Bull. Environ. Contam. Toxicol. (2003) 71:1026–1033
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DOI: 10.1007/s00128-003-8776-2

Environmental
Contamination
and Toxicology

Determination of Semivolatile Compounds in Drinking Water by Tandem Mass Spectrometric Detection

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Received: 2 October 2002/Accepted: 8 July 2003

In the eastern area of China, rapid economic development has resulted in serious environmental problems, and increased consumption of fresh water coupled with enormous wastewater discharge worsened the situation. Therefore, more and more attention should be paid to the deterioration of water quality and the reduction of clean water resource for its importance in human living. Since the organic compounds are potential contaminants and could be harmful to human and ecosystems health, the study on organic contaminants in the groundwater environment become a hotspot in China. In fact, organochlorine pesticides (OCPs) and many kinds of additives were used widely in China in the past decades, and industrial effluents, dumping of urban residues were dumped into rivers and soils without necessary pretreatment (Ma et al., 2001). Naturally, many kinds of toxicants have been detected in the regional drinking water, and high efficient determination methods for trace hazardous organics in water samples are vital needed now to the performance of environmental management.

Presently, solid-phase extraction (SPE) is extensively applied to the extraction of organic compounds present in water samples for its convenience on organic solvent consuming and combined with gas chromatographic-mass spectrometry (GC-MS) (Junk and Richard, 1988; Font et al., 1993; Hennion and Pichon, 1994; Brinkman and Ureuls, 1996). The selected ion monitoring method (SIM) of GC-MS in the EI mode technique is commonly used to analyze organic compounds in many kinds of samples for its high qualitative and quantitative abilities. However, the SIM detection attainable of GC-MS is set by the levels of interfering ions from the matrix, which can obscure the signal from the target compounds.

Compared with SIM, tandem-mass spectrometry (MS-MS) has more advantages. In MS–MS mode a precursor ion is isolated inside the trap and fragmented later to obtain a pro-characteristic product spectrum. The sample matrix ions are excluded from the trap during the isolation step so improving the signal-to-noise ratio of the peaks, providing cleaner spectra. Thus, GC-MS-MS can effectively improve the selectivity of the technique with a drastic reduction of the background and without losing identification capability (Schachterle et al., 1994). In spite of the high sensitivity and selectivity of the technique, fewer papers on organic compounds

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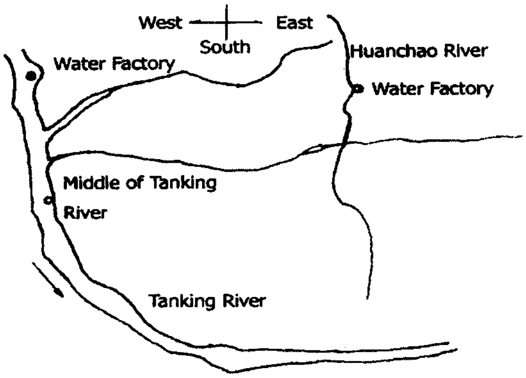

Figure 1. Water sampling locations.

analyzing in water samples by the GC-MS-MS associated with SPE were reported.

In this study, more than 20 semi-Volatile compounds have been analyzed qualitatively and quantitatively by tandem mass spectrometric in the drinking water sampling from two rivers both located in eastern part of Jiangsu Province, China in June 2002. Most of these organic compounds detected are in the hazardous compounds list of U.S. Environmental Protection Agency (USEPA) for their cancerogenicity and mutagenicity. The results could be applied to the water quality evaluation, and should be helpful for the inhabitants drinking and industrial planning and management in this area.

MATERIALS AND METHODS

The reagents, methanol, dichloromethane and pure water used were all HPLC grade. A mixture standard (USEPA 625 semi-volatile calibration mix, containing 54 semi-Volatile compounds) was purchased from Supelco Company, USA. SPE C18 cartridges (6g, 20ml) were purchased from Tedia Inc., USA. A 0.45μm micro-fiber filters were obtained from Toyo Roshi Kaisha Ltd., Japan. Anhydrous sodium sulfate was desiccated at 500°C for 4h before using.

