Journal of Chromatography, 636 (1993) 255–261
Elsevier Science Publishers B.V., Amsterdam

CHROM. 24 900

Glass fibre prefilter–XAD-2 sampling and gas chromatographic determination of airborne chlorophenols

Helena Kontsas and Christina Rosenberg*
Institute of Occupational Health, Topeliuksenkatu 41 a A, SF-00250 Helsinki (Finland)

Paavo Jäppinen
Enso-Gutzeit Oy, SF-55800 Imatra (Finland)

Marja-Liisa Riekkola
Department of Analytical Chemistry, University of Helsinki, Vuorikatu 20, SF-00100 Helsinki (Finland)

(First received November 24th, 1992; revised manuscript received January 22nd, 1993)

ABSTRACT

A procedure for air sampling and analysis of polychlorinated phenols was developed and used for field measurements at two pulp-bleaching plants. The sampler consisted of an XAD-2 resin tube with a glass fibre prefilter. The filter and the resin were separately eluted with toluene, followed by acetylation of the chlorophenols with a mixture (5:2) of acetic acid anhydride and pyridine and determination by capillary gas chromatography using electron-capture and mass-selective detection. The sampler was tested in the $\mu g/m^3$ range for desorption and collection efficiency. The collection efficiency of the sampling device was not affected by humidity (40–80%) or sampling rate (200–750 ml/min) for the tested compounds. Stability tests at +20, +4 and −20°C showed no degradation of the chlorophenols studied during 4 weeks. The detection limit was below the $\mu g/m^3$ range for 180-l air samples.

INTRODUCTION

Chlorophenols have been found in spent bleaching liquors and in waters and water organisms downstream of pulp-bleaching plants [1,2]. During the production of pulp, lignin is broken down into a variety of monomeric phenols, which are chlorinated in the bleaching process [3]. The total amount of chlorinated phenolics produced in the course of chlorine bleaching depends on the pH, temperature and the amount of chlorine and chlorine dioxide used in the process [4]. In all, over 250 chlorinated compounds have been identified in effluents from pulp mills [5].

Chlorophenols show moderate bioaccumulation, and their toxicity increases with increasing degree of chlorination. In humans, exposure to chlorophenols can cause nausea, headache and irritation of the eyes and respiratory tract [6].

A number of different sampling procedures have been used for airborne chlorophenols, including freezing and condensing by drawing air

* Corresponding author.

0021-9673/93/$06.00

through cooling traps [7], absorption in liquids and adsorption on silica gel or porous polymers [8–13]. The compounds are then desorbed with an appropriate organic solvent or by thermal desorption and determined using gas or liquid chromatography.

Chlorophenols can be analysed directly [14] or as derivatives. At low concentrations, however, direct chromatographic separation is hindered by adsorption problems characteristic of the analysis of polar compounds. To overcome such difficulties and, furthermore, to improve analytical sensitivity, *e.g.* to mono- and dichlorophenols [15], the compounds of interest are often converted into less polar derivatives prior to gas chromatographic analysis. The most common derivatization methods are alkylation, silylation and acylation. Of these, acylation produces considerably less interference than the other methods [16].

Although chlorophenols have been extensively studied in environmental matrices, little is known about the possible release of these compounds into the work environment, *e.g.* during bleaching of pulp. We therefore developed a simple sampling procedure and method of analysis for airborne di-, tri-, tetra- and pentachlorinated phenols. The systems were used for field measurements at a hardwood and a softwood bleaching plant using chlorine-containing bleaching agents. The chlorophenols monitored were 2,4- and 2,6-dichlorophenol (2,4-DCP and 2,6-DCP), 2,4,5- and 2,4,6-trichlorophenol (2,4,5-TCP and 2,4,6-TCP), 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP) and pentachlorophenol (PCP). These congeners were chosen on account of their occurrence in mill effluents [4,17–19].

