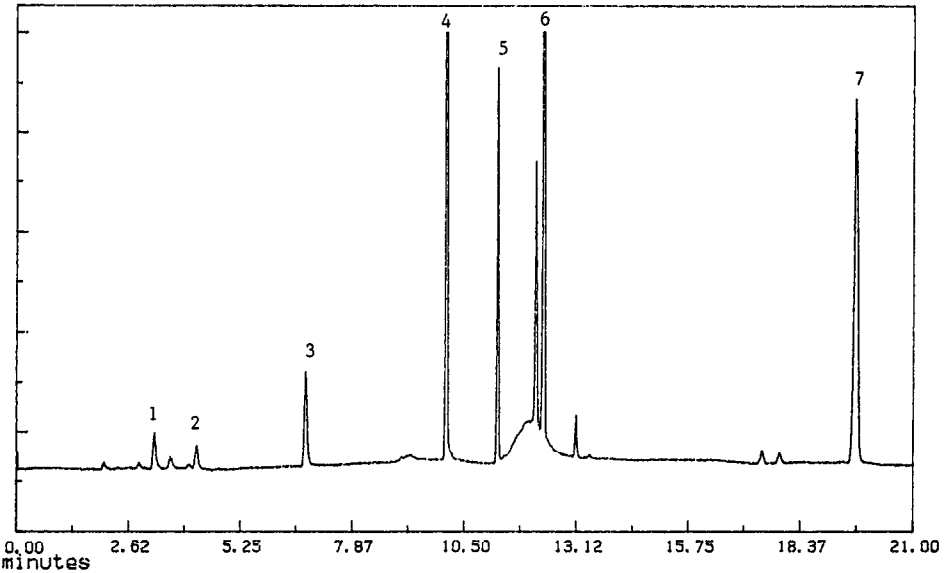


Fig. 6. Headspace gas chromatogram showing the detection of several substances at low concentration. Peaks: 1 = ethanol ($1.97 \mu\text{g/ml}$); 2 = isopropanol ($1.94 \mu\text{g/ml}$); 3 = tetrahydrofuran ($2.19 \mu\text{g/ml}$); 4 = toluene ($2.16 \mu\text{g/ml}$); 5 = *n*-butyl acetate ($2.17 \mu\text{g/ml}$); 6 = xylenes ($2.14 \mu\text{g/ml}$); 7 = *o*-dichlorobenzene ($3.24 \mu\text{g/ml}$).

TABLE II

LIMITS OF DETECTION OF THE HEADSPACE GC METHOD COMPARED WITH THE LIMITS SET BY THE SWISS CLEAN AIR ACT (1986)

Compound	Legal limit (mg/m^3)	Passive* (mg/m^3)	Active** (mg/m^3)
Ethylene oxide	5	0.50	0.12
<i>o</i> -Dichlorobenzene	20	0.60	0.06
Toluene	100	0.45	0.06
Ethanol	150	1.30	0.25

* Passive adsorption: 104 h sampling.

** Active adsorption: 8 h sampling at 1 l/h.

In this comprehensive headspace GC method the linearity range is very large. In general, satisfactory linearity is achieved in the concentration range needed for our emission measurements, which currently lies between 5 and 700 $\mu\text{g}/\text{ml}$. The linearity plots for most of the substances studied show correlation coefficients higher than 0.995.

An example of the signals detected using this method at low concentrations is given in Fig. 6. The signal-to-noise ratio is well above 3:1. The sensitivities achieved are compared with the requirements of ref. 1 in Table II. The use of a universal flame ionization detector, with both active and passive sampling, permits detection limits at least ten times better than those legally prescribed in Switzerland. The passive sampling alone allows determinations, for most compounds, at levels up to 100 times lower than those required by Swiss law. By modifying the sampling conditions, *e.g.*, sampling time, sampling gas flow-rate or sampler design, the sensitivity can easily be increased. The application of specific detectors permits a further lowering of the detection limits for specific substance groups.

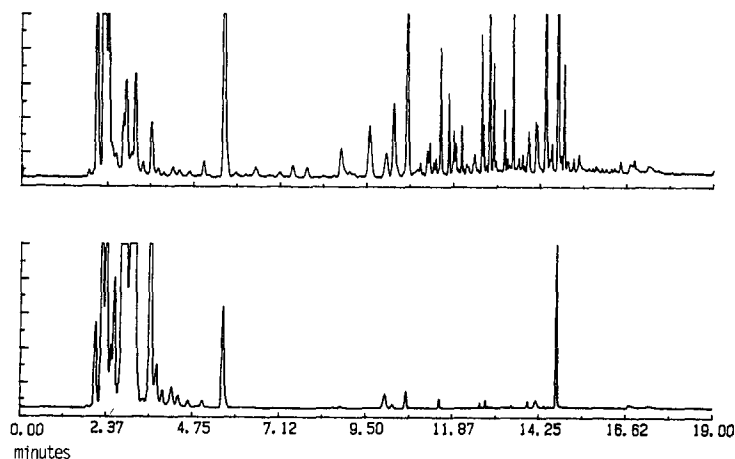


Fig. 7. Headspace gas chromatograms showing results of two consecutive 1 week samplings from a chimney stack.