Water samples used in this study were collected from three stations along Tanking River and Huanchao River, one station near the water factory of Huanchao River, and the other stations in the middle reach and water factory of Tanking River, respectively (Figure 1). In the area near both rivers, quite a few small factories, for instance, automobile, textile, chemical and electronic production, are scattered, and most drinking water of inhabitants come from the two rivers. It is well known as a part of economy active area of Jiangsu Province, China.

Water samples were collected in acid-washed glass bottles (4L of capacity) and stored in a refrigerator at 4°C. Prior to extraction by SPE, the water samples were passed through 0.45μm micro-fiber filters, then the samples were adjusted to pH 2 by 6 molar·l^{-1} hydrochloric acid. SPE cartridge was filled with 20ml dichloromethane and 20ml methanol, respectively. During extraction process, the flow of water sample was controlled at a maximum of 1l·h^{-1}, and the solid phase should not be dry. Elution was done three times with 20 ml of dichloromethane every time, and then anhydrous sodium sulfate had been added into the to absorb residential water. After that, elution was concentrated by a rotary evaporator to near 1.0ml. Quantitative determination was performed by external standard method.

Table 1. MS-MS parameters.

Compounds	Activation Time (min)	Parent ion (m/z)	m/z range	Product ion (m/z)
Phenol	11.23-11.53	94	92-96	66
1,3-dichlorobenzene	11.90-12.89	146	144-150	111
1,2-dichlorobenzene	11.90-12.89	146	144-150	111
1,4- dichlorobenzene	11.90-12.89	146	144-150	111
2,2'-oxybis(1-chloro)propane	12.89-13.59	121	120-122	66
2-propanamine,N-(1-methyl ethyl)-N-nitro	13.29-13.61	113	111-115	85
Nitro benzene	13.76-14.26	123	75-95,120-125	93
2-nitro phenol	14.75-15.00	139	107-111,137-142	109
2,4-dichloro phenol	15.44-15.70	162	96-100,160-165	126
1,2,4-trichloro benzene	15.70-15.90	182	178-185	180
4-chloro-3-methyl phenol	17.04-18.10	142	105-109,140-144	107
2,4,6-trinitro phenol	18.70-19.18	198	195-199	162
Dimethyl phthalate	19.95-20.58	163	161-167	133
2-methyl-1, 3-dinitrobenzene	20.58-20.92	183	161-167,181-185	165
Acenaphthylene	20.58-20.92	153	150-154,161-167	152
Acenaphthene	20.92-21.32	153	151-155	151
Pentachlorophenol	24.67-25.28	266	263-269	202
Phenanthrene	25.28-26.20	178	176-180	176
Anthracene	25.28-26.20	178	176-180	176
Carbazole	26.20-26.87	167	165-169	139
Dibutyl phthalate	26.87-28.28	149	147-150	121
Fluoranthene	28.28-31.00	202	226-230	200
Pyrene	28.28-31.00	202	20-204	201
Benzene[a]anthracene	32.63-33.67	228	226-230	228
Chysene	32.63-33.67	228	226-230	228
Bis(2-ethylhexyl) phthalate	33.67-34.29	149	165-169	121

The purified samples were analyzed by a CP-3800 gas chromatograph (DB-5MS capillary column with a film thickness of 0.25μm: 30m×0.25mm i.d. and auto injector) equipped with a Varian MS-MS (Varian CP-2200). The operation conditions of GC were injector, 250°C, and helium as carrier gas. Transfer line to the MS-MS was set to 240 °C, ionizing voltage was 70eV, and the temperature of the source was 180°C. oven temperature, initiated with 40°C, hold 5.0min, to 280°C at a rate of 8°C per minute, and hold 11min at 280°C; Injection volume was 1μl with splitting ratio 1:20.

For MS-MS, parameters are shown in Table 1. Dissociation of all compounds was waveform resonant.

