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OPTIMIZATION OF ANALYTICAL METHODS FOR THE DETERMINATION OF TRACE CONCENTRATIONS OF TOXIC POLLUTANTS IN DRINKING AND SURFACE WATERS

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ABSTRACT

Pollutants posing health risks to human health and to the aquatic environment often occur in drinking and surface waters, as a result of disinfection practices, agricultural and industrial activities, wastewater discharges. Toxic pollutants belong to different chemical categories, including chlorination by-products, volatile and semivolatile organic compounds, insecticides (organochlorine and organophosphorous), herbicides (triazines and substituted ureas), metals and organotin compounds. Optimization of different analytical methods needed for their laboratory determination is necessary, since most of these pollutants have toxic effects when they are present even at trace concentrations in water. The investigation described here includes optimization of analytical methods applied in the Water and Air Quality Laboratory of the University of the Aegean for determination of 130 toxic pollutants in water, by means of gas chromatography with ECD, NPD, FPD and MS detection, Purge and Trap concentration, high performance liquid chromatography (HPLC) with Diode Array Detection (DAD) and atomic absorption spectrometry (AAS). The methods described were selected for application to surface water and drinking water samples from Greece, after experimental modifications which resulted in the best analytical performance achievable with the particular instrumentation, expressed by the calculated recoveries and detection limits.

KEYWORDS: analytical methods, chlorination by-products, volatile organic compounds, insecticides, herbicides, metals, organotin compounds

INTRODUCTION

A large number of toxic pollutants have been detected in drinking and surface waters worldwide, raising concerns about possible impacts on the environment and human health. Toxic pollutants including volatile and semivolatile organic compounds (VOCs), organochlorine and organophosphorous insecticides, herbicides, metals and organotin compounds (OTs) are released from various human activities, such as agriculture and industry. Another major category of compounds, chlorination by-products (CBPs) are formed during water disinfection, by reactions of chlorine with natural organic matter (Fent and Hunn, 1995; Albanis et al., 1998; Cancho et al., 1999; Golfinopoulos and Nikolaou, 2001; Richardson 2002; Cerejeira et al., 2003).

Many toxic pollutants have been regulated by the European Union, the United States Environmental Protection Agency and the World Health Organization (EEC, 1982; WHO, 1995; USEPA, 1998; EC, 2000). In order to obtain information about their occurrence in water, their levels, their transport and fate and their possible transformations, sensitive analytical methods are a necessary tool. The optimization of different analytical methods for the determination of toxic pollutants is an issue of critical importance, since it affects the capability of screening, quantifying and even minimizing their concentrations in water (by legal measures) (Lekkas, 2000a).

This work presents the results of the optimization efforts for ten analytical methods for the determination of 130 toxic pollutants in water (Table 1). The techniques utilized include gas chromatography (GC) with ECD, NPD, FPD and MS detection, Purge and Trap, high performance liquid chromatography (HPLC) with Diode Array Detection (DAD) and atomic absorption spectrometry (AAS). The objective was to obtain reliable methods that can be applied on a routine basis, providing acceptable recoveries and low detection limits (DLs). These methods are applied in the Water and Air Quality Laboratory of the University of the Aegean, where CBPs are analyzed monthly in chlorinated drinking water from Athens (25 sampling stations) (Golfinopoulos and Nikolaou, 2001), and the other toxic pollutants are analyzed seasonally in the surface waters of Greece, from the 53 sampling stations of the National Monitoring Network (Lekkas, 2000a).

ANALYTICAL METHODS

Glassware. All glassware was washed with detergent, rinsed with tap water, ultrapure water (Millipore: Milli-Ro 5 plus and Milli Q plus 185) and acetone (Mallinckrodt Chemical Works St. Louis) and placed in an oven at 105 ^{O}C overnight.

Chlorination by-products

Sampling. Samples were collected in 40-ml amber glass bottles with polypropylene screw caps and TFE-faced septa (Pierce 13075), which were carefully filled just to overflow. The residual chlorine was quenched by addition of sodium sulfite for the volatile CBPs and ammonium chloride for HAAs (100 mg per liter of sample in both cases).

Standard solutions. Stock solutions of volatile CBPs were prepared in methanol purge and trap grade (Sigma-Aldrich) by addition of certified CBPs standards (Chemservice, purity > 99 %). The nine haloacetic acids (HAAs) and their methyl esters in methyl-tert-butyl ether (MTBE) were purchased from Supelco and were accompanied with certificates of analysis (purity > 99 %). All stock solutions were stored at 4 ^{O}C.

Sample preparation. A. Volatile CBPs. A modification of EPA Method 551.1 was performed (Nikolaou et al., 2002a). 6 g sodium sulfate anhydrous (Merck) and 2 ml MTBE (Merck) were added to 35 ml of CBPs solution in a 40-ml glass vial capped with PTFE-faced silica septum (Pierce 13075). The vial was sealed and shaken for 1 min and left undisturbed for 2 min. 1 μl of the ether phase was then injected into the GC.

