

Determination of Tetrabromobisphenol A in Soil by Liquid Chromatography-electrospray Ion Trap Mass Spectrometry

Jun Jin¹, Ying Wang, Hao Peng, Xiaoyan Tang

¹College of Life and Environmental Science, Central University For Nationalities, College of Environmental Science, Peking University

Introduction

Tetrabromobisphenol A ((4,4A-isopropylidenebis(2,6-dibromophenol), CAS 79-94-7, m.w.: 543.87, TBBPA) is widely used throughout the world as a flame retardant for building materials, paints, synthetic textiles, and plastic products, including epoxy resin electronic circuit boards and other electronic equipment. TBBPA currently accounts for about one third of the total usage of flame retardants. Despite the fact that TBBPA is usually chemically bound to a substrate, its high usage and limited water solubility may be expected to lead to persistence in the environment and possibly accumulation in biological systems. Due to its low water solubility, TBBPA has been detected in sediment and sewage sludge worldwide. Studies have shown that TBBPA can act as thyroid hormone-disrupting agents, as well as estrogens^{1,2}. In China, there are the number of TBBPA producing plants, especially in Jiangsu Province and Shangdong Province. However, almost no studies on the presence of TBBPA were reported in the environment in China. Trace amounts of TBBPA in environmental samples have been determined by GC-ECD or GC-MS. However, tedious pretreatments and derivatization as well as purification are necessary for the determination of TBBPA with GC³. In recent years, the instrumentations of liquid chromatography (LC) with MS or tandem MS (MS/MS) detection and the related techniques have been evolved rapidly, and so the LC-MS methods have been utilized to so many fields. Recently, the determination of TBBPA in sediment and biological samples by HPLC/MS were reported by two different research groups^{3,4}. The purpose of this research is also to develop a simple method for the determination of TBBPA in environmental soil samples. The method was applied to detect and quantify TBBPA in Chinese environmental samples.

Materials and Methods

All organic solvents and water were of LC-grade from Caledon Laboratories Ltd. (Ont, Canada). All other chemicals were of analytical grade. Nitrogen gas (99.999%) for drying and for MS were obtained from BABP Corporation (Beijing, China).

TBBPA standard was obtained from Shangdong TBBPA producing plant. Environmental soil samples were obtained outside one brominated flame retardants producing plant in 2005 at Shangdong Provinces. The 20 g environmental soil samples were analyzed for TBBPA by Liquid Chromatography-electrospray Ion Trap Mass Spectrometry (Agilent LC-MSD-Trap-XCT). Acquisition parameters of the LC-ESI interface of MSD were shown in Table 1. A reversed-phase C-18 (150mm x 4.6mm.i.d., particle size 5µm; SHIMADZU) column was used. Injection of samples was carried out automatically. Water (mobile phase A, 20%) and methanol (mobile phase B, 80%) were used as mobile phases. The flow-rate of the mobile phase and the column oven temperature were set at 0.8 mL/min and 40°C, respectively. The LC-MS was operated in the negative ESI mode.

Ultra-sonication was used for the extraction of TBBPA from environmental soil samples. Soil samples were extracted with 200 ml of acetone for 5 hours. After the filtered sample was evaporated by Rotary evaporator, the sample was applied to the preconditioned C18 SPE cartridge (Alltech 1.5ml, 100mg, USA). The SPE cartridge was washed with 2ml of methanol and 2ml of dichloromethane. TBBPA in the cartridge was eluted with 4ml of methanol, and the eluate was concentrated under a nitrogen stream. The solution was then placed in the auto-sampler of LC-MSD-Trap system.