Since the analytical quality control is concerned, blank analysis procedure was performed to reveal no impurities in the solvent and ensure stability of instrument. Parallel samples were performed at the same condition.

RESULTS AND DISCUSSION

For the analysis of organic compounds, appropriate excitation voltage of collision-induced dissociation (CID) is very important to get needed relative abundance ion by breaking the parent ion. Excitation voltage of CID was optimized to achieve maximum sensitivity, limit of determination (LOD) and precision. A signal at a signal-to-noise ratio of 3:1 is defined as the limit of detection. The mixture standard was determined at six concentration levels, $1\mu g{\cdot}l^{-1}$, $10\mu g{\cdot}l^{-1}$, $50\mu g{\cdot}l^{-1}$, $100\mu g{\cdot}l^{-1}$, $200\mu g{\cdot}l^{-1}$ and $1000\mu g{\cdot}l^{-1}$for adjusting excitation voltage CID, determining the LOD of the organic compounds and checking precision and stability of the analysis method. The data of CID, LOD, the relative standard deviation (RSD) and percentage recovery were summarized in Table 2.

LOD of most compounds ranged from $1\mu g{\cdot}l^{-1}$ to $5\mu g{\cdot}l^{-1}$ (Table 2). In some other similar MS-MS studies, LOD of some organic compounds, for instance, malathion was $14.5\mu g{\cdot}l^{-1}$ (Schachterle ea al., 1994), that of Ethoprophos, Dichloran, Chlorothalonil and Parathion-m etc. ranged from $0.1\mu g{\cdot}l^{-1}$ to $3\mu g{\cdot}l^{-1}$ (Martýnez et al., 2000), and that of Bezafibrate, Carbamazepine, Clofibric acid, Diazepam and Pentoxifylline etc. ranged from $11ug{\cdot}l^{-1}$ to $29ug{\cdot}l^{-1}$ (Sacher et al., 2001). Therefore, the excitation voltage of CID and LOD of compounds used in this study were quite suitable to analyze most compounds in the drinking water samples.

The recovery of organic compounds from water samples depends on factors of pH, samples volume, different sorbent and rate of water samples flow though the sorbent and so on (Font et al., 1993; Conquart and Hennion, 1991). In this study, the extraction process by SPE was controlled strictly according to the method of USEPA 625. The recoveries of the semi-Volatile compounds distributed from 31.8% to 86%. It might be interpreted that some organic compounds were difficult to be adsorbed by the C_{18} solid phase. Since most of RSD ranged from 3.0% to 13.6%, the analysis equipment was stabile and analysis method had good reproducibility and repeatability. Linearity of external standard curve of these semi-Volatile compounds were very good and the correlation coefficient (R) were higher than 0.991.

Table 2. CID, LOD, recovery and RSD of organic compounds with MS-MS.

Compounds	CID (V)	LOD ($ng \cdot l^{-1}$)	RSD (%)	Recovery (%)
Phenol	0.60	8.0	12.1	38
1,3-dichlorobenzene	0.50	3.0	3.4	69.0
1,2-dichlorobenzene	0.52	2.0	3.9	65.1
1,4- dichlorobenzene	0.50	2.0	3.0	53.8
2,2'-oxybis(1-chloro)propane	0.48	5.0	5.7	79.2
2-propanamine,N-(1-methyl ethyl)-N-nitro	0.40	1.6	5.1	60.3
Nitro benzene	0.20	30	8.1	42.6
2-nitro phenol	0.42	9.0	6.4	57.6
2,4-dichloro phenol	0.60	3.0	3.8	48.6
1,2,4-trichloro benzene	0.80	2.0	4.4	75.4
4-chloro-3-methyl phenol	0.70	13	6.2	63.1
2,4,6-trinitro phenol	0.80	4.0	8.7	56.9
Dimethyl phthalate	0.90	1.0	6.9	77.6
2-methyl-1, 3-dinitrobenzene	0.50	12	3.4	66.8
Acenaphthylene	1.0	0.4	5.2	76.5
Acenaphthene	1.0	0.6	5.9	72.4
Pentachlorophenol	0.74	21	6.6	73.0
Phenanthrene	0.90	0.7	4.8	67.5
Anthracene	0.88	1.0	8.9	64.9
Carbazole	0.90	2.0	10.6	52.8
Dibutyl phthalate	0.80	40	7.4	75.9
Fluoranthene	0.90	3.0	13.6	64.3
Pyrene	0.90	2.0	11.6	66.4
Benzene[a]anthracene	0.90	2.0	9.5	70.4
Chysene	0.92	2.0	5.8	61.6
Bis(2-ethylhexyl) phthalate	0.55	26	12.4	49.8