EXPERIMENTAL

Apparatus

Gas chromatograph. A Hewlett-Packard (HP) 5890A gas chromatograph equipped with an electron-capture detector (^{63}Ni) operating at 350°C or an HP-5970A mass-selective detector with electron impact (EI) ionization (70 eV) was used. The temperatures of the transfer line and ion source were 250°C and 180°C, respectively. The emission current was 0.3 mA. The mass-selective detector was operated in the selective-ion monitoring (SIM) mode. The following ion pairs were monitored: dichlorophenols m/z 162/164, trichlorophenols m/z 196/198, tetrachlorophenol m/z 230/232 and pentachlorophenol m/z 266/268. A fused-silica capillary column (HP-5), 25 m × 0.32 mm I.D., coated with diphenyl–dimethyl (5:95) polysiloxane (0.17 μm film thickness) was used with electron-capture detection (ECD). An equivalent but 50-m-long column directly coupled to the ion source was used with mass-selective detection (MS). The column temperature programme, identical for both columns, was as follows: 0.5 min at 75°C, heating to 200°C at 7°C/min, 1 min at 200°C, heating to 250°C at 15°C/min, 1 min at 250°C. Helium was used as carrier gas at flow-rates of 2 ml/min (ECD) and 1.55 ml/min (MS).

An autoinjector was used to introduce 1 μl samples into the gas chromatograph. The injector was operated in splitless mode with an inlet temperature of 220°C and a splitless time of 0.5 min (ECD) or with an inlet temperature of 230°C and a splitless time of 0.75 min (MS).

Materials

Chemicals. All solvents were of analytical grade and purchased from Merck (Darmstadt, Germany), except methyl-*tert.*-butyl ether, which was HPLC grade and purchased from Rathburn (Walkerburn, UK). Borax, potassium hydrogenphosphate, potassium carbonate, sodium hydroxide, sodium sulphate and acetic acid anhydride were of analytical grade (Merck). Pyridine was obtained from Pierce (Rockford, IL, USA). XAD-2 resins (Servachrom XAD-2 cat. No. 42821, Serdolit AD-2 cat. No. 42821, Serdolit AD-2 cat. No. 42420) were purchased from Serva (Heidelberg, Germany), commercial XAD-2 tubes (cat. No. 226-30) from SKC (Eighty Four, PA, USA) and silica and C_{18} adsorbent tubes (Bond-Elut, 1 cm^3) from Analytichem (Harbor City, CA, USA). 2,4-DCP was obtained from Ega-Chemie (Steinheim, Germany) and 2,6-DCP, 2,4,5-, 2,4,6-TCP, 2,3,4,6-TeCP and PCP from Fluka (Buchs, Switzerland). Glass fibre filters (binderfree, 13 mm) were from Gelman (Ann Arbor, MI, USA), filter holders (cat. No. SX001300) from Millipore

(Molsheim, France) and silanized glass wool from Ohio Valley Speciality Chemicals (Marietta, OH, USA).

Acetylation reagent. The acetylation reagents were prepared immediately before use by mixing acetic acid anhydride and pyridine in the following ratios: 2:5, 5:2 and 1:1.

Buffer solutions. Solutions of 0.1 *M* Borax, 1 *M* potassium hydrogenphosphate (pH adjusted to 7 with sodium hydroxide) [20] and 0.1 *M* potassium carbonate were prepared in distilled water.

Purification of XAD resins. The XAD resins were subjected to intensive cleanup before use as follows: 100 g of resin were washed twice with 300 ml of distilled water and twice with 300 ml of methanol and extracted for 6 h with diethyl ether in a Soxhlet apparatus. The resin was dried at 60°C for 12 h and stored in a desiccator [21].

Procedure

Preparation of chlorophenol standard solutions. Stock solutions of each of the chlorophenols were prepared in hexane. From these solutions, working standard mixtures of four different concentration levels, 25, 50, 100 and 250 pg of each chlorophenol per μl, were prepared in each of the following solvents: ethyl acetate, hexane, toluene, dichloromethane and methyl-*tert.*-butyl ether. 2,3,6-TCP was used as an internal standard at a concentration of 46.5 pg/μl.

Acetylation reaction. Optimum reaction conditions were studied by adding 100 μl of acetylation reagent (2:5, 5:2 or 1:1) to 1 ml of standard in either ethyl acetate or hexane and agitating for 2 min. Buffer (2 ml) was added at the same time or after the acetylation reaction to remove excess acetylation reagent. Three buffers, borax, potassium hydrogenphosphate and potassium carbonate, were tested.

Regarding chlorophenols collected with commercial XAD-2 tubes, the acetylated and buffer-extracted organic phase was purified further by solid phase extraction in prepacked silica and reversed-phase (C_{18}) columns. Briefly, the silica column was wetted with 1 ml of hexane, after which the acetylated sample in 1 ml of hexane was added and the derivatives eluted with 1 ml of hexane. The total hexane fraction was recovered. The C_{18} column was wetted with 1 ml of hexane, the acetylated sample added in 1 ml of hexane and the derivatives eluted with 1 ml of ethyl acetate.