B. HAAs. Acidic methanol esterification was applied (Nikolaou et al., 2002b). 30 ml of sample were poured into a 40-ml amber glass vial and the following reagents were added: surrogate standard 1 (5 μl of a solution of 2-bromopropionic acid 60 mg l^{-1} in MTBE), 3 ml concentrated sulfuric acid (Merck) (so that pH < 0.5), 12 g of anhydrous sodium sulfate (Merck), 3 g copper (II) sulfate pentahydrate (Merck) and 2 ml MTBE. The vial was sealed, shaken for 2 minutes, and allowed to stand for 5 minutes. 900 μl of the extract was transferred into a 14-ml vial containing 2 ml solution of sulfuric acid in methanol (10 %). After addition of surrogate standard 2 (1 μl solution of 2,3-dibromopropionic acid 60 mg l^{-1} in MTBE), the vial was placed in a water bath at 50 ^{O}C for 1 h. Then it was cooled to 4 ^{O}C for 10 min and 5 ml of a copper (II) sulfate pentahydrate / anhydrous

Table 1. Toxic pollutants analyzed with the optimized analytical methods

CBPs	VOCs (continued)	Insecticides	Herbicides
Volatile CBPs	32.Dichloromethane	**Organochlorine**	96.Simazine
1.Chloroform*	33.trans-1,2- Dichloroethene	64.Heptachlor	97.Atrazine
2.Dichlorobromomethane*	34.1,1-Dichloroethane	65.Heptachlor epoxide	98.Monolinuron
3.Dibromochloromethane*	35.cis- 1,2- Dichloroethene	66.α-Endosulfan	99.Linuron
4.Bromoform*	36.1,1,1-Trichloroethane	67.β-Endosulfan	100.Diuron
5.Monochloroacetonitrile	37.Benzene	68.Endosulfan sulfate	101.Metobromuron
6.Trichloroacetonitrile	38.1,2-Dichloropropane	69.Endrin aldehyde	102.Terbuthylazine
7.Dichloroacetonitrile	39.Toluene	70.Methoxychlor	103.Prometryn
8.Chloral hydrate	40.1,1,2-Trichloroethane	71.Endrin ketone	104.Cyanazine
9.1,1-Dichloropropanone	41.1,2-Dibromoethane	72.DDT	105.Chlorotoluron
10.Monobromoacetonitrile	42.Chlorobenzene	73.HCH	106.DeisopropylAtrazine
11.Chloropicrin	43.Ethylbenzene	74.Aldrin	107.Metamitron
12.Bromochloroacetonitrile	44.(m + p)-Xylenes	75.Dieldrin	108.Chloridazon
13. Trichloropropanone	45.o-Xylene	76.Endrin	109.DesethylAtrazine
14.1,3-Dichloropropanone	46.Isopropylbenzene	77.Isodrin	**Metals**
15.Dibromoacetonitrile	47.2-Chlorotoluene	**Organophosphorous**	110.As
Haloacetic acids	48.4-Chlorotoluene	78.Methamidophos	111.Cd
16.Monochloroacetic	49.1,3-Dichlorobenzene	79.Mevinphos	112.Hg
17.Monobromoacetic	50.1,4-Dichlorobenzene	80.Omethoate	113.Cr
18.Dichloroacetic	51.1,2-Dichlorobenzene	81.Demeton (O+S)	114.Cu
19.Bromochloroacetic	52.Napthalene	82.Demeton-S-Methyl	115.Co
20.Trichloroacetic	53.Bromochloromethane	83.Dimethoate	116.Fe
21.Dibromoacetic	54.Dibromomethane	84.Disulfoton	117.Pb
22.Bromodichloroacetic	2.Dichlorobromomethane*	85.Parathion methyl	118.Mn
23.Dibromochloroacetic	3.Dibromochloromethane*	86.Fenitrothion	119.Mo
24.Tribromoacetic acid	55.2,2-Dichloropropane	87.Malathion	120.Ni
VOCs	56.1,1-Dichloropropene	88.Fenthion	121.V
25.Carbon tetrachloride	57.1,3-Dichloropropane	89.Parathion ethyl	122.Zn
26.Hexachlorobenzene	4.Bromoform*	90.Triazophos	123.Ti
27.Hexachlorobutadiene	58.Bromobenzene	91.Azinphos methyl	124.Ba
1.Chloroform*	59.n-Propylbenzene	92.Azinphos ethyl	125.Al
28.1,2-Dichloroethane	60.tert-Butylbenzene	93.Coumaphos	**Organotins**
29.Trichloroethylene	61.sec-Butylbenzene	94.Phoxim	126. Monobutyltin
30.Tetrachloroethylene	62.1,3,5-Trimethylbenzene	**Phenols**	128. Tributyltin
		95. Pentachloro-phenol	129. Diphenyltin
			130. Triphenyltin

* These compounds belong to the category of CBPs and are analyzed both in drinking and surface water

sodium sulfate solution 50 g l^{-1} and 100 g l^{-1} respectively in ultrapure water was added. The vial was shaken again for 2 minutes and allowed to stand for 5 minutes. 1 μl of the final extract was injected into the GC.

