ELSEVIER

Journal of Chromatography A, 774 (1997) 333–347

JOURNAL OF CHROMATOGRAPHY A

Analytical methods for the determination of organochlorine compounds
Application to environmental samples in the Slovak Republic

Marta Veningerová*, Viktor Prachar, Jana Kovačičová, Ján Uhnák

Institute of Preventive and Clinical Medicine, Limbová 14, 833 01 Bratislava, Slovak Republic

Abstract

The paper deals with the isolation of chlorinated phenols, benzenes and insecticides from water, soil and vegetable samples. A review of the current procedures is presented. Solid-phase extraction on Empore extraction discs was experimentally evaluated for isolation of the compounds from surface and ground waters. For the isolation of chlorophenols from soil and vegetable samples, a method of simultaneous steam distillation/extraction was elaborated which proved to be also applicable for waste waters and sludges. Chlorinated insecticides and benzenes were extracted from soil and vegetable samples with the Soxhlet procedure. Final determinations were carried out by GC–electron-capture detection. The recoveries of the methods were well over 70%, with relative standard deviations below 14%. Samples of surface and ground waters, soil and vegetables, mostly from the vicinity of chemical and municipal waste dumping sites, were analysed. The highest contamination levels were found for chlorinated phenols in surface water from the vicinity of a former chemical waste dumping place where the concentrations of 2,6-dichlorophenol and pentachlorophenol were 4.3 and 3.9 $\mu g\ l^{-1}$, respectively.

Keywords: Water analysis; Soil; Environmental analysis; Vegetables; Food analysis; Organochlorine compounds; Benzenes; Phenols; Chlorophenols; Pesticides

1. Introduction

Chlorinated insecticides, benzenes and phenols represent an important group of environmental contaminants. When used as pesticides, deodorants, repellents, dielectric fluids, etc., they enter the environment directly as a result of human industrial and agricultural activities and also from chemical and municipal waste deposits. Apart from being manufactured for their specific uses, chlorinated benzenes and phenols are also formed by the biotic and non-biotic transformation of pesticides, especially of phenoxyalkanoic herbicides, hexachlorobenzene and hexachlorocyclohexane. Another method of their formation is by chlorination of aromatic compounds during treatment of drinking and waste waters with active chlorine [1–4].

Chlorinated phenols are very soluble in organic solvents such as benzene, hexane, or isooctane. The lipophilic character increases with increasing number of chlorine atoms in the molecule, thus contributing to the bioaccumulation of higher chlorinated phenols. Solubility in water changes depending on the acidity. Sodium and potassium salts are by four orders of magnitude more water soluble than the original compounds. These characteristics are utilized in the analysis of chlorophenols but they also influence the toxicological properties. The water solubility of

*Corresponding author.

0021-9673/97/$17.00
PII S0021-9673(97)00359-2

chlorinated pesticides is very limited. They are very soluble in organic solvents and highly persistent in environmental compartments and biological materials [5–7].

The toxic effect of chlororganic compounds seems to be linked to a chain reaction of their gradual dechlorination in body fluids and the formation of free radicals interfering with subcellular structures. The formation of peroxides and other products of lipid oxidation results in enzyme deactivation and liver dystrophy [8–11]. Chronic toxicity studies showed carcinogenic properties in some chlorinated insecticides, benzenes and phenols [12–14]. Higher chlorinated phenols have immunosuppressive effects, are nephrotoxic and interfere with blood formation [15–18]. Chlorinated phenols are excreted from the organism mainly in urine, partially free and partially in the form of their sulphate and glucuronide conjugates [4,8]. Chlorinated phenols are known for their pronounced organoleptic characteristics [19], the taste threshold ranging between 0.040–30 $\mu g\ l^{-1}$ and smell threshold between 30–1600 $\mu g\ l^{-1}$. This is important for setting their maximum tolerable concentrations in drinking water [20].

The discharge of chlororganic compounds into the environment can be minimized providing the principles of good manufacturing practice and good agricultural practice are observed. However, considerable amounts of these compounds can occasionally enter the environment by accident and from old chemical waste dumping sites.

The aim of the present work was to elaborate methods for isolation of chlorinated phenols, benzenes and insecticides from water, soil and crops. Samples of such materials taken in the vicinity of a former dumping site of a chemical factory manufacturing hexachlorocyclohexane (HCH), hexachlorobenzene (HCB) and 1,1,1-trichloro-2,2-bis-(4-chlorophenyl) ethane (DDT) as well as in the vicinity of a municipal waste dumping site located in western Slovakia were then analyzed. In addition, surface waters from the rivers Danube and Váh were also analyzed.

2. Review of analytical methods

The philosophy of the recent published methods for the determination of chlororganic compounds in environmental samples is concentrated mainly on the development of universal, rapid and high capacity methods capable of analysing as many different pollutants in as many matrices as possible (multiresidue–multimatrix techniques). In addition to this, advanced highly reliable techniques for confirming positive results found with the screening methods are required. The criteria of quality assurance and quality control are gaining more and more importance. We have included in this section only the most significant papers, considering the above aspects.

2.1. Chlorinated phenols

Most of the analytical methods use acidification of the sample to convert the chlorinated phenols to their non-ionised form, liquid–liquid extraction into an organic solvent and a clean-up procedure [4,21,22]. For this purpose, toluene and/or dichloromethane are the commonly used solvents. Although the recoveries of these methods are generally very acceptable, they are extremely time and solvent consuming. The problems associated with the formation of emulsion or foam when surface or waste waters are extracted also present a serious limitation.

An efficient screening method capable of recovering basic/neutral and acidic organic pollutants which covers also pentachlorophenol has been recently reported [23]. The procedure involves solvent extraction with sonication, solid-phase clean-up and quantitative analysis by gas chromatography–ion-trap mass spectrometry. The recovery of pentachlorophenol reached 81%. Quality data control indicated that the accuracy and precision of this method is comparable to the US Environmnetal Protection Agency (EPA) methods for waste samples. In 1987, Lee et al. [24] reported on a method for quantitative and isomer-specific analysis of pentachlorophenol and nineteen other chlorophenols in sediments. After acidification, the samples were Soxhlet-extracted with a acetone–hexane mixture and re-extracted into 2% $KHCO_3$. For quantitative GC–MS analysis of acetate derivatives, selected ion monitoring was used. Recoveries of dichloro- and higher chlorinated phenols varied between 80 and 95%, and those of monochlorophenols between 65 and 85%.

Other procedures are based on the relatively high

volatility of chlorinated phenols which enables us to combine the advantages of steam distillation and extraction in one step [25,26]. The extracts are sufficiently free from co-extractives and no clean-up on sorbents is required when the chlorophenols are analysed in free form.