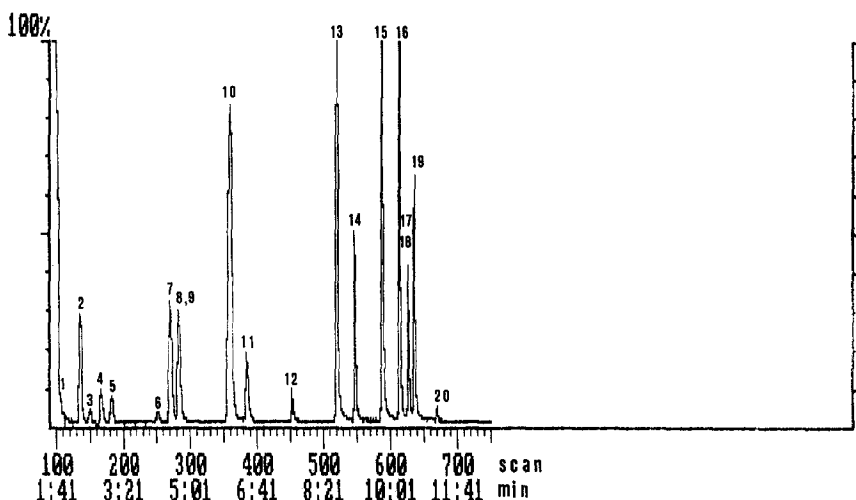


Fig. 8. Mass chromatogram of the gases in the extraction flue of a wastewater collector. Peaks: 1 = methanol; 2 = diethyl ether; 3 = ethanol; 4 = acetone; 5 = dichloromethane; 6 = *n*-propanol; 7 = ethyl acetate; 8 = tetrahydrofuran; 9 = 2-butanone; 10 = isopropyl acetate; 11 = *sec.*-butanol; 12 = *n*-butanol; 13 = toluene; 14 = tetrachloroethylene; 15 = *n*-butyl acetate; 16 = di-*n*-butyl ether; 17 = chlorobenzene; 18 = *p*-xylene; 19 = *o*-xylene; 20 = *m*-xylene.

Coupling of headspace GC with MS

Most of our products are manufactured in batches using multi-purpose plants and the emissions at any individual measuring point can vary considerably. Fig. 7 shows a typical example, both chromatograms being of samples taken from the same flue during two consecutive weeks with diffusive sampling for 1 week in each instance. It is not only the sample composition that can change but also the relative concentrations in a given sampling operation, and these factors complicate both qualitative and quantitative analysis.

Coupling of headspace GC with MS has proved to be of particular value for the identification of components. Fig. 8 shows the mass chromatogram of a sample drawn from the extraction flue of an industrial effluent system, where up to 20 components were identified. In addition to the identification possibilities offered by the ion-trap detector, this particular system coupling allows two-dimensional quantitation, which gives a useful increase in reliability for the evaluation of priority substances.

CONCLUSIONS

The application headspace GC to the determination of organic gases and vapours in emissions has the following advantages:

(1) Sampling can be performed with high-capacity adsorbents. This allows long-term sampling and is also suitable for short-term sampling in the presence of high concentrations.

(2) The substance range is simplified in that only the more volatile components are submitted to chromatographic analysis. The greater part of organic emissions in

chemical industry consists of such compounds which, consequently, have a preferential position in our examination.

(3) The eluents used in headspace GC interfere minimally in the chromatographic analysis.

(4) The sensitivity of the method is well suited to the control requirements of current Swiss law and a sensitivity increase can be achieved without complex modifications.

(5) Headspace GC can be highly automated and, consequently, it can cope with a high sample throughput.

(6) The method presented here, is a commercially viable off-line technique of the measurement of organic pollutants in industrial emissions.

ACKNOWLEDGEMENTS

The authors thank F. Vantrepol and C. Reber for dedicated technical assistance, U. Gruntz for generous advice and support and W. Habersaat for linguistic suggestions.

REFERENCES

- 1 *Luftreinhalte-Verordnung (LRV) der Schweiz*, 16 December, 1985, in effect 1 March, 1986 (SR 814.318.142.1).
- 2 J. T. Y. Yeh, *Chem. Eng.*, 20 (1986) 55-68.
- 3 F. A. Bencsath, K. Drysch, D. List and H. Weichardt, *Applied Chromatography*, Perkin-Elmer, Norwalk, CT, 1978, 32E.
- 4 R. G. Melcher, T.L. Peters and H. W. Emmel, *Top. Curr. Chem.*, 134, (1986) 59-123.
- 5 K. Figge, A. M. Dommroese, W. Rabel and W. Zerhau, *Fresenius' Z. Anal. Chem.*, 327 (1987) 279-292.
- 6 D. G. Taylor (Editor), *NIOSH Manual of Analytical Methods*, Vols. 1-7, National Technical Information Service, Springfield, VA, 1980.
- 7 G. O. Nelson and C. A. Harder, *Am. Ind. Hyg. Assoc. J.*, 35 (1974) 391-410.
- 8 G. O. Nelson and C. A. Harder, *Am. Ind. Hyg. Assoc. J.*, 37 (1976) 205-215.
- 9 K. Figge, W. Rabel and A. Wieck, *Fresenius' Z. Anal. Chem.*, 327 (1987) 261-278.
- 10 J. Namiesnik, T. Gorecki and E. Kozlowski, *Sci. Total Environ.*, 38 (1984) 225-258.
- 11 L. Weber and U. Knecht, *Fresenius' Z. Anal. Chem.*, 321 (1985) 544-548.
- 12 B. Kolb and P. Pospisil, *Applied Chromatography*, Perkin-Elmer, Norwalk, CT, 1978, 33E.
- 13 B. Kolb, *Headspace-Gaschromatographie mit Kapillar-Trennsäulen*, Vogel-Verlag, Würzburg, 1986.