Analytical. A Hewlett Packard Gas Chromatograph 5890 Series II with a 63Ni Electron Capture Detector (ECD) was used. The carrier gas was helium and the make-up gas nitrogen. The column used was fused silica DB-1, 30 m x 0.32 mm i.d. x 0.25 μm film thickness. The injection technique was split/splitless. The analytical conditions of the gas chromatograph are presented in Table 2

Table 2. Analytical conditions for the determination of CBPs

Carrier gas flow:	*1.6 ml min-1*
Oven temperature:	*35 ^{O}C (9 min), with 1 ^{O}C min-1 to 40 ^{O}C (3 min), with 6 ^{O}C min-1 to220 ^{O}C (10 min)*
Injector temperature:	*175 ^{O}C*
Split ratio:	*1:25*
Detector temperature:	*300 ^{O}C*

Table 3. Recoveries and detection limits for CBPs

Compound	Concentration range (μg l^{-1})	Recovery range (%)	DLs (μg l^{-1})	Compound	Concentration range (μg l^{-1})	Recovery range (%)	DLs (μg l^{-1})
CHCl3	*0.5-20.0*	*90.0-110.8*	*0.010*	*1,1,1-TCP*	*0.5-20.0*	*75.8-111.3*	*0.040*
CHCl2Br	*0.5-20.0*	*87.6-110.8*	*0.005*	*1,3-DCP*	*0.5-20.0*	*88-100*	*0.070*
CHClBr2	*0.5-20.0*	*92.0-107.5*	*0.007*	*DBAN*	*0.5-20.0*	*92.6-121.2*	*0.070*
CHBr3	*0.5-20.0*	*94.7-112.8*	*0.010*	*MCA*	*1.5-9.0*	*25.0-126.0*	*0.20*
MCAN	*0.5-20.0*	*60.4-139*	*0.040*	*MBA*	*1-6.0*	*78.8-123.7*	*0.05*
TCAN	*0.5-20.0*	*97.2-118.2*	*0.070*	*DCA*	*1.5-9.0*	*89.7-104.8*	*0.02*
DCAN	*0.5-20.0*	*62.6-124.3*	*0.007*	*BCA*	*1-6.0*	*94.7-109.4*	*0.02*
CH	*0.5-20.0*	*86.7-144.5*	*0.007*	*TCA*	*0.5-3*	*87.8-117.7*	*0.01*
1,1-DCP	*0.5-20.0*	*83.7-120*	*0.040*	*DBA*	*0.5-3*	*97.1-141.1*	*0.02*
MBAN	*0.5-20.0*	*87.9-131.2*	*0.040*	*BDCA*	*1.0-6.0*	*89.9-126.0*	*0.10*
CP	*0.5-20.0*	*58.7-124.2*	*0.040*	*DBCA*	*2.5-15.0*	*78.1-135.9*	*0.20*
BCAN	*0.5-20.0*	*82.5-143.2*	*0.040*	*TBA*	*5-30.0*	*89.5-109*	*0.20*

and a representative chromatogram in Figure 1. Recoveries ranged from 87.6 % to 112.8 % for THMs, from 60.4 % to 144.5 % for the other CBPs and from 78.1 % to 123.7 % for HAAs (Table 3). Low recoveries of MCAN, 1,3-DCP and MCA have also been reported in the literature. 1,3-DCP is a volatile compound with decomposition trends, while the derivatization of MCA has been reported to be problematic by use of different derivatization agents (Cancho et al., 1999, Chen and Weisel, 1998). The DLs (estimated for signal-to-noise ratio 3/1) ranged from 0.005 μg l^{-1} to 0.070 μg l^{-1} for the volatile CBPs and from 0.01 to 0.2 μg l^{-1} for HAAs, therefore the method provides accurate measurements for the range of CBPs usually existing in drinking water, which generally has been reported to be above 0.5 μg l^{-1} for most of the compounds (Lekkas, 2003). The main advantages of these methods are the small sample volume required, which is convenient for routine (monthly) analysis, and the small amount of solvents used, which results in lower cost and lower analysis time since evaporation of the extracts is not necessary.

Volatile and semivolatile organic compounds (VOCs)

Sampling. Duplicate samples for VOCs measurement were collected in 40-ml glass vials and were capped with PTFE-faced silica septum (Pierce 13075). The vials were carefully filled just to overflow. HCl (4 drops 6 N/40 ml) was added to each water sample to prevent biodegradation and dehydrohalogenation.