Sampling device. The sampling system consisted of a glass fibre filter mounted in a filter holder in front of a resin tube (70 × 4 mm I.D.) containing 150 mg of XAD-2. The resin was plugged with glass wool at both ends.

Desorption efficiency. The efficiency of desorption from the adsorbent was investigated using the phase equilibrium technique by applying known amounts of the chlorophenols to the resin. The resin (150 mg) was placed in a screw-capped test tube and 1 ml of standard solution containing 25, 100 or 250 pg/μl of each chlorophenol was added and allowed to stand for 1 h before treatment. The glass fibre filter and the commercial XAD-2 tube were tested in a similar way.

Collection efficiency. Collection efficiency and possible breakthrough were tested by evaporation of the chlorophenols to produce a test atmosphere. A standard solution (10 μl) in hexane containing 25 ng/μl of each chlorophenol was injected into glass wool packed in a glass tube (130 × 4 mm I.D.), which was then heated to 90°C. This tube, a sampling device and a back-up resin tube were connected in series and humidified air was drawn through the system for 4 h at 200, 500 or 750 ml/min. An air flow of known rate and relative humidity (40 or 80%) was obtained by humidifying the air in a bath of distilled water and diluting it with dry air in a mixing chamber (10 l) fitted with a relative humidity meter (Vaisala HMI 32, Helsinki, Finland).

Stability tests. For stability testing, glass fibre filters and XAD-2 tubes were spiked with 10 μl of a standard solution containing 25 ng/μl of each chlorophenol. The tubes were stoppered, placed in plastic bags and stored at +20, +4 or −20°C for 1, 2 or 4 weeks before analysis.

Field sampling and sample treatment. Sampling of workplace air was carried out at one hardwood and one softwood bleaching plant using chlorine-containing bleaching agents. Air was sampled for 4 h at a flow-rate of 750 ml/min.

Samples were collected at different bleaching stages near the washing drums at a height of 1.5 m from floor level. After sampling, the sampling devices were stoppered and placed in a plastic bag. In the laboratory, the samples were stored in a freezer (−20°C) until further treatment.

For analysis, the glass fibre filter and the resin plug were transferred to separate test tubes. Toluene (1 ml) containing the internal standard was added to each test tube, and the tubes were allowed to stand for 1 h. The solvent was then transferred to another test tube, mixed with 100 μl of the acetylation reagent (5:2) and agitated for 2 min. The mixture was allowed to stand for 10 min, after which 2 ml of 0.1 *M* potassium carbonate was added and the tube shaken for 2 min. After separation of the phases, the organic layer was transferred to another test tube and dried with sodium sulphate. The extract was then transferred to autosampler bottles for gas chromatography.

RESULTS AND DISCUSSION

Acetylation reaction

According to Ballesteros *et al.* [22], the optimum temperature for acetylation is over 40°C. Pekari *et al.* [23] determined 2,4,6-TCP from urine, using acetylation without heat treatment. They extracted the urine with hexane and shook the organic phase with borax buffer and acetylation reagent (acetic acid anhydride and pyridine, 2:5) for 5 min. In the present study, however, simultaneous buffer extraction and acetylation resulted in an incomplete reaction. We initially attempted acetylation with ethyl acetate or hexane as the solvent and borax as the extraction buffer. It was difficult to achieve reproducible results with ethyl acetate, because the water solubility of this solvent hampers its quantitative removal from the buffer solution. Hexane did not exhibit these problems and thus was used. In the following experiments, acetylation reagent containing two parts acetic acid anhydride and five parts pyridine was added simultaneously with borax buffer to the standard solution in hexane, and the mixture was agitated for 2 min. According to the analysis, 16–35% of the TCPs and 20% of the 2,3,4,6-TeCP remained unreacted, whereas the DCPs and the PCP were almost completely derivatized. The reagent blank showed an interference peak that co-eluted with the acetylated PCP. Hereafter 2,4,6-TCP was used as a test compound to study the acetylation reaction.

