Simultaneous determination of 4-\textit{tert}-octylphenol, 4-nonylphenol and bisphenol A in Guanting Reservoir using gas chromatography-mass spectrometry with selected ion monitoring

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Abstract: The wide occurrence of estrogenic compounds 4-\textit{tert}-octylphenol, 4-nonylphenol, bisphenol A in surface water of Guanting Reservoir was successfully determined. The target compounds in water samples were preconcentrated by liquid-liquid extraction with dichloromethane, derivatized by trifluoroacetic anhydride, and quantified by gas chromatography-mass spectrometry (GC-MS) with selected ion monitoring (SIM). In the selected seven sampling sites (S1–S7), the concentration of NP in sample S7 was significantly higher than the other in reservoir. The status of pollution in S3 and S7 were much more serious. The concentrations of OP, NP and BPA were in the range of 44.5–48.8, 221.6–349.6 and 30.2–82.7 ng/L, respectively. The pollutants were mainly inputted from the upper river and released from sediments in Guanting Reservoir.

Keywords: 4-\textit{tert}-octylphenol; 4-nonylphenol; bisphenol A; Guanting Reservoir; GC-MS-SIM

Introduction

In the last decade, there is an important topic of great interest in studying endocrine disrupters (Sonenshine, 1998). In particular, the estrogenic-like activity of 4-\textit{tert}-octylphenol (OP), 4-nonylphenol (NP) and bisphenol A (BPA) had been discovered, and raised concern over their role in endocrine disruption effects were observed in aquatic biota (Klotz, 1996). OP and NP could be detected in rivers and estuaries where a feminization of fish was observed (Blackburn, 1995), whereas BPA was also determined from sewage influent, effluent and sludge (Fürhacker, 2000). In vitro and partly in vivo studies have demonstrated the estrogenic activity of NP, OP and BPA (Soto, 1991; Jabling, 1993), and confirmed the estrogenic potential of these compounds even in low concentrations.

OP and NP were released into the environment mainly as metabolites of alkylphenol ethoxylates (APEOs) (Ariel, 1994). Precursor APEOs were widely used as nonionic surfactants in industrial, agriculture and domestic applications (Renner, 1997). BPA frequently used as a monomer in the manufacture of epoxy resins and polycarbonate plastics (Lee, 2002). Because of their widespread application, the ubiquitous occurrence, persistence and toxicity of these phenolic xenoestrogens have also documented extensively in various environmental samples (Kuch, 2001; Bolz, 2000).

Guanting Reservoir is located at the northwest of Beijing. It dammed Sunggan River, Yang River and Gui River, and finally flowed into Yongding River. As the first large-scale reservoir in China, Guanting Reservoir played an important role in water supply for Beijing. Since 1972, the water quality of reservoir has deteriorated gradually (Liang, 2003). In the following three decades, the body of water has been exposed to series pollutions, and lost its function as the source of drinking water in 1997. With the shortage of drinking water in Beijing, Guanting Reservoir is reconsidered as the reserve source of potable water.

During the past decade, the occurrence of heavy metal, total nitrogen, total phosphorous (Liu, 2002), HCH, DDT, PCB (Ma, 2001; Wang, 2003), PAHs (Jiang, 2002), organotin compounds (Liu, 2003) and other organic pollutants in Guanting Reservoir have been investigated. To understand the pollution levels of alkylphenol compounds in Guanting Reservoir, simultaneous determination of NP, OP and BPA have been carried out by the gas chromatography-mass spectrometry with selected ion monitoring in this study.

1 Materials and methods

1.1 Apparatus and reagents

An Agilent 6890 gas chromatography (GC) coupled with 5973 mass spectrometry (MS) detection was used to analyze target compounds. GC separation was performed on a HP-1 MS fused-silica capillary column (60 m × 0.25 mm i. d.; film thickness 0.25 μm). Helium, used as carrier gas, was controlled at a flow rate of 1.0 ml/min in a constant flow...
mode. The injection was operated in pulsed splitless mode at a temperature of 250°C. The oven temperature program used was as follows: the initial temperature was 80°C, kept for 2 min, raised to 180°C at 15°C/min, to 190°C at 5°C/min, to 280°C at 20°C/min and held for 3 min. As to the MSD parameters, electron impact ionization was set at 70 eV, the temperatures of interface, source and quadrupole were 280, 230 and 150°C, respectively.

Pesticide grade dichloromethane and n-hexane were purchased from Fisher scientific (New Jersey, U.S.A.). Acetone was of analytical reagent and was distilled before use. De-ionized water was double redistilled by quartz distiller. NP and OP were obtained from Tokyo Kasei Kogyo Co. Ltd., Japan. BPA was purchased from Acrors Organics (NJ). Trifluoroacetic anhydride (TFAA) was obtained from Koch-Light Laboratories Ltd., England. Priority grade sodium chloride, and analytical grade 1, 2, 4-trichlorobenzene (TBB), hydrochloric acid and sodium sulfate anhydrous were obtained from Beijing Chemicals Corporation. In the whole analytical process only glassware were used and flushed with acetone and methanol before use.

1.2 Sampling

To investigate the contaminated levels of OP, NP and BPA in water samples from Guanting Reservoir, seven different sampling sites were selected and shown in Fig. 1. Samples were collected in 4 L of preconditioned amber glass bottles on September 20, 2003. Samples were filtered through 0.45 μm cellulose acetate membranes in order to remove algae, zooplankton and suspended particles. Water samples were extracted immediately after sampling and filtering.