Supercritical fluid extraction (SFE) has been proven to be a modern and efficient alternative for extraction of solid samples. An in situ supercritical fluid extraction and derivatization procedure for the determination of pentachlorophenol and related compounds in soil and sediment has been recently reported [27]. Phenols are extracted and acetylated in an one-step procedure with supercritical carbon dioxide in the presence of triethylamine and acetic anhydride. The recovery of the method ranged from 90% for 2,3,5,6-tetrachlorophenol to 104% for 2,3,4,5-tetrachlorophenol. This procedure is proven to be a reliable and rapid screening method for chlorinated phenols in soil contaminated by the wood preserving chemicals. A tandem supercritical fluid extraction–liquid chromatography system [28] seems to be a very progressive and favourable approach to the determination of chlorinated phenols in various solid matrices such as soil, wood and biological tissue. This system permits a direct introduction of supercritical fluid extracts into the liquid chromatograph, allowing quantitation down to the sub-parts per million (w/w) levels. The recoveries for chlorinated phenols from wood using SFE–HPLC technique varied from 84.7% for pentachlorophenol to 101.1 for 2,6-dichlorophenol.

Solid-phase extraction belongs also to the frequently used techniques because it is fast, safe and more efficient than the traditional liquid–liquid extraction. A variety of sorbents have been reported for the solid-phase extraction of chlorophenols such as phenyl-, octyl- and octadecylsilica bonded phases. The dependencies of recovery on the eluent volume, sample pH and sample volume were investigated, and the octadecylsilica (C_{18}) bonded phase was found to be the most efficient [29]. Fingler et al. found that the C_6, C_8, C_{18} reversed-phase adsorption for accumulation of lower chlorinated phenols as well as pentachlorophenol from water appeared to be efficient, reproducible and sensitive [30]. Various polymeric sorbents such as PRP-1, Amberlite XAD-4 and anion-exchange resins have also been reported.

The use of the Empore disks presents a new solid-phase extraction approach for a rapid and efficient isolation of organic contaminants from aqueous matrices. Its use offers to the analysts advantages in ease and specificity of elution that was not available with solvent extraction and/or solid-phase preparation techniques to such an extent [31]. The recoveries from the Empore disks are comparable to those obtained by liquid–liquid extraction using dichloromethane.

In solid-phase microextraction (SPME) sorbent-coated silica fibers are used to extract analytes from aqueous and gaseous samples. After extraction, the fibers are directly transferred to the GC injector, where the analytes are thermally desorbed and subsequently separated and quantified. This is a fast and simple analytical technique, which does not require solvents. The method based on poly-(acrylate)-coated fibers has been developed for the isolation of phenols which is capable of sub parts per billion limit of detection [32]. The SPME of phenolic compounds from the headspace over water has also been investigated in this study.

In capillary gas chromatographic separation of chlorinated phenols with commonly used stationary phases, peak tailing presents one of the serious problems. This results from the adsorption of polar analytes on the stationary phase. Derivatization of the substances under study is the recommended way to solve these problems. Methods using derivatization with diazomethane, acetic anhydride [25,33], methyl iodide [34], pentafluorbenzylbromide [25,35] or trimethylsulfoniumhydroxide [36] have been reported.

2.2. Chlorinated benzenes and chlorinated insecticides

The frequently used isolation technique for recovering chlorinated benzenes and chlorinated insecticides from environmental samples in the past as in present is a simple liquid–liquid extraction. Pentane, hexane, and a 1:1 mixture of diethyl ether or petroleumether and cyclohexane have been found to be the most effective extraction solvents for chlorinated benzenes [37,38]. Six liquid–liquid extraction methods for pesticide isolation in soils samples were tested and evaluated by Steinwandter [39]. Treatment overnight with BF_3-methanol prior to extraction was

found to be the most efficient method for recovery of hexachlorocyclohexane isomers.

The extraction of chlorobenzenes from aquatic sediments or soil can be achieved by Soxhlet extraction. The sewage sludges were Soxhlet extracted for 6 h with a mixture of hexane–acetone (2:1) in a full glass system [40]. The recoveries of chlorinated benzenes other than monochlorobenzene were 80–98%. The recovery of monochlorobenzene (MCB) was only 37%. MCB also gave a poor response on electron-capture detection (ECD). The municipal and industrial sludges were analysed also for various types of organic compounds inclusive chlorinated pesticides [41]. After liquid–liquid extraction, a procedure using various types of extraction mixtures and clean-up with gel permeation chromatography (Bio-Beads S-X3, 200-400 mesh) was performed. Capillary gas chromatography with ECD was used for quantitation. The recoveries of this method ranged from 87% for *p,p'*-DDE to 102% for *p,p'*-DDT. The limit of determination was 2 $\mu g\ kg^{-1}$.

As in the case of chlorinated phenols [23] an efficient and rapid screening method for neutral and acidic extractable organic pollutants in sediments should be mentioned. The use of a water soluble organic solvent (acetonitrile) for sediment extraction improves the recovery without pH adjustment or drying. The recoveries of this method met or exceeded EPA Method 8270 acceptance criteria. Matz et al. [42] brought an efficient alternative for determining chlororganic compounds in soil. Their procedure is based on a mobile headspace-gas chromatography–mass spectrometry method. A special modified headspace insert was used in this study. The headspace method is suitable for the contaminated soil with concentrations ranging from 0.1 to 100 $mg\ kg^{-1}$.

A rapid, efficient high-performance liquid chromatography (HPLC) method for isolating more than thirty various chlororganic contaminants from tissue and sediment extracts has been reported in 1988 [43]. The method was based on use of a size-exclusion column for separating the analytes of interest from interfering compounds in the sample matrix. The fractions were then analysed using capillary gas chromatography with electron capture, flame ionisation and/or mass selective detection. The HPLC clean-up method has several advantages compared to the conventional methods, e.g., increased efficiency, improved precision, the ability to monitor chromatographic conditions as well as the potential for automating the analyses. In addition to this, this HPLC method may be applicable to a variety of environmental samples.

The need for an inexpensive, simple and fast clean-up procedure for routine use in analysis of aqueous samples has led to the application of solid-phase extraction technique. The most widely used sorbent for nonpolar interactions is an octadecyl silica matrix. In a study by Bengtsson and Ramberg [44] river water samples fortified with sixty-two pesticides underwent solid-phase extraction using C_{18} as a bulk sorbent. For chlororganic pesticides analysed by GC with ECD the recoveries reached 99%.

A favourable method for the determination of a large group of pesticides in water covering also chlororganic insecticides by GC–MS with electron impact ionisation was developed in 1994 [45]. The preconcentration of 500 ml of water using membrane extraction on discs with C_{18}-bonded silica or styrene–divinylbenzene copolymer allowed the determination of pesticides at low $\mu g\ l^{-1}$ levels. The advantage of the high sensitivity of capillary GC with ECD is limited by the lower identification power of this technique. The coupling of GC with MS seems to be the most specific method for this type of analyses. The mass spectra under positive and negative chemical ionisation are also obtained in this study. Higher sensitivity with negative chemical ionisation was obtained for most compounds under study. The recoveries were over 85% for most compounds and the limits of detection ranged between 0.06 and 0.2 $\mu g\ l^{-1}$ in the full scan mode.