Changing the acetylation reagent to five parts acetic acid anhydride and two parts pyridine improved the reaction, but it was still incomplete (Table I). Increasing the reaction time from 2 to 10 or 20 min did not improve the result, nor did the use of a 1:1 reagent mixture. Acetic acid anhydride alone yielded over 90% derivatization, but at the same time there was a 16-fold increase in the interference peak co-migrating with PCP. When the buffer solution was added 2 min after the 2:5 acetylation reagent, almost complete derivatization was achieved. The 5:2 reagent gave a quantitative acetylation reaction, and the interference peak was clearly diminished. To establish optimum derivatization conditions, further experiments were done with potassium carbonate or potassium hydrogenphosphate as the extraction buffer. The use of these buffers produced reagent blank chromatograms almost devoid of interfering peaks, potassium carbonate being superior in this respect.

Desorption efficiency

The results of the desorption efficiency tests are presented in Table II. Initially, a batch of

TABLE I

FORMATION (%) OF AN ACETYL DERIVATIVE FROM 2,4,6-TRICHLOROPHENOL (25 pg/μl) DEPENDING ON ACETYLATION REAGENT COMPOSITION AND TIMING OF BORAX BUFFER EXTRACTION

Acetic acid anhydride: pyridine/time of buffer extraction	Acetylated form (%)	Unreacted form (%)
2:5/simultaneously	55	45
5:2/simultaneously	87	13
1:1/simultaneously	77	23
Acetic acid anhydride/ simultaneously	91	9
2:5/after acetylation	98	2
5:2/simultaneously	100	0

TABLE II

DESORPTION EFFICIENCY (%) OF CHLOROPHENOLS FROM XAD-2 RESIN AND GLASS FIBRE FILTER[a]

AG = Analytical grade; RG = research grade; MTBE = methyl-*tert.*-butyl ether

Chlorophenol	Servachrom XAD-2 (AG)/ECD, hexane[b]	Serdolit AD-2 (RG)/ECD, hexane[c]	Serdolit AD-2 (AG)/ECD		Serdolit AD-2 (AG)/MS, toluene[f]
			Hexane[d]	MTBE[e]	
2,4-DCP	81–86	14–37	36–46	116	87–97
2,6-DCP	80–89	26–60	49–67	115	97–110
2,4,5-TCP	84–104	9–10	14–32	101	78–97
2,4,6-TCP	93–100	12–26	36–57	100	98–113
2,3,4,6-TeCP	102–107	4	3–14	62	73–103
PCP	98–100	2–4	4–13	28	40–96 50–82[g]

[a] The chlorophenols were added at three levels (25, 100 and 250 ng of each chlorophenol) to 150 mg of resin, extracted with an organic solvent, acetylated with 5:2 acetylation reagent, purified with potassium carbonate buffer and determined by GC–ECD or GC–MSD. The values represent means of a minimum of two measurements at each level, with the exception of [c] and [e], where only two levels, 25 and 250 ng, and one level, 250 ng, respectively, were used.

[b] $n = 22$.

[c] $n = 4$.

[d] $n = 12$.

[e] $n = 1$.

[f] $n = 6$.

[g] Glass fibre prefilter.

analytical-grade resin, XAD-2 (Servachrom) dating from 1984, was used with hexane as the desorption solvent, resulting in excellent recovery (80–107%). Later, a new batch of analytical-grade resin purchased in 1990, AD-2 (Serdolit), yielded poor recoveries, especially of TeCP and PCP (3–14%). A new batch of research-grade resin, AD-2 (Serdolit), having the same catalogue number as the initial analytical-grade XAD-2 exhibited still poorer recovery (2–4%) with hexane. The reason for these inadequate recoveries could not be found. Commercial XAD-2 tubes were also used in desorption efficiency tests. These tubes produced immense amounts of impurities when desorbed with hexane. The impurities could not be removed even with an additional cleanup step by solid phase extraction with either silica or C_{18} columns.

Dichloromethane was examined as an alternative solvent to desorb the chlorophenols. Satisfactory recoveries were achieved with both new XAD-2 resins. However, this solvent caused severe degradation of the chromatographic column after only a few injections. This was avoided by replacing dichloromethane with hexane after the desorption step. As a drawback, there was a 20–30% loss of DCPs and TCPs and a 10% loss of TeCP. PCP was not affected when dichloromethane was evaporated with a gentle stream of nitrogen.

The use of methyl-*tert.*-butyl ether for desorption improved the recovery of DCP, TCP and TeCP (62–116%) from the analytical-grade Serdolit AD-2 resin, but the recovery of PCP was still low (28%, Table II). Good desorption of DCP, TCP and TeCP from the resin (73–113%) and PCP from the glass fibre filter (50–82%) was achieved with toluene, which was thus chosen as the desorption solvent.

