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Determination of 2,6-di-*tert*-butyl-hydroxytoluene and its transformation products in indoor dust and sediment by gas chromatography–mass spectrometry coupled with precolumn derivatization

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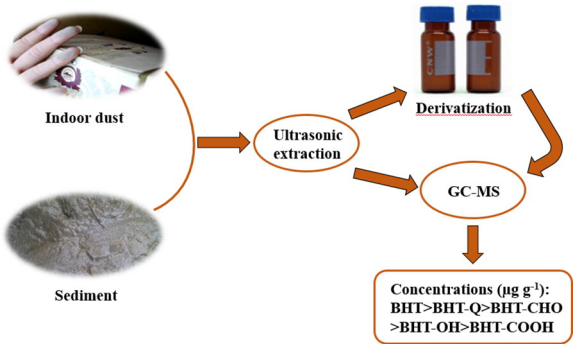
HIGHLIGHTS

- GC–MS coupled with derivatization method was established for BHT and transformation products.
- The method was successfully applied to indoor dust and sediment samples.
- Different profiles indicated the various transformation pathways among transformation products.

GRAPHICAL ABSTRACT



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ABSTRACT

We developed an analytical method to simultaneously determine 2,6-di-*tert*-butyl-hydroxytoluene (BHT) and its four transformation products in indoor dust and sediment samples. BHT, 2,6-di-*tert*-butylcyclohexa-2,5-diene-1,4-dione (BHT-Q), and 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (BHT-CHO) were measured by gas chromatography–mass spectrometry (GC–MS) after ultrasonic extraction with hexane/dichloromethane (1:3), while 2,6-di-*tert*-butyl-4-(hydroxymethyl) phenol (BHT-OH) and 3,5-di-*tert*-butyl-4-hydroxybenzoic acid (BHT-COOH) were derivatized using *N*, *O*-bis (trimethylsilyl) trifluoroacetamide before GC–MS analysis. The limits of detection (LODs) and quantification (LOQs) of the developed method were 0.02–0.34 and 0.08–1.14 ng g^{-1}. The recoveries for BHT and its transformation products were 71.1–118% with relative standard deviations < 10.6% at different spiking levels. The method was applied to indoor dust and sediment samples, showing that BHT was found in all samples with concentrations being 0.22–47.37 μg g^{-1} in dust and 0.09–6.93 μg g^{-1} in sediment. BHT-Q was the dominant transformation product, followed by BHT-CHO, BHT-OH, and BHT-COOH. Different metabolite profiles for BHT indicated various transformation pathways, making it necessary to study their transformation mechanism and environmental behaviors in the future studies.

1. Introduction

Synthetic phenolic antioxidants (SPAs) are widely used as additives and preservatives to prevent fat degradation and prolong the shelf-life of many consumer products, including fat-containing foods, plastics,

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and paints (Rodil et al., 2012; Cacho et al., 2015; Wang et al., 2016). As one of the most frequently used SPAs, 2,6-di-*tert*-butyl-hydroxytoluene (BHT) is widely used in food and cosmetic industry. It has been reported that the BHT contents in >1700 cosmetic formulations were as high as 0.5% (Lanigan and Yamarik, 2002). BHT is unstable in the environment and can be transformed through oxidation of alkyl substituent, π-system, or photo-degradation (Matsuo et al., 1984; Fernández-Álvarez et al., 2009). The transformation products include 2,6-di-*tert*-butylcyclohexa-2,5-diene-1,4-dione (BHT-Q), 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (BHT-CHO), 2,6-di-*tert*-butyl-4-(hydroxymethyl) phenol (BHT-OH) and 3,5-di-*tert*-butyl-4-hydroxybenzoic acid (BHT-COOH).

There are increasing concerns regarding the potential toxicity of BHT and its transformation products (BHTs). BHT may exert toxic effect, such as lung damage and melanoma metastasis in mice (Gal et al., 2015), hepatic necrosis, nephrotoxicity and hemorrhagic death in rats (Nakagawa et al., 1984; Nakagawa and Tayama, 1988). BHT-CHO, has been linked to DNA damage and apoptosis in human cells. For example, BHT transformation products induced DNA strand breaks in Burkitt's lymphoma cell line BJAB and human myelogenous leukemic cell line HL 60. In addition, apoptosis was observed based on internucleosomal DNA fragmentation through H_2O_2 generation (Oikawa et al., 1998). Given the toxicity of BHTs, it is necessary to study their environmental occurrence and fate, which is important for accurate risk assessment for human exposure.

BHT and its transformation products can be released into environment through daily use of BHT-containing household products (Lanigan and Yamarik, 2002). These compounds are often absorbed onto indoor dust due to their high hydrophobicity (e.g., log Kow of BHT = 5.32) (Liu et al., 2017). For example, BHT was detected in dust sample from 75 resident houses in Jinan city, China, showing concentrations of 163–1840 ng g^{-1}. Although mounting evidence showed that dust ingestion is a significant exposure routes for human for many contaminants (Richards et al., 2016; Meng et al., 2016; Wei et al., 2015), there are limited data about accumulation levels of BHTs in indoor dust. In addition, similar to other organic contaminants, BHT-containing effluent from wastewater treatment plants can be released into sediment (Liu et al., 2015). Studies have reported the occurrence of BHTs in several environmental matrixes, such as foodstuffs, sludge, and surface water (Liu et al., 2015; Kim et al., 2016). However, no information is available about levels of BHTs in sediment.