The modern SPME technique was successfully applied also for chlorinated insecticides. A fused-silica fiber 1 cm long coated with 100 μm of nonpolar polydimethylsiloxane stationary phase was used to extract the analytes from water samples over a concentration range of 0.001 to 100 $ng\ ml^{-1}$ [46]. Limits of detection varied in the levels from $ng\ l^{-1}$ for flame ionisation detection (FID) to sub $ng\ l^{-1}$ using MS or ECD. This SPME technique has been proven to be a viable and rapid alternative for the quantitative and qualitative analysis of organochlorines from aqueous environmental samples.

3. Experimental

A method for the determination of chlorinated phenols: pentachlorophenol (PCP), isomers of tetrachlorophenol (2,3,5,6-, 2,3,4,5-TeCP), trichlorophenol (2,3,5-, 2,4,6-, 2,3,6-TCP), dichlorophenol (2,4-, 2,6-DCP), chlorinated benzenes: hexachlorobenzene (HCB), pentachlorobenzene (PeCB), isomers of tetrachlorobenzene (1,2,3,5-, 1,2,4,5-TeCB), trichlorobenzene (1,3,5-, 1,2,4-, 1,2,3-TCB), dichlorobenzene (1,4- 1,3-, 1,2-DCB) and insecticides: DDE, DDT, isomers of hexachlorocyclohexane (α, β-, γ-, δ-HCH) in water, soil and crops was developed.

3.1. Chlorinated phenols

3.1.1. Isolation

3.1.1.1. Water

Isolation by simultaneous distillation and extraction with water vapour and toluene. Place the water sample (0.2–1 l) to which the internal standard is added (40 μl 2,6-dibromophenol, 1.0 μg ml^{-1}) in a round bottom flask and adjust the pH to 1 with 5 *M* HCl. Add 15 ml toluene and 15 ml saturated NaCl solution, connect the flask to a modified distillation column [47] equipped with a safety absorber containing 5 ml 0.1 *M* NaOH and heat to boil. The apparatus is described in detail in our work [35]. The water vapour and toluene distillation of the analytes occurs within 1.5 h and in the attached column the toluene phase is enriched with the compounds analyzed. Allow the system to cool down and drain the organic phase by a side valve into a separatory funnel containing 100 ml distilled water. The content of the safety absorber is also added to the separatory funnel. Extract the phenols by intensive shaking into the alkaline aqueous phase and then discard the organic phase. Adjust the pH of the aqueous phase to 1 with 5 *M* sulphuric acid and re-extract the phenols with three portions of dichloromethane (50, 25, 25 ml). Evaporate the joint extracts to a low volume and derivatize using the procedure described in Section 3.1.2.

For recovery studies, distilled water spiked with water solutions of the respective compounds was processed in the same way. The spiking was at the level of 0.001, 0.010 and 0.100 μg l^{-1} for all compounds except the DCP isomers which were spiked at the level of 0.01–1.00 μg l^{-1}.

Isolation by solid-phase extraction on Empore extraction discs. The 47 mm SDB Empore Extraction discs (polystyrene–divinylbenzene copolymer, Varian) were used. Prior to use, the disc is adjusted as follows: place the disc onto a layer of glass beads in a beaker and add acetone. Soak the disc for 1 h and repeat with fresh acetone. Afterwards, center the disc in the filtering apparatus and prewash with 10 ml of acetone. After 5 min, remove acetone by vacuum, apply 20 ml of methanol to the disc and allow to soak into the disc for 5 min. Remove methanol by rinsing with 25 ml water.

Filter the sample (0.2–0.5 l) if necessary, adjust to pH 2 with 5 *M* HCl, apply onto the adjusted disc and pass through under vacuum. After air-drying, elute the analytes from the disc with 20 ml methanol. Evaporate the eluate under vacuum to about 0.5 ml at 40°C and derivatize as described in Section 3.1.2.

3.1.1.2. Soil

Place the sample (20 g) into a round bottom flask, add the internal standard 2,6-DBP and 100 ml water and adjust the pH to 1 with 5 *M* HCl. Add 15 ml of saturated NaCl solution and 15 ml toluene and attach the flask to the distillation column as described in Section 3.1.1 on Water.

For recovery studies, 20 g soil samples spiked to 0.01, 0.10 and 1.00 mg kg^{-1} were analyzed.

3.1.1.3. Vegetables

Weigh a 20 g analytical sample of the homogenized vegetable into a round bottom flask. Add 2,6-DBP internal standard and 100 ml of 0.1 *M* KOH water solution and heat the flask to boil moderately under reflux for 30 min. After cooling, adjust the pH to 1 with 5 *M* HCl, add 15 ml of saturated NaCl solution and 15 ml toluene, attach to the distillation column and process the sample as described in Section 3.1.1 on Water.

3.1.2. Derivatization

Place the joint dichloromethane extracts resulting from the procedure in Section 3.1.1 in a 50 ml conical flask, evaporate just to dryness by a gentle stream of nitrogen and immediately dissolve the

residue in 4 ml acetone. Add 30 μl of 30% K_2CO_3 water solution and 200 μl of 1% acetone solution of pentafluorobenzyl bromide (PFBBr) and heat the flask under reflux for 1 h. When the derivatization is completed, take the solution down to approximately 0.5 ml with a stream of nitrogen. To remove the traces of acetone, dissolve the residue in 2 ml hexane and again evaporate to dryness. Then dissolve the residue in 1 ml hexane and clean up on activated Florisil column. Elute the analytes with 30 ml of 15% dichlormethane in toluene, filter the eluate through anhydrous sodium sulphate, evaporate to 1 ml with nitrogen and analyze by GC.

3.1.3. GC determination

For separation and determination of the PFB derivatives of chlorophenols, a HP 5890 GC equipped with a ^{63}Ni ECD was used. A 30 m×0.25 mm I.D., 0.25 μm film thickness fused-silica capillary column was used, the stationary phase was SPB-5 (5% phenyl-methylsilicone). Column temperature program: from 70°C (2 min) with a gradient 30°C min^{-1} to 105°C (10 min), then 4°C min^{-1} to 240°C which was held for 10 min. Carrier gas nitrogen, column head pressure 70 kPa, detector temperature 300°C, make-up gas nitrogen, flow 15.3 ml min^{-1}. Injector temperature 250°C. All injections were made in the splitless mode.

3.2. Chlorinated insecticides and benzenes

3.2.1. Isolation and clean-up

3.2.1.1. Water

Chlorinated insecticides. Solid-phase extraction on Empore discs was used for the isolation. Empore extraction discs with silica gel modified with octadecyl (C_{18}), 47 mm, by Varian were employed. Disc adjustment: wet the disc with 20 ml of a methylene chloride–ethyl acetate (1:1) mixture and allow to stand for 5 min without vacuum. Then dry the disc under vacuum. Add 2 ml methanol, allow to stand for 5 min with the vacuum off. When methanol drains through the disc so that only a 0.5 cm layer remains, apply 0.2–1 l water sample with the internal standard aldrin (50 μl, concentration 10 μg ml^{-1}) and draw under vacuum through the disc. Soak the disc with 20 ml ethyl acetate and allow to drain during 5 min into a flask, then apply 25 ml methylene chloride onto the disk, leave on the disc with vacuum off and drain. Filter the joint eluates through anhydrous sodium sulphate and take down to 1 ml with a gentle stream of nitrogen. The resulting solution is analyzed by GC–ECD. If necessary, the samples may be additionally cleaned up on a Florisil column as described in Section 3.2.1 on Soil.