Over twenty semi-volatile compounds were determined from three station samples. The qualitative and quantitative results were shown in Table 3.

As shown in Table 3, 24,19 and 20 kinds of organic compounds were found in Huanchao River, Tanking River (F) and Tanking River (M), respectively. The result showed the kinds of the semi-Volatile compounds in Huanchao River were more than that of Tanking River. The semi-Volatile compounds concentration were in the range of 0.001 to 0.1$\mu g\ l^{-1}$ and the pollutant levels of Huanchao River was higher than that in the two other stations. Although has fewer factories beside Huanchao River, it is smaller than Tanking River so that the concentrations of the compounds were higher than that in Tanking River. At last Huanchao River flow into the Tanking River, the compounds of Huanchao River are diluted effectively by the Tanking River.

Table 3. Qualitative and quantitative results for semi-volatile compounds.

Compound	Concentration ($\mu g \cdot l^{-1}$) Huanchao River	Tanking River (F)	Tanking River (M)
Phenol	0.053	0.033	0.044
1,3-dichlorobenzene	0.0005	0.0013	n.d.
1,2-dichlorobenzene	0.054	0.054	0.035
1,4- dichlorobenzene	0.030	0.021	0.018
2,2'-oxybis(1-chloro)propane	0.080	0.045	0.059
2-propanamine,N-(1-methyl ethyl)-N-nitro	0.045	0.028	0.029
Nitro benzene	0.102	0.038	0.023
2-nitro phenol	0.015	0.0083	0.0033
2,4-dichloro phenol	0.078	n.d.	n.d.
1,2,4-trichloro benzene	0.019	0.003	0.010
4-chloro-3-methyl phenol	n.d.	0.0010	n.d.
2,4,6-trinitro phenol	0.036	0.0063	0.0055
Dimethyl phthalate	0.015	0.0038	0.0038
2-methyl-1, 3-dinitrobenzene	0.075	0.066	0.022
Acenaphthylene	0.0035	0.0028	0.0015
Acenaphthene	n.d.	n.d.	0.0025
Pentachlorophenol	0.104	0.059	0.092
Phenanthrene	0.007	0.003	0.0025
Anthracene	0.009	0.0033	0.0033
Carbazole	0.0053	n.d.	0.0005
Dibutyl phthalate	0.440	0.218	0.310
Fluoranthene	0.009	0.0013	0.0015
Pyrene	0.0005	n.d.	n.d.
Benzene[a]anthracene	0.0018	n.d.	n.d.
Chysene	0.0010	n.d.	n.d.

