

Stir bar sorptive extraction and thermal desorption-gas chromatography-mass spectrometry for trace analysis of benzophenone and its derivatives in water sample

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Abstract

A simple and highly sensitive method called stir bar sorptive extraction (SBSE) and thermal desorption (TD)-gas chromatography-mass spectrometry (GC-MS), which is used for the determination of trace amounts of benzophenone (BP) and its derivatives, 2-hydroxy-4-methoxybenzophenone (BP-3) and 2-hydroxy-4-methoxy-4'-methylbenzophenone (BP-10), in river water samples, is described. A stir bar coated with polydimethylsiloxane (PDMS) is added to a 10 ml water sample and stirring is carried out for 120 min at room temperature (25 °C) in a vial. Then, the PDMS stir bar is subjected to TD-GC-MS. The detection limit is 0.5–1 pg ml⁻¹ for BPs. The method shows good linearity and the correlation coefficients are higher than 0.997 for all the analytes. The average recoveries of the BPs are equal to or higher than 98.5% (R.S.D.: 1.5–5.1%). This simple, accurate, sensitive and selective analytical method may be used in the determination of trace amounts of BPs in river water samples.
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1. Introduction

Benzophenone (BP) and its derivatives are the most commonly used sunscreen agents in cosmetics. However, various studies have revealed the estrogenic activity of BPs [1–3]. Therefore, BPs are considered to be endocrine disrupting chemicals (EDCs). To evaluate the potential risks of BPs, their determination requires highly sensitive and reliable methods. In the present study, we focused on the combined determination of BP, 2-hydroxy-4-methoxybenzophenone (oxybenzone, BP-3) and 2-hydroxy-4-methoxy-4'-methylbenzophenone (BP-10).

Several analytical methods for the determination of BPs in water and cosmetic samples have been reported, including liquid chromatography (LC) with UV detection, diode array detection (DAD) and mass spectrometry (MS) [4–8]. However, LC has low resolution and is frequently affected by the sample matrix. On the other hand, gas chromatography-mass spectrometry (GC-MS) was initially used for the determination of BPs [8–11].

Such sample preparation as online continuous liquid-liquid extraction (LLE) [9] and solid-phase extraction (SPE) [7,8] have been developed for the determination of BPs. However, LLE requires large volumes of organic solvents and additional concentration steps. On the other hand, although SPE requires small volumes of organic solvents, the manual version is tedious and time-consuming. Recently, solid-phase micro extraction

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(SPME) has been successfully used for the determination of BPs in water and urine samples [10,11]. However, the sensitivity of the above methods remains low. Because SPME with polydimethylsiloxane (PDMS) is by nature an equilibration technique that is based on the partitioning of an analyte between the stationary phase and the aqueous sample, the enrichment is dependent on the distribution coefficients of the analyte in the two phases. Therefore, the water/PDMS phase ratio is very important for sorptive extraction. The limited enrichment on the SPME fiber is mainly due to the volume of the PDMS phase (typically 0.5 μl or less), and increasing the volume of PDMS relative to the aqueous matrix is expected to markedly increase the enrichment of the analyte. Recently, a new sorptive extraction technique that uses a stir bar coated with PDMS was developed [12] and is known as stir bar sorptive extraction (SBSE). Its main advantages are high sensitivity and wide application range that includes volatile aromatics, halogenated solvents, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, preservatives, odor compounds and organotin compounds [12–18]. In addition, we have reported the determination of several EDCs in water samples and human biological samples [19–26].

The aim of this study was to determine trace amounts of BPs in water samples by the SBSE and TD-GC-MS method, which is simple, accurate and highly sensitive. The developed method was applied to river water samples.

2. Experimental

2.1. Materials and reagents

Benzophenone (BP) of environmental analytical grade and BP- d_{10} as internal standard were purchased from Kanto Chemical Inc. (Tokyo, Japan). 2-Hydroxy-4-methoxybenzophenone (oxybenzone, BP-3) was purchased from Sigma–Aldrich Co. (St. Louis, MO, USA). 2-Hydroxy-4-methoxy-4'-methylbenzophenone (BP-10) was purchased from Lancaster Synthesis (Morecambe, England). The chemical structures are shown in Fig. 1. The other reagents were purchased from Wako Pure Chemical Inc. (Osaka, Japan). The water purification system used was a Milli-Q gradient A 10 with an EDS polisher (Millipore, Bedford, MA, USA).

Stock solutions ($1.0 \mu\text{g ml}^{-1}$) of BP, BP-3 and BP-10 standards were prepared by methanol. More than six-point calibrations (2, 5, 10, 20, 50, 100, 200, 500, 1000, 2000 and 5000 pg ml^{-1}) were prepared by the addition of purified water

and performed daily for all samples with the internal standards by using the SBSE method.

2.2. Instrumentation

TD was performed with a Gerstel TDS 2 thermodesorption system equipped with a Gerstel TDS A autosampler and a Gerstel Cooled Injection System (CIS) 4 programmable temperature vaporization (PTV) inlet. GC-MS was performed with an Agilent 6890N gas chromatograph equipped with a 5973N mass-selective detector with an ultra ion source (Agilent Technologies).

Stir bars coated with a 0.5 mm-thick PDMS layer (24 μl ; TwisterTM; a magnetic stirring rod is placed inside a glass jacket and coated with PDMS) were obtained from Gerstel (Mülheim an der Ruhr, Germany). The stir bars were conditioned for 1 h at 300 °C in a flow of helium. Then, the stir bars were kept in new 2 ml vials until immediately prior to use. The stir bars could be used more than 50 times with appropriate re-conditioning (the stir bars were conditioned for 1 h at 300 °C in a flow of helium). For the extraction, a 20 ml headspace vial from Agilent Technologies (Palo Alto, CA, USA) was used.

2.3. TD-GC-MS conditions

The TDS 2 temperature was programmed to increase from 20 °C (held for 1 min) to 250 °C (held for 5 min) at 60 °C min^{-1} . The desorbed compounds were cryofocused in the CIS 4 at -150 °C. After the desorption, the CIS 4 temperature was programmed to increase from -150 to 300 °C (held for 10 min) at 12 °C s^{-1} to inject the trapped compounds into the analytical column. Once an analyte is trapped by means of temperature control, the entire quantity is subjected to GC-MS. Injection was performed in the solvent vent mode. The separations were conducted on a DB-5ms fused silica column (30 m \times 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific, Agilent Technologies). The oven temperature was programmed to increase from 60 to 300 °C (held for 4 min) at 15 °C min^{-1} . Helium was used as the carrier gas at a flow rate of 1.2 ml min^{-1} . The mass spectrometer was operated in the selected ion-monitoring (SIM) mode with electron ionization (ionization voltage: 70 eV).

2.4. Water samples

River water was sampled from two sites (points A and B) at Tama River, Tokyo, Japan. All samples were stored at 4 °C prior to use.

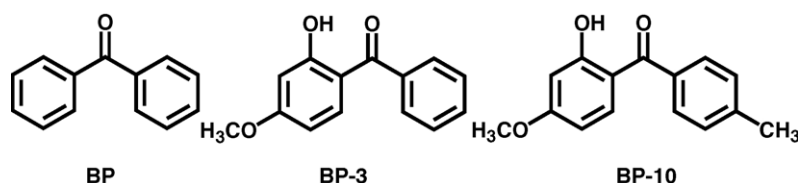


Fig. 1. Chemical structures of BPs.

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