Chlorinated benzenes. Solid-phase extraction on Empore discs was used. The same type of extraction discs was used as for the chlorophenols. Prior to use, pre-wash the disc with 20 ml acetone and let soak without vacuum for 5 min. Draw acetone through the disc and repeat the procedure. Add 20 ml methylene chloride and allow to stand without vacuum for 5 min. Draw methylene chloride through the disc. With vacuum on, draw air through disc for 1 min. Condition disc by adding 20 ml methanol and allowing to stand without vacuum for 5 min, add 100 ml water to methanol covering the disk. Draw most of the water through the disc. Release vacuum, leaving a layer of water above the disc. Apply the water sample (0.2–0.5 l) with 5 μl of the aldrin internal standard (concentration 10 μg ml^{-1}) onto the disc, then apply vacuum. Draw the water sample through the disc, then wash the disc with 30 ml distilled water. Dry the disc by drawing air under vacuum and elute the analytes with 30 ml methylene chloride without vacuum for 5 min. Apply vacuum and draw the solution into a flask. Repeat the elution with another 20 ml of methylene chloride. Remove water from the joint eluates by filtering through anhydrous sodium sulphate, take down to 1 ml with nitrogen and analyze by GC–ECD.

3.2.1.2. Soil

Soil sample (20 g) is deactivated with 25% water for 12 h in a tightly closed dark glass jar prior to the extraction. Aldrin is used as internal standard (50 μl of a 10 μg ml^{-1} solution).

Procedure: to bind the excess water, add siloxide to the deactivated soil sample in an amount sufficient for obtaining free-flowing powder. Place the sample in extraction cellulose thimble (Whatman) in a Soxhlet extractor and extract with 250 ml hexane for 8 h. Clean up the extract on a column made of 14 g Florisil and use 200 ml of 15% dichlormethane in hexane to elute the chlorinated benzenes and insec-

ticides [48]. Evaporate the eluate at 40°C on a vacuum rotary evaporator and analyze the compounds by GC–ECD according to Section 3.2.2.

3.2.1.3. Vegetables

Weigh a 20 g analytical sample from the homogenized vegetable, add the internal standard aldrin (50 μl, concentration 10 μg ml^{-1}) and enough siloxide to bind the water. Extract the vegetable-siloxide homogenate with hexane [48] in extraction cellulose thimble (Whatman) in a Soxhlet apparatus for 8 h. Proceed further as described in Section 3.2.1 on Soil.

3.2.2. GC determination

A 25 m×0.35 mm I.D., 0.33 μm film thickness HP-1 (methyl silicone) fused-silica capillary column was employed. Column temperature program: 60°C for 2 min, then 30°C min^{-1} to 175°C, hold for 2 min, then 0.5°C min^{-1} to 185°C, hold for 2 min, then 15°C min^{-1} to the final temperature 270°C which was held for 10 min.

Carrier gas was nitrogen, column head pressure 70 kPa, detector temperature 300°C, make-up gas nitrogen, flow 12 ml min^{-1}. Injector temperature was 250°C. All injections were made in the splitless mode.

4. Results and discussion

4.1. Analytical methods

Two methods were evaluated for the *isolation of chlorophenols* from water samples: steam distillation with toluene in a special apparatus and SPE using the SDB Empore extraction discs.

The steam distillation method proved to be suitable for all water samples including waste waters and sludge. These, however, must be hydrolyzed with KOH prior to the distillation as described for the vegetable samples. The distillation/extraction is then carried out following the adjustment of the pH to 1. With this extraction procedure, there is no problem connected to the formation of emulsions which is the main drawback of the occasionally used liquid–liquid extraction technique.

The recoveries of the steam distillation extraction method found in model experiments ranged from 75.94 to 89.69% in the concentration range of 0.01–1.0 μg l^{-1} of dichlorophenols and 0.001 to 0.1 μg l^{-1} of the higher chlorophenols. The relative standard deviation (R.S.D.) was below 8.5% (Table 1). The results are the average of ten replicate analyses.

The extraction on the SDB Empore discs is faster for the isolation of the chlorophenols from ground and surface waters but samples containing solid particles must be filtered prior to the extraction. For the extraction of very impure samples, the steam distillation/extraction is the method of choice. The recoveries of the extraction on Empore discs ranged between 74.14 and 97.92% and the R.S.D. was 2.48–9.15%.

The Empore discs also proved to be more advantageous than the solid-phase columns with modified silica gel [49] because of their higher stability in a broad pH range. Thus, higher recoveries of all compounds under study could be obtained.

The simultaneous steam distillation/toluene extraction followed by clean up by liquid–liquid partitioning at changing pH and derivatization with PFBBr proved to be suitable for the isolation of chlorophenols from soils and vegetables (carrot, parsley, cabbage, kale, tomatoes, onion, kohlrabi). The recoveries calculated from ten replicate analyses of soil spiked with 0.01 to 1.0 mg kg^{-1} of the respective chlorophenols were 71.31 to 85.05%, with R.S.D.s ranging from 2.58 to 13.28%. The recoveries from vegetable samples at the levels of 0.01 to 1.0 mg kg^{-1} were 71.1 to 89.65%, R.S.D. 3.86 to 11.28% (Table 2).

Table 1 also gives the limits of quantification (LOQs) for the GC–ECD analyses of the PFB derivatives of chlorophenols in water which are 0.0003 to 0.0006 μg l^{-1} for different compounds. In vegetables and soil, the LOQ is in the range of 0.0005–0.0009 mg kg^{-1} (Table 2).

Acetylation is a frequently used derivatization method for chlorophenols, however, we find the derivatization with PFBBr [50] quite fast and quantitative. The PFB derivatives are stable and easy to chromatograph and they are very sensitive to EC detection. The sensitivity of the detection is greatly increased compared to the parent compounds. The reaction of chlorophenols with PFBBr was base catalyzed by K_2CO_3. The optimum conversion

Table 1
Characteristics of the analytical method for determination of chlorinated phenols from water sample-comparison of isolation by extraction on Empore disc and distillation technique