Standard solutions. The accuracy of determinations is routinely checked by using standard solutions containing known amounts of VOCs. Standard solutions are prepared in ultrapure water by injecting known volumes of certified VOCs standards in methanol (Chemservice, purity > 99 %).

Analytical. The determination of VOCs is carried out by a modification of purge and trap-gas chromatography-mass spectrometry method (PAT-GC-MS) (Kostopoulou et al., 2000). The VOCs are analyzed using a Hewlett Packard Purge and Trap Concentrator 7695 fitted with a 30 cm absorbent trap (VOCARB3000), a Hewlett Packard Gas Chromatograph 5890 Series II and a Hewlett Packard Mass Spectrometer HP5971 MSD. The column used for the chromatographic separation of VOCs is a 60 m x 0.32 mm i.d. x 1.8 μm i.d. film thickness fused silica capillary HP VOC. Helium is used as the carrier gas, and the injection technique is split/splitless. The analytical conditions are shown in Table 4 and a representative chromatogram in Figure 2. The recoveries and detection limits of the compounds (estimated for signal-to-noise ratio 3/1) are presented in Table 5. The recoveries are relatively low, but it must be taken into account that the compounds are volatile and that the concentrations measured were very low. Several of these coumpounds cannot be determined with liquid-liquid extraction or with headspace GC-MS, as proved in our previous research (Golfinopoulos et al., 2001). The major advantages of the method is the elimination of the sample preparation step, and the elimination of use of toxic solvents. The detection limits, using the Selected Ion Monitoring (SIM) mode, range from 0.01 μg l^{-1} to 0.25 μg l^{-1}.

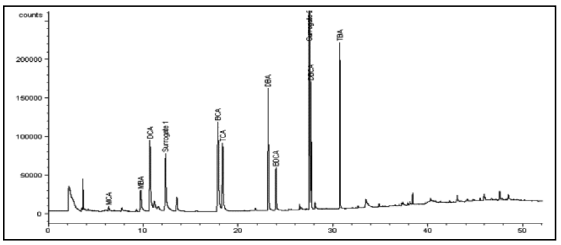

Figure 1: Typical GC-ECD chromatogram of derivatized HAAs standard solution, concentration 3-30 μg l^{-1}.

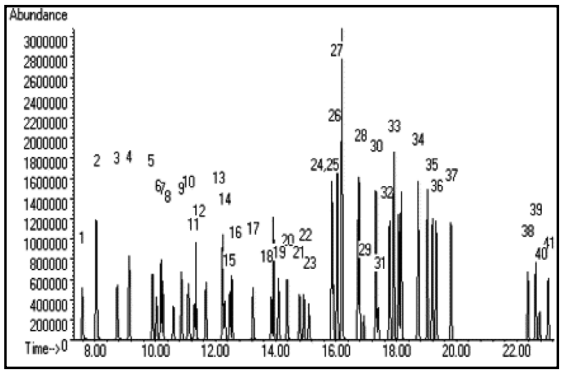

Figure 2: Typical PAT-GC-MS of VOCs standard solution, concentration 10 μg $^{l-1}$.

Insecticides

Sampling. Water samples are collected in 1-l amber glass vials. They are pre-filtered through 0.45 μm glass fiber to eliminate particulate matter and acidified with hydrochloric acid (6N) to pH = 2, in order to inhibit biological activity.

Sample preparation. Solid-phase extraction procedure (SPE) is applied. Methanol modifier (10 ml) is added to 1l water samples to allow better extraction (Albanis et al., 1998). SPE disks of 47 mm diameter and 0,5 mm thickness, containing 500 mg of the bonded phase (octadecyl -C18- bonded silica), are used for sample preparation. The disks are conditioned with acetone 10 ml for 30 min and placed in the conventional Millipore apparatus. Prior the extraction they are washed with 10 ml of ethyl acetate followed by 10 ml of dichloromethane under vacuum and with 10 ml of methanol with the vacuum off. The SPE disks are not allowed to become dry, as recommended (Albanis et al., 1998). The water samples are mixed well and allowed to percolate through the disks with a flow rate of 30 ml min^{-1} under vacuum. The insecticides trapped in the disk are collected by using 2 x 5 ml of ethyl acetate as eluting solvent. The eluted fractions are evaporated to 0.5 ml in a gentle stream of nitrogen.