![Fig. 1 Sampling sites in Guanting Reservoir](image)

1.3 Extraction and derivatization procedure

15 g NaCl were added to 300 ml water sample and its pH was adjusted to less than 2 with several drops of 50% HCl (v/v). Extraction was performed with 3 × 20 ml of dichloromethane, shaken violently for three minutes each time. The combined organic phase was dehydrated with anhydrous sodium sulfate, reduced by rotary evaporation to a volume of about 1 ml, then transferred to a reaction vial and gently evaporated to dryness under a stream of high pure nitrogen. Derivatization was rapidly performed with 100 μl of TFAA (Varcois, 2000). The reaction vial was sealed and kept in 30°C water bath for 10 min, then sonicated for 10 min in 30°C water bath. The products were evaporated to dryness under a stream of nitrogen. The residues were redissolved in 100 μl of n-hexane containing 0.4 mg/L of TBB as internal standard of quantitative analysis (Rinken, 2001). An aliquot of 1 μl of the derivatized resultants was injected for GC-MS analysis.

2 Results and discussion

2.1 Identification and quantification of the analytes by GC-MS

The retention time of the target compounds were obtained and confirmed by GC-MS in the scan mode under the above-described operation conditions. One peak of the derivatized OP(OD-TFAO), fourteen peaks of the derivatized NP(NP-TFAO) and one peak of the derivatized BPA(BPA-TFAO) were observed respectively in the chromatogram. By means of full scan mass spectra and retention times, and with the help of the NIST98 standard mass spectral library, the characteristic ions of the derivatized analytes were obtained and identified from the derivatized standards stock solution. Based on the mass spectra, the selected characteristic ions were m/z 231, 203, 302 for OP-TFAO; m/z 203, 217, 231, 245, 259 for NP-TFAO; m/z 405, 406, 420 for BPA-TFAO.

The typical parameters of the derivatized analytes were selected and listed in Table 1. The m/z values including internal standard TBB, m/z 235, 314, 316 were applied for quantification and confirmation of the target compounds. The mass spectrometer was operated in a selected ion-monitoring (SIM) mode to detect the trifluoroacetates derivatives of the analytes in standards and water samples. All characteristic signals of the derivatized analytes were obtained and shown in Fig. 2.

The analytes were quantified by comparing the peak area of their derivatives with the peak area of the internal standard TBB. However, fourteen peaks of NP-TFAO were attributed to their different isomers, some of individual peaks contained several isomers and did not represent pure isomers. For quantifying the NP, the peak areas of the fourteen selected peaks had to be wholly integrated, and then compared the summed area with the peak area of TBB. The responses were calculated by integrating with RTI integrator.

Stock solutions containing all analytes at accurately concentration were diluted with double distilled water. With the proposed procedure, calibration curves of all analytes were established. The regression equations and correlation coefficients (R^2) of OP, NP and BPA were A_{OP} = 0.0263 C_{OP} - 1.1092 (R^2 = 0.9943), A_{NP} = 0.0255 C_{NP} - 1.8611 (R^2 = 0.9908), A_{BPA} = 0.0196 C_{BPA} - 0.5054 (R^2 = 0.9961), respectively. Where A is relative response of
the target compound, \( C \) represents its concentration accordingly. According to these equations, concentrations of the analytes in water samples can be calculated.

2.2 Distribution of the target compounds in Guanting Reservoir

The target compounds of all water samples in Guanting Reservoir were determined by GC-MS-SIM, and quantified by the established calibration curve. The determined concentrations of OP, NP and BPA were in the range of 44.5–48.8, 221.6–349.6 and 30.2–82.7 ng/L, with a mean value of 46.5, 267.1 and 48.4 ng/L, and a median value of 45.8, 240.2 and 40.8 ng/L, respectively. The distribution of OP, NP and BPA in Guanting Reservoir is shown in Fig. 3. In the sampling sites of S3 and S7 the concentrations of NP were significantly higher than those of the other water samples in the reservoir. The concentration of BPA in sample S3 was the highest. There was no evident difference in the concentrations of OP in all samples. As a whole, the concentrations of NP were higher than that of OP and BPA in all water samples. The occurrences of contaminants in S3 and S7 were worse than the other sites.

With the development of industry and agriculture, many factories such as fur factory, paper mills, agrochemical factories built in upper rivers discharged the sewage into rivers and finally entered into the reservoir, which led to the high input of pollutants in the past decades. Yang River and Sanggan River converged and firstly flowed through the site S7 situated in the west of Guanting Reservoir. And with the persistent of the drought, the water depth of the reservoir was getting shallower; the water quality of the reservoir became worse and worse. Therefore, there were two sources of pollutants were obtained from investigation and the determined results. One is inputted pollutants come from the factories built at the headwaters. The prominent level of NP in S7 supported this result, and many studies on determining the other organic compounds such as HCH, DDT, PAHs, PCB, atrazine (Ren, 2002) and organotin compounds have also confirmed it. Another pollution source is likely to be released from the sediments in Guanting Reservoir. The possibility of the second pollution from sediments and the water shortage of the reservoir resulted in similar levels of OP.
3 Conclusions

In this study, the occurrence of OP, NP and BPA in surface water of Guanting Reservoir was successfully determined by GC-MS-SIM method after derivatizing by trifluoroacetic anhydride. The levels of OP, NP and BPA in all samples were determined. The concentrations of OP, NP and BPA were determined in the range of 44.5–48.8, 221.6–349.6 and 30.22–82.7 ng/L, respectively. The pollution sources were mainly inputting pollutants from upper rivers and releasing pollutants from sediments. As the reserved water source of Beijing in the future, the further control of water quality and reduce OP, NP and BPA contamination is urgently required.

References:


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