Compounds	LOQ ($\mu g\ l^{-1}$)	Concentration ($\mu g\ l^{-1}$)	Recovery±R.S.D. Distillation method (%)	Recovery±R.S.D. SPE method (%)
2,4-DCP	0.0004	0.010	81.44±4.44	97.92±4.73
		0.100	81.46±7.61	85.43±2.82
		1.000	79.11±4.61	84.94±3.68
2,6-DCP	0.0004	0.010	81.40±5.36	96.96±4.56
		0.100	81.58±6.89	86.09±3.02
		1.000	78.36±7.12	78.77±5.38
2,3,5-TCP	0.0003	0.001	79.39±8.50	88.29±2.58
		0.010	76.94±4.86	80.42±3.73
		0.100	75.94±4.33	77.90±9.15
2,4,6-TCP	0.0003	0.001	83.35±6.92	84.90±6.36
		0.010	80.16±4.99	79.31±4.75
		0.100	78.87±6.42	74.73±4.83
2,4,5-TCP	0.0003	0.001	89.69±8.48	85.25±2.48
		0.010	86.13±3.36	79.98±7.80
		0.100	82.56±4.25	75.57±5.16
2,3,6-TCP	0.0003	0.001	85.57±6.73	87.02±3.85
		0.010	79.78±5.35	79.39±3.93
		0.100	76.87±3.92	74.14±5.04
2,3,5,6-TeCP	0.0003	0.001	84.70±3.25	89.42±5.77
		0.010	80.35±4.03	84.04±5.14
		0.100	79.27±6.43	77.07±4.23
2,3,4,5-TeCP	0.0003	0.001	80.57±5.25	86.75±7.14
		0.010	78.55±5.36	85.88±6.59
		0.100	76.40±4.21	76.09±5.13
PCP	0.0006	0.001	80.91±4.94	96.83±4.18
		0.010	80.44±6.51	85.34±6.48
		0.100	79.96±6.20	84.54±6.47

$n = 10$ parallel determination, LOQ: limit of quantification.
DCP: dichlorophenol, TCP: trichlorophenol, TeCP: tetrachlorophenol, PCP: pentachlorophenol.

occurred at heating to 60°C for 1 h under reflux. The drawback of this method is its unspecifity. The by-products formed must be removed prior to GC analysis on a Florisil column or, alternatively, by gel permeation chromatography on a Presep column [33].

For the *isolation of chlorinated insecticides* (isomers of HCH, DDE and DDT) from water samples, solid-phase extraction on Empore C_{18} discs was employed. The recoveries of the compounds under study in the concentration in the range of 0.005–1.0 $\mu g\ l^{-1}$ for DDE and DDT and 0.001–0.1 $\mu g\ l^{-1}$ for the other compounds ranged from 70.81 to 81.63%, the R.S.D. was 4.76 to 13.58% (Table 3). The LOQ with this method is from 0.0009 to 0.005 $\mu g\ l^{-1}$ for the different compounds. For groundwater samples, SPE on Separcol C_{18} columns was also successfully used, the recoveries ranged between 89.35 and

Table 2
Characteristics of the analytical method for determination of chlorinated phenols in soil and vegetables by simultaneous distillation and extraction with water vapour and toluene

Compounds	LOQ (mg kg^{-1})	Concentration (mg kg^{-1})	Recovery±R.S.D. from soil (%)	Recovery±R.S.D. from vegetables (%)
2,4-DCP	0.0008	0.010	74.11±7.04	78.69±8.46
		0.100	71.31±5.12	80.83±8.20
		1.000	83.64±6.24	84.86±5.40
2,6-DCP	0.0008	0.010	72.24±9.15	71.10±5.15
		0.100	71.99±9.15	79.74±5.44
		1.000	84.08±4.46	84.56±6.95
2,3,5-TCP	0.0005	0.010	73.02±6.42	75.49±7.97
		0.100	73.63±9.98	80.26±9.91
		1.000	82.93±3.58	89.65±6.31
2,4,6-TCP	0.0005	0.010	73.20±9.63	74.24±6.41
		0.100	76.38±9.82	80.81±10.32
		1.000	81.72±4.96	85.50±4.97
2,4,5-TCP	0.0005	0.010	72.75±13.28	75.69±8.07
		0.100	78.61±8.56	81.20±10.96
		1.000	77.63±2.58	80.32±5.57
2,3,6-TCP	0.0005	0.010	74.10±8.50	76.37±5.09
		0.100	78.04±5.54	81.93±9.19
		1.000	85.05±3.50	86.06±5.69
2,3,5,6-TeCP	0.0005	0.010	73.74±10.32	76.69±4.13
		0.100	78.75±7.49	80.33±7.59
		1.000	81.01±8.89	83.70±8.65
2,3,4,5-TeCP	0.0005	0.010	72.82±9.24	76.08±6.41
		0.100	78.47±9.94	81.43±6.51
		1.000	76.82±4.46	79.50±3.86
PCP	0.0009	0.010	74.54±8.38	77.22±11.28
		0.100	75.23±7.96	81.59±6.58
		1.000	78.69±7.71	80.46±9.96

$n = 10$ parallel determination, LOQ: limit of quantification.
DCP: dichlorophenol, TCP: trichlorophenol, TeCP: tetrachlorophenol, PCP: pentachlorophenol.

103.25%. However, these columns could not be used for more polluted waters.

Chlorinated benzenes (HCB, PeCB, isomers of DCB, TCB and TeCB) were extracted from the waters by SPE on the SDB Empore discs. The results of the recovery studies are in Table 3. The recoveries of the respective chlorobenzenes were 63.81 to 80.10%, R.S.D. 4.61 to 11.71%. The model samples were spiked at 0.005 to 0.5 μg l^{-1} with the dichlorobenzenes and 0.001 to 0.1 μg l^{-1} with the other chlorobenzenes. The LOQs ranged between 0.001 and 0.005 μg l^{-1}.

For the isolation of chlorinated insecticides and benzenes from soils samples, supercritical fluid extraction with supercritical carbon dioxide is frequently used. Soxhlet extraction with acetone–hexane mixtures [40] are also frequently used. We have compared several ways of extraction [48] and

Table 3
Characteristics of the analytical method for determination of chlorinated insecticides and benzenes in water by extraction on Empore discs

Compounds	LOQ ($\mu g\ l^{-1}$)	Concentration ($\mu g\ l^{-1}$)	Recovery±R.S.D. (%)
α-HCH	0.0009	0.001	76.53±8.68
		0.010	80.10±4.76
		0.100	76.18±9.09
β-HCH	0.0010	0.001	76.94±10.35
		0.010	76.26±11.67
		0.100	76.43±7.25
γ-HCH	0.0009	0.001	76.86±13.58
		0.010	79.04±8.79
		0.100	76.74±9.52
δ-HCH	0.0009	0.001	72.03±6.65
		0.010	75.61±9.59
		0.100	76.73±10.41
DDE	0.0020	0.005	72.35±8.78
		0.050	79.75±9.84
		0.500	81.63±10.23
DDT	0.0050	0.010	70.81±10.31
		0.100	77.05±9.46
		1.000	80.14±10.29
1,4-+1,3-DCB	0.005	0.005	68.92±7.76
		0.050	75.72±5.78
		0.500	77.39±7.60
1,2-DCB	0.002	0.005	67.41±9.11
		0.050	76.45±7.15
		0.500	76.95±4.61
1,3,5-TCB	0.001	0.001	66.22±9.07
		0.010	74.37±8.08
		0.100	77.28±8.69
1,2,4-TCB	0.001	0.001	63.81±11.71
		0.010	73.49±8.08
		0.100	76.64±6.73
1,2,3-TCB	0.001	0.001	65.91±8.31
		0.010	75.66±8.22
		0.100	77.90±7.93
1,2,3,5-−1,2,4,5-TeCB	0.001	0.001	64.61±7.3
		0.010	73.97±9.21
		0.100	78.37±6.83
PeCB	0.001	0.001	67.57±9.83
		0.010	72.57±7.43
		0.100	79.18±6.92
HCB	0.001	0.001	71.85±9.02
		0.010	76.59±11.47
		0.100	80.10±7.76

$n = 10$ parallel determination, LOQ: limit of quantification.
HCH: hexachlorocyclohexane, DDE: 1,1-dichloro-2,2-bis-(4-chlorophenyl) ethylene; DDT: 1,1,1-trichloro-2,2-bis-(4-chlorophenyl) ethane, DCB: dichlorobenzene, TCB: trichlorobenzene, TeCB: tetrachlorobenzene, PeCP: pentachlorobenzene, HCB: hexachlorobenzene.