Analytical. The insecticide residues are analyzed by Gas Chromatography (GC) method using a Hewlett Packard Gas Chromatograph 5890 Series II, supported by a Nitrogen Phosphorus Detector (NPD) for the organophosphorus insecticides and an Electron Capture Detector (ECD) for the organochlorine insecticides. A 30 m x 0.32 mm i.d x 0.25 μm film thickness fused silica capillary (DB-5) is used for the chromatographic separation of the organophosphorus insecticides and a 30 m x 0.53 mm i.d x 0.5 μm film thickness fused silica capillary (HP-608) is used for the chromatographic separation of the organochlorine insecticides. The analytical conditions for determination of insecticides are given in Table 6 and a representative chromatogram in Figure 3. The detection limit for the organochlorine insecticides is 0.002 μg l^{-1} and for the organophosphorus insecticides 0.003 μg l^{-1} except for methamidophos, meviphos, demeton (O+S), demeton-S-methyl, dimethoate (0.005 μg l^{-1}) and omethoate (0.05 μg l^{-1}). In the case of insecticides, minimization of sample volume or elimination of the evaporation step is not possible, since the regulatory limits (76/464/EEC) are very low, demanding detection limits similar to those obtained by the analysis of 1-l water sample.

Table 4. Purge and trap-GC-MS method - analytical conditions

Purge:	*40 ml min^{-1} He, 11 min, ambient temperature*
Desorb:	*30 ml min^{-1} He, 180 ^{O}C for 4 min (preheat 175 ^{O}C)*
Bake:	*220 ^{O}C for 10 min*
Temperatures:	*Line 200 ^{O}C, Valve 200 ^{O}C, Moisture Contr. Syst. (MCS) Line 200 ^{O}C*
Carrier gas flow	*1 ml min^{-1}*
Oven temperature	*35 ^{O}C for 3 min , 10 ^{O}C min-1 to 235 ^{O}C*
Injector temperature	*200 ^{O}C*
Split ratio	*1:25*
Solvent delay	*0*
MS operating mode	*SIM*
EMV	*2200*

Table 5. Recoveries and detection limits for VOCs (concentrations 0.5-10 μg l^{-1})

Compound	Recovery range (%)	DLs range (μg l^{-1})	Compound	Recovery range (%)	DLs (μg l^{-1})
cis-1,2-dichloroethene	*47-120*	*0.25*	*Tetrachloroethene*	*47-130*	*0.1*
Dichloromethane	*62-160*	*0.05*	*1,2-dibromoethane*	*67-130*	*0.1*
1,1-dichloroethene	*54-141*	*0.1*	*Chlorobenzene*	*57-140*	*0.05*
1,1-dichloroethane	*55-130*	*0.1*	*Ethylbenzene*	*49-145*	*0.05*
trans-1,2-dichloroethene	*59-140*	*0.25*	*(m+p)-xylenes*	*49-147*	*0.05*
2,2-dichloropropane	*50-125*	*0.05*	*o-xylene*	*53-137*	*0.05*
Chloroform	*58-135*	*0.1*	*Bromoform*	*67-135*	*0.1*
Bromochloromethane	*63-152*	*0.25*	*Isopropylbenzene*	*47-125*	*0.05*
1,1,1-trichloroethane	*49-125*	*0.1*	*Bromobenzene*	*60-140*	*0.1*
1,2-dichloroethane	*65-125*	*0.1*	*n-propylbenzene*	*46-125*	*0.05*
Carbon tetrachloride	*48-135*	*0.1*	*1,3,5-trimethylbenzene*	*51-140*	*0.25*
Benzene	*50-147*	*0.1*	*1,3-dichlorobenzene*	*57-132*	*0.05*
Trichloroethene	*58-135*	*0.05*	*1,4-dichlorobenzene*	*59-135*	*0.05*
Dibromomethane	*66-140*	*0.25*	*1,2-dichlorobenzene*	*61-137*	*0.1*
Dichlorobromomethane	*60-160*	*0.05*	*1,2,4-trichlorobenzene*	*63-140*	*0.01*
1,1,2-trichloroethane	*66-135*	*0.1*	*Napthalene*	*76-140*	*0.05*
1,3-dichloropropane	*65-125*	*0.05*	*Hexachlorobutadiene*	*46-127*	*0.25*
Chlorodibromomethane	*64-132*	*0.1*	*1,2,3-trichlorobenzene*	*65-140*	*0.01*

However, ethyl acetate, which has been reported to be a low toxicity solvent has been selected, and proved to provide good chromatography results.

The percent recoveries of the insecticides at concentration levels 0.02 - 0.4 μg l^{-1} are presented in Table 7. The recoveries generally ranged from 40.3 % (heptachlor) to 145.3 % (dieldrin). Lower recoveries were observed for DDT and its metabolites (26.8 % - 123.3 %), HCH (34.8 %-168.2 %) and isodrin (19.8 % - 83.2 %). The fact that the insecticide concentrations tested were very low, in combination with possible impurities during the SPE exctraction procedure can explain the poor recoveries observed in these cases.

Previous study for similar concentration levels, using C18 cartridges, had also resulted in low recoveries for DDT and its metabolites (28.6 % - 82.0 %), but showed higher recovery for HCH (85.8 - 145.3) and lower recovery for aldrin (37.2 % - 49.7 %) compared to the present method (Golfinopoulos et al., 2003).

Herbicides and Phoxim

Sampling. Water samples are collected in 1-l amber glass vials and are filtered through 0.7 μm glass microfiber filter.