Reliable analytical method is important to understand environmental occurrence and fate of contaminants. Couples of analytical methods have been developed for analysis of BHTs in foodstuffs and food packaging materials (Kim et al., 2016; Andre et al., 2010; Xu et al., 2016), but method for BHTs in dust and sediment is scarce. High performance liquid chromatography (HPLC) and gas chromatography (GC) are the most common methods (Kulawik et al., 2013). However, HPLC method needs improvement for its sensitivity. For instance, BHTs in cheese and bread spread were determined by reversed–phase HPLC with low sensitivity (limit of detection = 0.5 mg L^{-1}) (Saad et al., 2007). HPLC–tandem mass spectrometry (MS/MS) showed good selectivity and sensitivity (Liu et al., 2015), but they are expensive and not suitable for analysis of hydrophobic BHT. Thus, GC–MS seems a good choice to determine BHTs with the characteristics of low expense and easy manipulation. In general, compounds containing polar groups (e.g., —OH, and —COOH) need to be derivatized to improve their chromatographic properties and separation on the GC column (Guo et al., 2006). Therefore, derivatization is necessary for polar BHT-OH and BHT-COOH. For example, Rodil et al. (2010) determined BHTs in water by solid phase extraction–derivatization–GC–MS method. This method showed satisfactory sensitivity (0.1–0.9 μg L^{-1}) and recovery (80–110%).

In this paper, we developed an analytical method to determine BHTs in indoor dust and sediment by GC–MS coupled with derivatization. The optimal derivatization and extraction conditions were investigated. Its applicability to 11 indoor dust samples from Nanjing and 26 sediment samples from Tai Lake, China was tested, showing satisfactory recovery and detection limits.

2. Materials and methods

2.1. Chemicals and reagents

Target chemicals and their structures are shown in supporting information as Table S1. The standards of BHT, BHT-Q, BHT-CHO, BHT-OH and BHT-COOH (BHTs) were purchased from CNW Technologies GmbH (Düsseldorf, Germany) with purity of 98%. Individual stock solutions of BHTs were prepared in methanol at a concentration of 2000 mg L^{-1}. The derivatization reagents, *N*-methyl-*N*-trimethylsilyl-trifluoroacetamide (MSTFA), *N*-methyl-*N*-(*tert*butyldimethylsilyl)-trifluoroacetamide (MTBSTFA), and *N*, *O*-bis (trimethylsilyl) trifluoroacetamide (BSTFA) (98%), were purchased from Regis Technologies, Inc. (Morton Grove, US). Sodium sulfate anhydrous from Nanjing Chemical Reagent co., LTD (Nanjing, China) was baked at 660 °C for 6 h and stored in a sealed desiccator. Ultrapure water (18.2 MΩ·cm) was prepared by a Milli-Q system (Millipore, Billerica, USA). All solvents (e.g., dichloromethane and hexane) obtained from Merck (Mollet del Vallés, Barcelona, Spain) and J.T. Baker (Phillipsburg, NJ, USA) were pesticide residue grade.

2.2. Samples collection and extraction optimization

Indoor dust samples were collected from 11 houses in Nanjing, China. Dust was collected from floor of living room and bedroom, and furniture surface using brushes. All dust samples were packed in clean aluminum foil and transported to laboratory immediately after collection. Dust samples were homogenized and sieved through stainless sieve to collect particles <125 μm. A total of 26 sediment samples were collected from seven locations in Tai Lake, including Zhushan bay, MeiLiang bay, Gong lake, coastal zone, central zone, Xu lake, and the eastern Tai Lake. Latitude and longitude coordinates of sampling points in Tai Lake are shown in Table S2. The sediment samples were freeze-dried, homogenized, and sieved through a 120-mesh stainless steel sieve. All the samples were stored at −20 °C until analysis.

To optimize the extraction method, dust samples were extracted by different solvents, including hexane, hexane: acetone (1:1, v/v), hexane: dichloromethane (1:1), hexane: dichloromethane (1:3), and ethanol. The detailed extraction conditions are listed in Table S3. The samples were placed in 50 mL glass centrifuge tubes and extracted by solvent with the best performance (i.e., hexane: dichloromethane (1:3)) in three cycles of 15 min in a sonicator. The samples were centrifuged for 5 min at 3000 rpm, and the supernatant from the three cycles was combined. The extract was dehydrated through anhydrous sodium sulfate column and evaporated to almost dryness under a stream of nitrogen. The extract was then reconstituted in 300 μL hexane, an aliquot of 100 μL of which was subject to GC–MS analysis for BHT, BHT-Q, and BHT-CHO. The other 200 μL solution was subject to derivatization to measure BHT-OH and BHT-COOH. The optimal derivatization conditions were investigated, including the selection of derivatization reagents, the amount of derivatization reagent, derivatization temperature, and reaction time.

2.3. Instrumental analysis and quality control

BHTs were analyzed using a GC (Agilent Technologies 7890A) coupled with a MS (Agilent Technologies 5977A) in the ion monitoring mode. The temperature of the injector was 280 °C, and a fused-silica capillary column (HP-5MS; 30 m × 250 μm i.d., 0.25 μm film thickness) was used for separation. High purity helium (purity ≥ 99.999%) was used as carrier gas with a constant flow of 1 mL min^{-1}. Oven temperature program was set initially at 45 °C for 1 min, first ramped to 270 °C at 10 °C min^{-1}, and finally ramped to 290 °C at 25 °C min^{-1} (held for