Table 4
Characteristics of the analytical method for determination of the chlorinated insecticides and benzenes in soil and vegetables

Compounds	LOQ (mg kg^{-1})	Concentration (mg kg^{-1})	Recovery±R.S.D. from soil (%)	Recovery±R.S.D. from vegetables (%)
α-HCH	0.001	0.001	82.21±8.21	82.23±8.99
		0.010	83.24±9.35	82.28±9.25
		0.100	84.41±9.12	83.00±8.24
β-HCH	0.001	0.001	84.55±8.21	82.13±10.23
		0.010	82.78±10.25	82.33±9.97
		0.100	85.54±5.51	84.84±7.99
γ-HCH	0.001	0.001	86.32±7.24	85.46±9.74
		0.010	86.35±8.24	85.36±8.99
		0.100	86.98±7.28	86.12±4.28
δ-HCH	0.001	0.001	77.35±8.63	79.32±9.12
		0.010	78.39±8.92	80.24±11.11
		0.100	78.89±9.26	81.10±8.25
DDE	0.005	0.005	84.12±11.31	79.21±9.94
		0.050	85.12±9.96	79.44±11.08
		0.500	85.31±8.92	81.03±9.57
DDT	0.005	0.010	80.21±7.31	79.98±9.79
		0.100	81.31±6.49	84.03±8.79
		1.000	84.12±8.12	84.87±10.38
1,4-+1,3-DCB	0.001	0.005	72.11±8.14	70.77±9.22
		0.050	73.24±4.52	72.35±8.41
		0.500	73.84±9.21	76.44±6.22
1,2-DCB	0.001	0.005	70.35±10.23	72.24±8.22
		0.050	70.88±10.21	72.34±6.88
		0.500	71.01±10.44	76.33±7.85
1,3,5-TCB	0.001	0.001	69.99±11.22	74.23±8.03
		0.010	70.12±9.82	76.33±8.21
		0.100	71.01±8.44	77.11±7.12
1,2,4-TCB	0.001	0.001	69.99±10.00	72.06±8.22
		0.010	69.89±10.22	79.01±11.04
		0.100	70.97±9.98	78.99±8.44
1,2,3-TCB	0.001	0.001	72.04±9.88	75.88±7.33
		0.010	71.02±9.22	79.49±11.01
		0.100	70.33±6.85	79.01±6.35
TeCB[a]	0.001	0.001	70.23±9.99	70.84±8.45
		0.010	69.99±8.51	74.54±8.41
		0.100	71.00±7.99	76.34±8.99
PeCB	0.001	0.001	70.88±10.48	71.11±8.41
		0.010	72.99±10.39	73.21±8.59
		0.100	73.55±9.81	74.21±7.12
HCB	0.001	0.001	76.02±9.74	70.65±8.15
		0.010	76.21±9.04	71.54±7.99
		0.100	75.06±8.44	74.43±8.94

$n = 10$ parallel determination, LOQ: limit of quantification.
HCH: hexachlorocyclohexane, DDE: 1,1-dichloro-2,2-bis-(4-chlorophenyl) ethylene; DDT: 1,1,1-trichloro-2,2-bis-(4-chlorophenyl) ethane, DCB: dichlorobenzene, TCB: trichlorobenzene, TeCB: tetrachlorobenzene (1,2,3,5-+1,2,4,5-)[a], PeCP: pentachlorobenzene, HCB: hexachlorobenzene.

achieved the least amount of interfering co-extractives and the best recoveries of chlorobenzenes from soil by Soxhlet extraction with hexane. The soil sample had been pre-treated by de-activating with water, the excess water had been bonded with siloxide. The recoveries of chlorobenzenes were 69.89–76.21%, R.S.D. 4.52–11.22%. For chlorinated insecticides, the recoveries were from 77.35 to 86.98% and the R.S.D. was 5.51–11.31% (Table 4).

Table 4 summarize the recoveries of chlorinated benzenes and insecticides in vegetable samples at the levels of chlorobenzenes from 0.001 to 0.50 mg kg^{-1} and those of chlorinated insecticides from 0.001 to 1.0 mg kg^{-1}. The recoveries of chlorobenzenes ranged between 70.65–79.49%, R.S.D. 6.22–11.04%. For chlorinated insecticides, the recoveries were 79.21–86.12%, R.S.D. 4.28–11.11%.

In general, the recoveries of the methods were adequate i.e., well over 70% in most cases, with the only exception of the lowest levels of chlorobenzenes in water where the recoveries were between 64 and 69%. However, the R.S.D. values were below 12% even for these analyses (Table 3).

For the validation of analytical methods the soil and vegetable samples from non contaminated areas were used. The concentrations of compounds under study ranged from <0.0001 to 0.001 mg kg^{-1}.

4.2. Levels of chlororoganic compounds in real samples

The methods described were used for determining the levels of contamination of ground and surface water from localities contaminated by agrochemical and communal wastes, soils from these localities and vegetables grown there. The waters from the rivers Danube and Váh have also been analyzed [51]. The results of the analyses of ground and surface waters are summarized in Tables 5 and 6.

As can be seen, the highest levels were found for

Table 5
Levels of chlorinated compounds in ground and surface waters

Compounds	Ground water (μg l^{-1})			Surface water (μg l^{-1})		
	Average	Maximum	90th%	Average	Maximum	90th%
2,4-DCP	0.025	0.077	0.068	1.224	6.971	2.707
2,6-DCP	0.118	0.450	0.154	0.390	4.340	1.440
2,3,5-TCP	0.045	0.141	0.062	0.055	0.629	0.189
2,4,6-TCP	0.048	0.250	0.055	0.073	1.431	0.170
2,3,6-TCP	0.002	0.018	0.003	0.047	3.110	0.033
TeCP[b]	0.030	0.066	0.045	0.016	0.446	0.037
PCP	0.071	0.321	0.113	0.484	3.942	1.258
1,4-+1,3-DCB	ND	ND	ND	0.028	0.490	0.097
1,2-DCB	0.022	0.070	0.038	0.011	0.131	0.034
1,3,5-TCB	0.003	0.006	0.005	0.003	0.045	0.009
1,2,4-TCB	0.002	0.008	0.004	0.005	0.060	0.012
1,2,3-TCB	0.001	0.009	0.003	0.013	0.104	0.033
TeCB[a]	0.011	0.032	0.016	0.006	0.130	0.013
PeCB	0.006	0.038	0.007	0.018	0.349	0.054
HCB	0.001	0.005	0.004	0.012	0.107	0.037
α-HCH	0.001	0.008	0.003	0.015	0.156	0.077
β-HCH	0.001	0.009	0.003	0.020	0.113	0.033
γ-HCH	ND	0.005	ND	0.029	0.122	0.054
δ-HCH	0.002	0.019	ND	0.005	0.047	0.007
DDE	0.004	0.021	0.006	0.125	0.674	0.491
DDT	0.016	0.066	0.032	0.041	0.553	0.150