Table 1. ESI(-)/MS Acquisition Parameters

Dry Temp	325°C	Skim 1	-40.0 Volt	Octopole RF Amplitude	194.5 Vpp
Nebulizer	50.00 psi	Skim 2	5.0 Volt	Capillary Exit	-132.3 Volt

An external calibration was used for the quantification of TBBPA. A linear calibration curve of area vs concentration with four or five solvent based standards was settled at each sequence of the analysis; the unknowns in the sequence were thus related to that curve. The concentration of TBBPA in standard solutions (methanol) ranged from 41 ng/ml to 6600 ng/ml; linear regressions showed R^2 was 0.9975. Average recoveries for the extraction of TBBPA in environmental soil samples spiked at the 17.8pg/g to 17.8ng/g TBBPA level ranged from 40.3% to 91.4%.

Results and Discussion

The first step in the development of the method was to establish the mass spectrum of TBBPA in negative ion mode by infusing a solution of the standard compound. The mass spectrum acquired in full scan (mass range of 300–800) is illustrated in Figure 1. The parent mass was $m/z = 542.8$ corresponding to the $[M-H]^-$ ion. We acquired a mass spectrum in MS-MS (ion trap) mode with the parent ion $m/z = 542.8$. The two daughters ions at $m/z = 525.7$ and $m/z = 445.7$ are the most intense (Figure 2). A third daughter ion at $m/z = 417.8$ and the fourth daughter ion at $m/z = 290.8$ is attributed to the loss of a dibromophenol moiety with a rearrangement of the propyl group to give the 4-isopropylene-2,6-dibromophenol (Figure 2).

The ion chromatogram and mass spectrum (negative ion mode) for an environmental soil sample taken outside the TBBPA producing plant is shown in Figure 3 and Figure 4. The concentration for the soil sample taken outside the TBBPA producing plant was 1.15 ng/g wet weight. The data suggest TBBPA may be emitted from point sources such as brominated flame retardants production facilities. The proposed LC-MSD-Trap method for the determination of TBBPA in soil samples is simpler than the previous GC methods because the derivatization step is not necessary. This results in a simple procedure, rapid analysis, and high reproducibility. Solid-phase extraction (SPE) offers efficient methods with lower solvent consumption, less risk of contamination, and higher selectivity. Extraction can be performed directly on wet soil with a single clean-up step without derivatization. Our study demonstrates the effectiveness of liquid chromatography with ion trap MS detection for the quantification of TBBPA in soil.