Standard solutions. All the solvents used are suitable for HPLC analysis. Analytical standards of

Table 6. Analytical conditions for determination of insecticides

Conditions	Organochlorine	Organophosphorous
Initial temperature (^{O}C) / Time (min)	*80 - 1*	*150 - 1*
Temperature increase rate (^{O}C min^{-1})	*30*	*2*
1st temperature step (^{O}C) / Time (min)	*180 - 0*	*180 - 0*
Temperature increase rate (^{O}C min^{-1})	*5*	*5*
2nd temperature step (^{O}C) / Time (min)	*200 - 0*	*200 - 0*
Temperature increase rate (^{O}C min^{-1})	*10*	*5*
3rd temperature step (^{O}C) / Time (min)	*260 - 3*	*250 - 7*
Injector temperature (^{O}C)	*250*	*240*
Detector temperature (^{O}C)	*300*	*280*
Carrier gas flow	*5 ml min^{-1} (He)*	*20 ml min^{-1} (He)*
Makeup gas flow	*40 ml min^{-1} (N_2)*	*1.5 ml min^{-1} (N_2)*
Hydrogen flow	*-*	*3.5 ml min-1 (H_2)*
Air flow	*-*	*100 - 120 ml min^{-1} (Air)*
Injection type	*On-column*	*On-column*

Table 7. Percent recoveries of insecticides (concentration levels 0.02 to 4 μg l^{-1})

Insecticides	Recovery range (%)	Insecticides	Recovery range (%)
HCB	*41.4-99.5*	*4,4-DDE*	*31.1-48.2*
a-HCH	*45.9-160.8*	*Dieldrin*	*59.6-145.3*
g-HCH	*47.4-148.8*	*Endrin*	*56.9-113.1*
b-HCH	*34.8-84.9*	*4,4-DDD*	*45.5-80.2*
Heptachlor	*40.3-114.0*	*b-Endosulfan*	*49.9-131.3*
d-HCH	*50.8-168.2*	*4,4-DDT*	*26.8-123.3*
Aldrin	*47.5-84.6*	*Endrin Aldehyde*	*52.9-132.4*
Isodrin	*19.8-83.2*	*Endosulfan Sulfate*	*48.9-122.5*
Heptachlor Epoxide	*49.9-126.8*	*Methoxychlor*	*57.8-127.6*
a-Endosulfan	*48.3-126.7*	*Endrin Ketone*	*54.6-124.5*

all the herbicides are supplied by Dr Ehrenstorfer, Germany and ChemService, USA.

Sample preparation. The sample (500 ml) is filtered through a GF/F 0.7 μm glass microfiber filter (Whatman, England). C18 cartridges (Waters, USA) are conditioned with 10 ml of methanol and 10 ml of ultra pure water and the sample is loaded with an approximate flow rate of 10 ml min^{-1}. The sorbent is washed with 5 ml of water, and the herbicides are eluted with 6 ml of acetonitrile. The acetonitrile is removed under a gentle stream of nitrogen, at 35 ^{O}C, and the herbicides are reconstituted with 1 ml of the initial mobile phase.

Analytical. The HPLC system consists of a 9012 pump, associated with a Polychrom 9065 diode-array detector (Varian, USA) and a Rheodyne 7161, 100 μl, loop injector (Rheodyne, USA). The column is a Zorbax SB - C18 4.6 mm x 15 cm (5 μm) connected with a Zorbax SB - C18 precolumn (Hewlett Packard, USA). Jones Chromatography, England supplied a 7980 column block heater. The temperature of the column is set at 40 ^{O}C. The chromatographic analysis is accomplished using a gradient program with a mobile phase of acetonitrile and water, at a flow rate of 1.2 ml min^{-1} (Kotrikla and Lekkas, 2001). The gradient program is 10 % acetonitrile to 100 % acetonitrile in 40 minutes. In order to attain maximum sensitivity, the quantitative measurements are made at 220 nm for triazines, at 244 nm for phenylureas and at 282 nm for phoxim with the external standard method and the correlation coefficients of the calibration graphs are always higher than 0.999. The recoveries of the compounds are calculated from spiked samples at concentrations of 0.1, 0.5 and 1.0 μg l^{-1}. The average recoveries and the coefficients of variation are: deisopropyl atrazine 12.8 (5.2), metamitron 36.7 (3.7), chloridazon 49.2 (2.9), desethyl atrazine 34.3 (3.8). Low recoveries for these polar compounds are reported in the literature (Sabik and Jeannot, 2000) due to their weak interactions with the non-polar octadecyl moieties of the C18 cartridges. For the rest of the compounds, the recoveries ranged between 65.4 and 104.6 % with an average value of 86.3 % and a maximum coefficient of variation 10.9 %.