ND: not determined (below LOQ).
DCP: dichlorophenol, TCP: trichlorophenol, TeCP: tetrachlorophenol (2,3,5,6-+2,3,4,5-)[b], PCP: pentachlorophenol, DCB: dichlorobenzene, TCB: trichlorobenzene, TeCB: tetrachlorobenzene (1,2,3,5-+1,2,4,5-)[a], PeCP: pentachlorobenzene, HCB: hexachlorobenzene, HCH: hexachlorocyclohexane, DDE: 1,1-dichloro-2,2-bis-(4-chlorophenyl) ethylene; DDT: 1,1,1-trichloro-2,2-bis-(4-chlorophenyl) ethane.

Table 6
Levels of chlorinated compounds in soil and vegetables

Compounds	Soil (mg kg^{-1})			Vegetables (mg kg^{-1})		
	Average	Maximum	90th%	Average	Maximum	90th%
2,4-DCP	0.011	0.014	0.012	0.067	0.730	0.273
2,6-DCP	0.005	0.014	0.009	0.065	0.515	0.229
2,3,5-TCP	0.001	0.004	0.002	0.011	0.368	0.027
2,4,6-TCP	0.001	0.008	0.003	0.022	0.348	0.063
2,3,6-TCP	0.001	0.006	0.004	0.008	0.152	0.012
TeCP[b]	0.001	0.006	0.004	0.004	0.062	0.011
PCP	0.002	0.007	0.006	0.017	0.211	0.058
1,4-+1,3-DCB	0.001	0.008	0.005	0.008	0.076	0.033
1,2-DCB	ND	ND	ND	ND	0.009	0.001
1,3,5-TCB	0.001	0.008	0.003	0.026	0.800	0.008
1,2,4-TCB	0.021	0.095	0.046	0.002	0,038	0.006
1,2,3-TCB	0.004	0.012	0.008	0.010	0.081	0.052
TeCB[a]	0.044	0.098	0.067	0.008	0.126	0.036
PeCB	0.007	0.017	0.012	0.001	0.018	0.003
HCB	0.013	0.026	0.018	0.003	0.058	0.007
α-HCH	0.007	0.014	0.009	0.003	0.058	0.009
β-HCH	ND	ND	ND	ND	ND	ND
γ-HCH	0.001	0.062	0.023	0.007	0.183	0.008
δ-HCH	0.004	0.008	0.005	0.003	0.016	0.003
DDE	0.006	0.056	0.014	0.009	0.087	0.035
DDT	0.005	0.059	0.020	0.037	0.492	0.089

ND: not detected (below LOQ).
DCP: dichlorophenol, TCP: trichlorophenol, TeCP: tetrachlorophenol (2,3,5,6-+2,3,4,5-)[b],PCP: pentachlorophenol, DCB: dichlorobenzene, TCB: trichlorobenzene, TeCB: tetrachlorobenzene (1,2,3,5-+1,2,4,5-)[a], PeCP: pentachlorobenzene, HCB: hexachlorobenzene, HCH: hexachlorocyclohexane, DDE: 1,1-dichloro-2,2-bis-(4-chlorophenyl) ethylene, DDT: 1,1,1-trichloro-2,2-bis-(4-chlorophenyl) ethane.

chlorinated phenols which may be related to their higher water solubility in comparison with the other chlororganic compounds studied as well as to the fact that chlorinated insecticides have been excluded from manufacture and use for more than 20 years in Slovakia. From among the chlorophenols, 2,6-DCP and PCP levels were the highest in ground water in terms of the average content as well as in terms of the 90th percentile. The maximum levels of 2,4,6-TCP were also higher in comparison with the other chlorophenols. In surface waters, the average levels of 2,4-DCP were the highest, followed by 2,6-DCP and PCP average levels which were two to three times lower. The same is true for the 90th percentile. In terms of maximum levels, 2,4,6-TCP and 2,3,6-TCP findings were higher than the other chlorophenols, the levels being in the order of μg l^{-1}. This is especially important for 2,4,6-TCP which is classified as a carcinogen.

From among the chlorobenzenes and chlorinated insecticides, the highest average, maximum and 90th percentile levels in ground water were found for 1,2-DCB and DDT. In surface waters, the 1,4-+1,3-DCB and the DDT and DDE levels were the highest [51].

The results concerning the levels of the chlororganic contaminants in the soil and the vegetables are summarized in Table 6. In the soil, even the maximum concentrations did not exceed 0.1 mg kg^{-1}. However, in spite of the fact that the soils samples originated from a locality which was a former dumping site of a chemical plant, it should be considered that the upper soil layer used for vegetable cultivation (20 cm) had been brought in from an uncontaminated area, several years after the dumping site had been abandoned.

The results of the analyses of vegetables concern the samples from the chemical waste dumping site as well as those from the vicinity of the communal waste dumping site. The chlorophenol levels in the

vegetables were somewhat higher for the DCP isomers, both in the average and the maximum values and in the 90th percentiles. The TCP and PCP levels were also relatively high. For chlorobenzenes and chlorinated insecticides, DDT and 1,3,5-TCB were the compounds occurring at the highest levels. In comparison with our previous results of the analyses of vegetable samples from a regular food supply [52], the levels of DDT and DDE in the present samples were somewhat higher. There is no marked difference between the levels of chlorobenzenes in the regular food supply and those found in vegetables grown in the vicinity of the chemical and communal dumping sites.

5. Conclusions

In the recent years, an important development has been observed in the methodology of isolation, separation and identification of chlorinated organic compounds in the environment, in particular in drinking and surface waters and in foods. Trace concentrations of chlorinated pesticides can be analyzed by capillary gas–liquid chromatography with sensitive and selective detection techniques, following the isolation with the modern techniques of solid-phase extraction and supercritical fluid extraction. Based on our experience, solid-phase extraction on Empore discs is the method of choice for the isolation of chlorophenols, chlorobenzenes and chlorinated insecticides from water samples. For soil and vegetable samples, the steam distillation/extraction technique and Soxhlet extraction were found to be more convenient.