Collection efficiency

Collection efficiency studies using only the adsorbent tube showed that PCP was not retained on the XAD-2 resin, even at air flow-rates as low as 200 ml/min. In subsequent experiments with a glass fibre prefilter, PCP was recovered from the prefilter. These results contradict previ-

ously reported studies [13] in which the XAD-2 resin alone was used for sampling of TCP, TeCP and PCP.

No breakthrough of DCP, TCP and TeCP was observed with the XAD-2 tube tested at sampling flow-rates ranging from 200 to 750 ml/min for 4 h in either 40% or 80% relative humidity test atmospheres. The collection efficiency in the 40% test atmosphere was 55–78% for DCP, 53–79% for TCP and 47–52% for TeCP ($n = 5$). The corresponding values for the 80% test atmosphere were 58–96%, 55–86% and 40–69% ($n = 5$). The collection efficiency of PCP with the glass fibre filter ranged from 88 to 108% and from 47 to 96% when the relative humidity was 40% ($n = 5$) and 80% ($n = 5$), respectively.

Stability tests

Storage of spiked resins (DCP, TCP and TeCP) and glass fibre filters (PCP) caused no degradation of the chlorophenols during 4 weeks at +20, +4 or −20°C.

Gas chromatography

The sensitivity of ECD for halogenated compounds makes its use rational for trace analysis of chlorophenols. Nevertheless, the inherent selectivity offered by the SIM technique renders MS more attractive. The fragmentation pattern and the ratio of the ions chosen add a second dimension to the identity of the compounds, in addition to retention time. In the EI fragmentation process, the acetyl group is lost from the acetylated chlorophenol, followed by hydrogen rearrangement. This corresponds to the loss of m/z 42 typical for acetates [24]. Monitoring of the resulting intense fragments, $M^+ = M_{deriv} - CH_2{=}C{=}O$, yielded characteristic ion clustering caused by the chlorine isotopes. The ions used were DCP m/z 162/164, TCP m/z 196/198, TeCP m/z 230/232 and PCP m/z 266/268. The relative abundances were 100/66, 100/99, 75/100 and 100/67, respectively. The ions represent $M^+/M^+ + 2$, for DCP, TCP and TeCP, and $M^+ + 2/M^+ + 4$ for PCP.

The instrumental limits of detection for the ECD and MSD were calculated by dividing the concentration of the lowest chlorophenol standard used in recovery studies by the signal-to-noise ratio and multiplying the quotient by 3, which was used as a safety factor. The instrumental detection limits were similar for the two instruments (Table III). Limits of determination calculated for 180-l air samples for GC–ECD and GC–MSD are presented in Table III.

TABLE III

INSTRUMENTAL LIMIT OF DETECTION AND LIMIT OF DETERMINATION OF THE CHLOROPHENOLS BY GC–ECD AND GC–MSD

Chlorophenol	Instrumental limit of detection (pg/μl)		Limit of determination (ng/m^3)[a]	
	ECD	MS	ECD	MS
2,4-DCP	6.8	3.6	38	20
2,6-DCP	13.0	4.1	72	23
2,4,5-TCP	2.2	1.6	12	9
2,4,6-TCP	1.5	1.6	8	9
2,3,4,6-TeCP	2.0	3.4	11	19
PCP	1.6	3.1	9	17

[a] Calculated for a 180-l air sample.

Field sampling

Over 50 air samples were collected at the bleaching plants. At the softwood bleaching plant, use of chlorine and chlorine dioxide in a ratio of 1:1 at the first chlorination stage resulted in PCP being found in 20% of the samples. The concentrations ranged from 17 to 40 ng/m^3. No other chlorophenols were found. When chlorine dioxide alone was used in the bleaching, no PCP was detected. The hardwood bleaching plant only utilized chlorine dioxide at the first chlorination stage. Here PCP was found in only 10% of the samples, the concentrations ranging from 40 to 115 ng/m^3. The better selectivity of the MS-SIM technique compared with ECD was evident in the analysis of the field samples, with the latter yielding false-positive results for DCPs, TCPs and TeCP in several samples.