The detection limits are: 0.025 μg l^{-1} for simazine, cyanazine, atrazine, terbuthylazine, prometryne, 0.040 μg l^{-1} for chlorotoluron, monolinuron, diuron, metobromuron and linuron, 0.5 μg l^{-1} for phoxim and 0.2 μg l^{-1} for deisopropyl-atrazine, metamitron, chloridazon and desethyl-atrazine. These values could be compared to the European legislation concerning the quality of water designated for human consumption: The EEC Directive 80/778, establishes the maximum admissible concentration of each individual pesticide at 0.1 μg l^{-1} and the total amount of pesticides at 0.5 μg l^{-1} (Council of the EEC, 1980). In surface water, these limits are an order of magnitude higher (1-3 μg l^{-1}). Although phoxim is an organophosphorous insecticide, it was included in the multiresidue method developed for the analysis of herbicides because the response of the HPLC/DAD was better compared to the GC / NPD system, as shown during preliminary experiments in our laboratory.

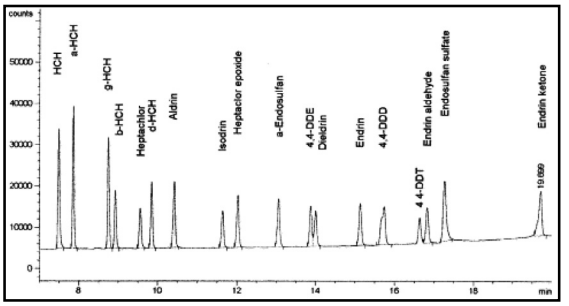

Figure 3: Typical GC-ECD chromatogram of standard solution of insecticides, concentration 10 μg l^{-1}.

Table 8. Analytical lines used for the determination of metals with AAS

Metal	As	Cd	Cr	Cu	Co	Fe	Pb	Mn
Line (nm)	193	228.8	357.9	324.8	242.5	248.3	283.3	279.5
Metal	Mo	Ni	Va	Zn	Ti	Ba	Al	Hg*
Line (nm)	313.3	232	318.4	213.9	364.3	553.6	309.3	253.7

Table 9. Detection limits for metals

Metal	As	Cd	Cr	Cu	Co	Fe	Pb	Mn
DL (μg l^{-1})	1	0.025	0.18	0.36	0.8	1	0.8	0.27
Metal	Mo	Ni	Va	Zn	Ti	Ba	Al	
DL (μg l^{-1})	0.13	0.40	1	0.35	15	11	16	

Table 10. Analytical conditions for the determination of Hg with AAS- FI/MHS

Wavelength	253.7 (HCL Mercury lamp)	Reagents:	
Slit	0.7 nm (Low)	Carrier solution	3 % (v/v) HCL
Integration time	20 sec.	Reducing agent	1.1 % $SnCl_2$ in 3 % (v/v) HCL
Data processing	Smoothing: 0,5 sec.	Sample solution	Hg^{2+} in acidified solution.
Cell temperature	100 ^{O}C	Flow of carrier gas	95 ml min^{-1}
Sample volume	500 μl	Replicates per sample	5

Pentachlorophenol (PCP)

Sampling. Water samples are collected in 1–l amber glass vials and kept at 4 ^{O}C.

Standards. Certified PCP standards from Restek and Chemservice are used. The standard solutions are prepared in methanol.

Sample preparation. Samples are acidified to pH < 2 with HCl and filtered through a GF/F 0.7 μm glass microfiber filter (Whatman, England). C18 cartridges (Waters, USA) are conditioned with 10 ml acetonitrile, 10 ml methanol and 5 ml buffer solution (pH 2.5) and the sample is loaded with an approximate flow rate of 10 ml min^{-1}. The sorbent dries for 5 min and PCP is eluted with 4x2 ml methanol. The methanol is removed under a gentle stream of nitrogen until the volume reaches 1 ml.

Analytical. The analysis is accomplished by use of the HPLC/DAD system described above. The mobile phase consists of (A) buffer solution KH2PO4-H3PO4 1mM, pH = 2.5 and (B) methanol. The gradient program is the following: t=0 min, 80 % A, 20 % B > t=15 min, 40 % A, 60 % B > t=18 min,10 % A, 90 % B

The mobile phase flow rate is 1.5 ml min^{-1}, the injected sample volume 100 μl and the column is kept at ambient temperature (20 0C). PCP is detected at wavelength 302 nm. The mean recovery of pentachlorophenol is 86.5 % and the DL 0.92 μg l^{-1}.

Metals

Sampling. Water samples are collected in 500-ml polyethylene vials and are acidified with HNO_3 to pH 1.