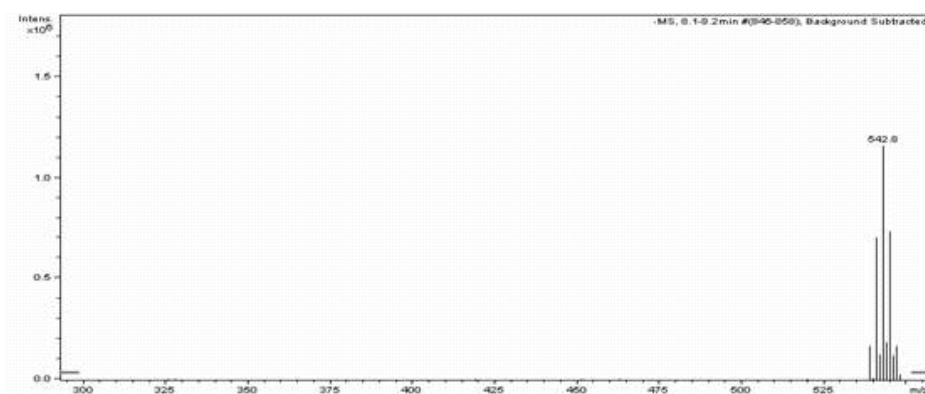


Figure 1. ESI-MS mass spectrum (negative ion mode) of TBBPA standard sample

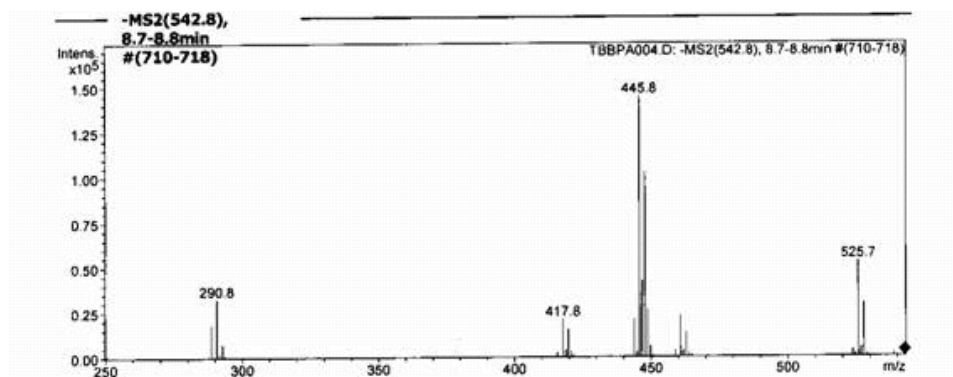


Figure 2. MS/MS (ion trap) fragmentation mass spectrum (negative ion mode) of TBBPA. Precursor ion of MS/MS is m/z 542.8.

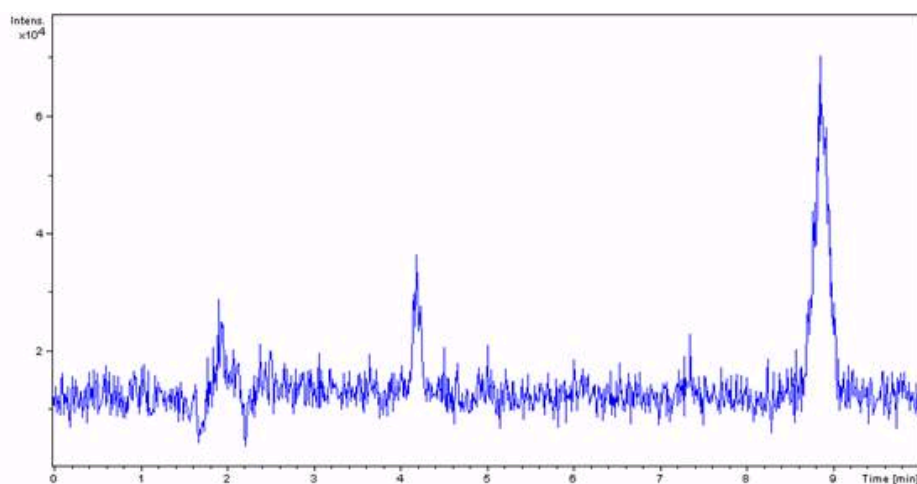


Figure 3. Ion chromatogram of soil sample taken outside the TBBPA producing plant

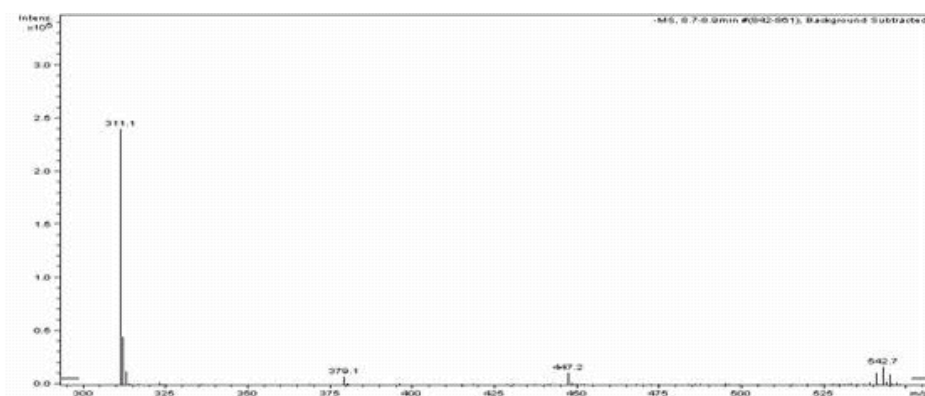


Figure 4. Mass spectrum of TBBPA (negative ion mode) in soil sample taken outside the TBBPA producing plant

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