The formation of chlorophenols during the bleaching of pulp has been found to be dependent on various factors, especially on the chlorination agents used. In a Swedish survey [25], airborne 2,3,4,6-TeCP and PCP were detected at

a softwood bleaching plant using only chlorine at the first chlorination stage. Traces of 2,4,6-TCP were observed when a 1:1 mixture of chlorine and chlorine dioxide was used. Both 2,4,6-TCP and 2,3,4,6-TeCP were also detected at a hardwood bleaching plant using a 1:1 mixture. The concentrations reported in the Swedish study were of the same order of magnitude as in the present study.

CONCLUSIONS

A sampling device, consisting of an XAD-2 resin tube with a glass fibre prefilter, allowing simultaneous sampling of airborne di-, tri-, tetra- and pentachlorophenols was developed. Gas chromatographic determination of acetylated chlorophenols by MS with the selective-ion monitoring technique is similar in sensitivity but superior in selectivity to ECD.

ACKNOWLEDGEMENTS

We wish to thank Ms. Ritva Wirmoila for skilful technical assistance. Financial support from the Finnish Work Environment Fund is gratefully acknowledged.

REFERENCES

1 K. Lindström and J. Nordin, *J. Chromatogr.*, 128 (1976) 13.
2 J. Paasivirta, *Kemia-Kemi*, 17 (1990) 34.
3 A.B. McKague, *J. Chromatogr.*, 208 (1981) 287.
4 H.-B. Lee, R.L. Hong-You and P.J.A. Fowlie, *J. Assoc. Off. Anal. Chem.*, 72 (1989) 979.
5 L.R. Suntio, W.Y. Shiu and D. Mackay, *Chemosphere*, 17 (1988) 1249.
6 WHO, *Environmental Health Criteria*, 93 (1989).
7 I. Gebefügi, H. Parlar and F. Korte, *Ecotoxicol. Environ. Safety*, 3 (1979) 269.
8 A. Dahms and W. Metzner, *Holz. Roh-Werkstoff*, 17 (1979) 331.
9 G.D. Kleinman, S.W. Horstman, D.A. Kalman, J. McKenzie and D. Stanzel, *Am. Ind. Hyg. Assoc. J.*, 47 (1986) 731.
10 T.P. Kauppinen and L. Lindroos, *Am. Ind. Hyg. Assoc. J.*, 46 (1985) 34.
11 A.S. Todd and C.Y. Timbie, *DHHS (NIOSH) Publ. No. 83-106*, 1983.
12 J.S. Warren, L.L. Lamparski, R.L. Johnson and R.M. Gooch, *Bull. Environ. Contam. Toxicol.*, 29 (1982) 719.
13 J.-O. Levin, C.-A. Nilsson, M. Burström and L. Carleborg, *Natl. Board of Occup. Safety and Health Report*, 24, 1978.
14 B.G. Reigner, J.F. Rigod and T.N. Tozer, *J. Chromatogr.*, 533 (1990) 111.
15 J. Hajšlová, V. Kocourek, I. Zemanová, F. Pudil and J. Davídek, *J. Chromatogr.*, 439 (1988) 307.
16 L. Renberg, *Natl. Swedish Environ. Protection Board Report*, 1410 (1981).
17 B. Starck, P.O. Bethge, M. Gerlov and E. Talka, *Pap. puu-papp. trä*, (1985) 745.
18 J. Paasivirta, K. Heinola, T. Humppi, A. Karjalainen, J. Knuutinen, K. Mäntykoski, R. Paukku, T. Piilola, K. Surma-Aho, J. Tarhanen, L. Welling and H. Vihonen, *Chemosphere*, 14 (1985) 469.
19 A.J. Sequeira and L.T. Taylor, *J. Chromatogr. Sci.*, 29 (1991) 351.
20 G. Scarping, C. Sangö and B.E.F. Smith, *J. Chromatogr.*, 208 (1981) 313.
21 K. Andersson, C. Hallgren, J.-O. Levin and C.A. Nilsson, *Anal. Chem.*, 56 (1984) 1730.
22 E. Ballesteros, M. Gallego and M. Valcárcel, *J. Chromatogr.*, 518 (1990) 59.
23 K. Pekari, C. Boudène and A. Aitio, *Arch. Toxicol.*, 59 (1986) 41.
24 K. Blau and G.S. King (Editors), *Handbook of Derivatives for Chromatography*, Heyden, Bristol, UK, 1977, p. 144.
25 A.-B. Antonsson, R. Bjurström, L. Rondahl and U. Rydevik, *Inst. för Vatten- och Luftvådsforskning Rapport, Swedish Environ. Res. Inst., ILV-Publ. B 966*, Stockholm, 1989.