References

[1] R. Engst, R.M. Macholz, M. Kujava, Res. Rev. 2 (1979) 71–95.
[2] R.M. Macholz, M. Kujawa, Res. Rev. 94 (1985) 119–149.
[3] I.C. MacRae, Rev. Environ. Contam. Toxicol. 109 (1989) 1–87.
[4] WHO, Pentachlorophenol, Environmental Health Criteria, No. 71, IPCS, Geneva, 1987.
[5] D.G. Crosby, K.I. Beynon, P.A. Greve, F. Korte, G.G. Still, J.W. Vonk, Pure Appl. Chem. 53 (1981) 1051–1080.
[6] L. Renberg, Gas Chromatographic Determination of Chlorophenols in Environmental Samples, National Swedish Environment Protection Board, Liber Tryck, Stockholm, 1981, pp. 1–58.
[7] K.L.E. Kaiser, I. Valdmanis, Can. J. Chem. 60 (1982) 2104–2106.
[8] WHO, Chlorophenols other than Pentachlorophenol, Environmental Health Criteria, No. 93, IPCS, Geneva, 1989.
[9] WHO, Chlorobenzenes other than Hexachlorobenzene, Environmental Health Criteria, No. 128, IPCS, Geneva, 1991.
[10] WHO, Lindane, Environmental Health Criteria, No. 124, IPCS, Geneva, 1991.
[11] V.M. Samokyszin, J.P. Freeman, K.R. Maddipati, R.V. Lioyd, Chem. Res. Toxicol. 8 (1995) 349–355.
[12] D.L. Houghton, L. Ritter, J. Am. Coll. Toxicol. 14 (1995) 71–89.
[13] R. Millikan, E. Devoto, B. Newman, D. Savitz, Breast Cancer Res. Treatment 35 (1995) 79–89.
[14] J.V. Holder and G. Stöhner, in: WHO, Lindane, Environmental Health Criteria, No. 124, IPCS, Geneva, 1991.
[15] A. Sorokin, J.L. Seris, B. Meunier, Science 268 (1995) 1163–1166.
[16] J.J.P. Bogaards, B. Vanommen, C.R. Wolf, P.J. Vanbladeren, Toxic. Appl. Pharmacol. 132 (1995) 44–52.
[17] L. Kohlmeier, M. Kohlmeier, Environ. Health Perspect. 103 (1995) 99–106.
[18] D. Kumar, P.K. Khan, S.P. Sinha, Food Chem. Toxicol. 33 (1995) 309–314.
[19] F. Dietz, J. Traud, Vom Wasser 51 (1978) 235–237.
[20] WHO, Guidelines for Drinking Water Quality, Vol. 1: Recomendations, Geneva, 1993.
[21] A. Jensen, G. Erikson, H. Kylin, Chemosphere 24 (1992) 229–245.
[22] W. Ebing, G. Richtarsky, Gesunde Pflanzen 38 (1986) 275–285.
[23] W.M. Davis, J.A. Coates, K.L. Garcia, L.L. Signorella, J.J. Delfino, J. Chromatogr. 643 (1993) 341–350.
[24] H.B. Lee, Y.D. Stokker, A.S.Y. Chau, J. Assoc. Off. Anal. Chem. 70 (1987) 1003–1008.
[25] V. Gajdušková, R. Ulrich and M. Jiaxisová, in E. Heinisch, A. Kettrup and S. Wenzel-Klein (Editors), Rueckstände chlorierter Phenole in Nahrungsketten, Schadstoffatlas Osteuropa, Ecomed. Forsch., 1994, pp. 104–107.
[26] M. Veningerová, V. Prachar, J. Uhnák, Fresenius Envir. Bull. 2 (1993) 386–393.
[27] H.B. Lee, T.E. Peart, R.L. Hong-You, J. Chromatogr. 605 (1992) 109–133.
[28] M.H. Liu, S. Kapilla, K.S. Nam, J. Chromatogr. 639 (1993) 151–157.
[29] J. Frébortová, V. Tatarkovičová, Analyst 119 (1994) 1519–1523.
[30] S. Fingler, V. Drevenkar, Ž. Vasilič, Mikrochim. Acta 11 (1987) 163–175.
[31] T. McDonnell, J. Rosenfeld, A. Rai-Firouz, J. Chromatogr. 629 (1993) 41–53.
[32] K.D. Buchholz, J. Pawliszyn, Anal. Chem. 66 (1994) 160–167.

[33] J. Hajšlová, V. Kocourek, I. Zemanová, F. Pudil, J. Davídek, J. Chromatogr. 439 (1988) 307–316.
[34] I. Cruz, D.E. Wells, Intern. J. Environ. Anal. Chem. 48 (1992) 101–113.
[35] M. Veningerová, V. Prachar, J. Uhnák, J. Kovačičová, Z. Lebensm. Unters. Forsch. 199 (1994) 317–321.
[36] M. Syhrem, G. Hanschmann and R. Heber, Chlorphenole-Derivatisierung und Bestimmung auf Moderne Art, GIT Fachz. Lab., Vol. 11, 1994, pp. 1234–1236.
[37] S. Fingler, V. Drevenkar, B. Tkalèeviè, Z. Šmit, Bull. Environ. Contam. Toxicol. 49 (1992) 805–812.
[38] US EPA, Health Assesment Document for Chlorinated Benzenes, Final Report No. EPA/600/8-84/015F, January 1985, Office of Health and Environmental Assesment, Washington, DC, USA.
[39] H. Steinwandter, Fresenius Z. Anal. Chem. 327 (1987) 309–311.
[40] M.J. Wang, K.C. Jones, Chemosphere 28 (1994) 1201–1210.
[41] P. Frost, R. Camenzind, A. Mägert, R. Bonjour, G. Karlaganis, J. Chromatogr. 643 (1993) 379–388.
[42] G. Matz, W. Schrödre and P. Kesners, in F. Arendt, M. Hinsenveld and W.J. van den Brink (Editors), Schnelle Vor-Ort Bodenanalytik: Ein Mobiles GC–MS Sytem im Vergleich mit Laborverfahren, Altlstensanierung 90, Kluwer, Dordrecht, Boston, London, 1990, pp. 869–876.
[43] M.M. Krahn, L.K. Moore, R.G. Bogar, C.A. Wigren, S.L. Chan, D.W. Brown, J. Chromatogr. 437 (1988) 161–175.
[44] S. Bengtsson, A. Ramberg, J. Chromatogr. Sci. 33 (1995) 554–556.
[45] C. Crespo, R.M. Marcé, F. Borrull, J. Chromatogr. A 670 (1994) 135–144.
[46] S. Magdic, J.B. Pawliszyn, J. Chromatogr. A 723 (1996) 111–122.
[47] G.P. Kann, T.S. Mah, N.I. Wade, J. Assoc. Off. Anal. Chem. 64 (1981) 1305–1308.
[48] M. Veningerová, J. Uhnák, Acta Hyg. Microbiol. 1 (1989) 63–88.
[49] Z. Vozňáková, I. Veterník, Sci. Tech. J. Projection, Implemnetation Planning Water Air Protect. 7 (1993) 40–43.
[50] B. Lee, A.S.Y. Chau, J. Assoc. Off. Anal. Chem. 67 (1984) 1086–1089.
[51] M. Veningerová, V. Prachar, J. Uhnák, J. Kovačičová, Fresenius Environ. Bull. 5 (1996) 361–368.
[52] M. Veningerová, J. Uhnák, V. Prachar, Fresenius Environ. Bull. 2 (1993) 735–744.