* F- water factory, M- middle of river
n.d. – no detectable

Millions people live in the area where the two rivers cross through, and some dozens of small chemical plants were located and producing several hundreds kinds of chemicals. The detected compounds in Table 3 were discharged mainly by the some little chemical factories. The survey illustrated quite a few kinds of halogenated benzene and phenols were presented in the two rivers and the concentration of pentachlorophenol was highest (0.104$\mu g \cdot l^{-1}$). As a mutagen and carcinogen, the phthalate chemicals were examined in water samples (Luks-betlei et al., 2001; Prokupkova et al., 2002). Only two kinds of phthalate were detected from the three stations samples. The concentrations of ten kinds of compounds in the middle reach of Tanking River were higher slightly than that in water factory station of Tanking River. It illustrated Huanchao River and other small rivers take organic pollutant into Tanking River, nevertheless the pollutants were diluted in Tanking River and concentrations of all the compounds were far lower than the water quality national standards of China. Compared with water quality of some main rivers such Jialing River, the concentrations of halogenated benzene in this study was about 5-10 times lower (Tang and Zheng, 2001). Though it was high water period of both rivers, the concentrations determined in this study were lower than those the same term in last 2 years. Therefore, the water in both rivers is quite safe as drinking water resource.

Recently, most areas in China, especially Jiangsu Province pay attention to environmental waste control and treatment. A large wastewater plant (1650t·d^{-1}) has been running for treatment of industry wastewater collected from the area studied here, therefore both of the two rivers received littler wastewater than before 1999, and remained quite clean and have self-cleaning ability.

Compared with other analytical technique such as GC-flame ionization detector (FID) and GC-ECD, GC-MS is predominant in qualitative analysis of organic compound by selected ion monitoring method (SIM). Though SIM-MS is also applied to quantitative analysis, it is difficult to solve the interference from complicated matrix and interfering peaks. The operation mode of GC-MS-MS is more selective than both GC–MS and GC–ECD, avoiding coelution problems between matrix and target peaks.

SPE extraction technique is commonly used to extraction of pesticide (Dong et al., 2000), steroids (Kelly, 2000), and other chemicals in water samples. It provides a simple, rapid, and reliable method for organic compound enrichment from water samples.

This research demonstrated that the use of SPE technique coupled with GC-MS-MS could provide a sensitive, rapid and accurate method for determination of semi-volatile compounds in water. The water quality of the two rivers, based on over data, is quite good.

REFERENCES

Brinkman UAT, Ureuls RJJ (1996) SPE for on-line samples treatment in capillary GC. GC-LC 14: 581-588

Dong YY, Sun C, Xu SF, Dai J, Fen JF, Jiang X, Wang LS (2000) Polychlorinated organic compounds (PCOPs) in the Yangtse river water samples using SPE and GC/ECD. Bull Contam Toxicol 64: 383-389

Font G, Manes J, Molto JC, Pico Y (1993) SPE in multi-residue pesticide analysis of water. J Chromatog 642: 135-142

Hennion MC, Pichon V (1994) SPE of polar organic pollutants from water. Environ Sci Technol 28: 576-584

Junk GA, Richard JJ (1988) Organic in water: SPE on a small scale. Anal Chem 60: 451-462

Kelly C (2000) Analysis of steroids in environmental water samples using solid phase extraction and ion-trap gas chromatography–mass spectrometry and gas chromatography–tandem mass spectrometry. J Chromatog 872: 309–314

Luks-betlei K, Popp P, Janoszka B, Paschke H (2001) Solid-phase microextraction of phthalates from water. J Chromatog 93: 93-101

Martýnez VJL, Pablos EMC, Frenich AG, Arrebola FJ (2000) Pesticide trace analysis using solid-phase extraction and gas chromatography with electron-capture and tandem mass spectrometric detection in water samples. J Chromatog 867:235-245

Ma M, Wang ZJ, Sodergren A (2001) Contamination of PCBs and organochlorinated pesticides in the sediment samples of Guanting reservoir and Yongding River. Environ Chem 20: 238-243 (in Chinese)

Schachterle S, RD, Mills JD (1994) Analysis of pesticide residues in food using gas chromatography-tandem mass spectrometry with a benchtop ion trap mass spectrometry. J Chromatog 688:185-193

Prokupkova G, Holadova K, Poustka J, Hajslova J (2002) Development of a solid-phase microextraction method for the determination of phthalic acid esters in water. Anal Chimica Acta: 457: 211-223

Tang L, Zheng ZG, (2001) Determination of substituted benzenes in water by double capillary gas chromatography. Environ Sci Technol 24: 41-43