Sample preparation. The total acid extractable matter of the metals As, Cd, Cr, Cu, Co, Fe, Mn, Mo, Ni, Pb, V and Zn is determined after digestion of samples for 12 hours in 70 ^{o}C (Haswell, 1991). The sample preparation for the determination of total and dissolved Hg is presented elsewhere (APHA, 1992; Perkin Elmer, 1990)

Analytical. The determination of the metals: As, Cd, Cr, Cu, Co, Fe, Mn, Mo, Ni, Pb, V and Zn (dissolved and total acid extractable) is made using a atomic absorption spectrophotometer equipped with a Zeeman THGA graphite furnace. The determination of Ba, Ti and Al is performed by Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES). The analytical lines used are presented in Table 8, and the detection limits in Table 9. For As, 1 μg Pd and for Cd and Pb, 1 μg Pl were used as chemical modifiers. Detailed analytical conditions are described elsewhere (Lekkas, 2000b; Perkin Elmer, 1982). The determination of Hg is made using an Atomic Absorption Spectrophotometer equipped with a Flow Injection Mercury/Hydride System (AAS- FI/MHS) (Perkin Elmer 5100 ZL with Perkin Elmer FIAS 100). The analytical conditions are presented in Table 10. The recovery of the method for Hg determination is 98.9 ± 4 % and the DL 0.2 μg l^{-1} (Pavlogeorgatos, 2001).

Table 11. Analytical conditions for determination of total organotin compounds

Stage	Temperature θ (°C)	Duration of temperature increase (sec)	Duration at temperature θ(sec)	Ar flow Ar flow(ml min^{-1})
Drying 1	120	5	5	250
Drying 2	130	15	15	250
Pyrolysis	1200	15	25	250
Vaporization	2000	0	4	0
Cleaning	2400	1	2	250

Organotins

Sampling. Water samples (1 l) are collected in dark glass bottles and immediately acidified with HCl to pH 2.

Sample preparation. A.Total Organotins. The procedure involves acidification of water samples with 50 ml of glacial acetic acid and extraction with 10 ml of toluene. After the extraction, the solvent layer is transferred in a glass bottle and is preconcentrated under a gentle air flow to 1 ml. Within this procedure tributyltin (TBT), triphenyltin (TPhT) and some dibutyltins (DBT) are extracted but not monobutyltin (MBT) or inorganic tin (Sn) (Dadfarnia et al., 1994). Recoveries tests are done in order to assure this hypothesis. The recoveries are for TBT (98 ± 4 %), TPhT (105 ± 2 %), DBT (76 ± 2), MBT (0 %), Sn (0 %).

B. Organotin speciation. The pH of 1 l of water sample is adjusted at 5.00 with 13.6 g of sodium acetate and few ml of acetic acid and it is transferred in a 1-l separation funnel. 2.5 ml of NaBEt4 0.4 % w/v (prepared every day) and 5 ml of hexane is added and the mixture is shaken manually for 10 min. After phase separation (20 min), the hexane phase is collected in a glass vial, protected from light and stored at -20 °C.

Analytical. A.Total Organotins. A Perkin Elmer atomic absorption spectrophotometer, model 5100 equipped with a Zeeman THGA graphite furnace is used. The operating conditions are lamp current 32 mA, wavelength 286.3 mm, slit 0.7 nm and rhenium has been chosen as chemical modifier. In order to achieve a lower detection limit the hot-injection technique has been utilized. The detection limit of the method is 0.001 μg l^{-1}. The analytical conditions for determination of organotins are presented in Table 11.

B. Organotin speciation. A Fisons GC 8000 with FPD Detector 800 is used. The column is DB-1 10 m x 0.32 mm, the carrier gas is He and the injection technique is split/splitless. The analytical conditions are presented elsewhere (Carlier-Pinasseau et al., 1996). The recoveries of the method range from 69.0 % - 72.4 % for MBT, 94.8 % - 98.6 % for DBT, 95.5 % - 103 % for TBT, 93.2 % - 101 % for DPT and 97.3 % - 105 % for TPT.

CONCLUSIONS

Analytical methods by means of GC with ECD, NPD, FPD and MS detection, PAT concentration, HPLC/DAD and AAS were optimized in order to be routinely used for the determination of trace concentrations of 130 toxic pollutants in drinking and surface water. Wherever possible, reduction of analysis time and amounts of toxic solvents use was attempted, either by small sample volume/elimination of the evaporation step (in the case of CBPs), or by use of the PAT technique for sample preparation (in the case of VOCs), or by selection of a low toxicity solvent such as ethyl acetate (in the case of insecticides). The recoveries and detection limits obtained for the determination of the majority of the compounds were satisfactory. Low recoveries observed in some cases are attributed to very low levels of concentrations tested, in combination with problems during the sample preparation procedure (in the cases of CBPs, insecticides and herbicides) or due to the volatility of the compounds (in the case of the PAT procedure). In conclusion, all extraction techniques described (solid phase extraction, liquid-liquid extraction and PAT) in combination with the chromatographic determination applied for the toxic pollutants resulted in the efficient isolation of the compounds from water samples. Although the recoveries of some of the compounds were low, the limits of detection complied with the European legislation concerning their occurrence in surface water.

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