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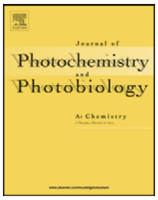

Research paper

Low temperature SPME device: A convenient and effective tool for investigating photodegradation of volatile analytes

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ABSTRACT

Hexachlorobenzene (HCB), a model volatile compound, was exposed to UV irradiation (16 W, 254 nm) after being sorbed in an internally cooled or low temperature solid-phase microextraction (LT-SPME) fibre. Photolysis took place directly on the polydimethylsiloxane coating of the LT-SPME fibre, yielding an “in situ” generation of photoproducts. Maintaining the temperature of the cold fibre at 0 °C eliminated, for the first time, problems of analyte losses due to volatilisation, inherent to the conventional room temperature photo-SPME studies. During the present studies, nearly complete photoremoval of HCB could be achieved within 20 min of irradiation. Photoreduction through photodechlorination was shown to be the main decay pathway in which lesser chlorinated congeners were sequentially formed as intermediates. Accordingly, initial generation of pentachlorobenzene was followed in order from 1,2,3,5-tetrachlorobenzene, 1,2,4,5-tetrachlorobenzene and 1,3,5-trichlorobenzene. The present findings were in agreement with previously reported results. Overall, the use of the LT-SPME device as a photoreaction support not only eliminated analyte losses but also greatly facilitated photochemical investigations of volatile compounds in general.

1. Introduction

Conventional solid-phase microextraction (SPME) is performed by exposing a fibre coated with a polymeric coating into a sample matrix, or to the sample headspace for a pre-determined pre-equilibrium or equilibrium time. The extraction process is completed once the analyte concentration has reached distribution equilibrium between the fibre coating and the sample matrix, as after this point the amount of analyte extracted remains constant within the limits of the experimental error [1]. In particular, the headspace sampling mode can be used to extract more volatile compounds from aqueous samples or complex matrices. In these cases, heating the sample at a high temperature whilst maintaining the fibre coating at a relatively low temperature were found to eliminate the negative effect of elevated extraction temperatures on the analyte distribution constant and thus increase sensitivity. The sampling strategy that evolved from this approach leaded to the development of the so-called internally cooled or low temperature solid-phase microextraction (LT-SPME) devices, which were recently miniaturized and automated [2]. The versatile and flexible character of SPME was also demonstrated when SPME fibre coatings were previously used as photoreaction supports and target analytes were exposed to light irradiation at room temperature after being sorbed in these SPME coatings [3,4]. Although photo-SPME proved to be a convenient photo-tool, a major limitation existed and these on-fibre studies could not be carried out for more volatile parent compounds or byproducts [4].

In current studies, hexachlorobenzene (HCB), a model volatile compound, was exposed to UV irradiation after being sorbed into a poly(dimethylsiloxane) (PDMS) coating serving as the reaction medium, located on internally cooled micro tubing of a SPME fibre maintained at temperatures close to 0 °C. Photolysis took place directly in the PDMS coating of the LT-SPME device, yielding an “in situ” generation of the photoproducts, allowing convenient introduction to GC and efficient determination of the primary volatile compound as well as its photoproducts without the need of any additional extraction steps (Fig. 1).

2. Experimental

2.1. Chemicals and sample preparation

All chemicals were of high purity and were purchased from Supelco or Fluka. Stock solutions at 1000 mg l^{-1} were prepared in acetone (Suprasolv grade for organic trace analysis; Merck) and spiked aqueous solutions were prepared from intermediate acetone

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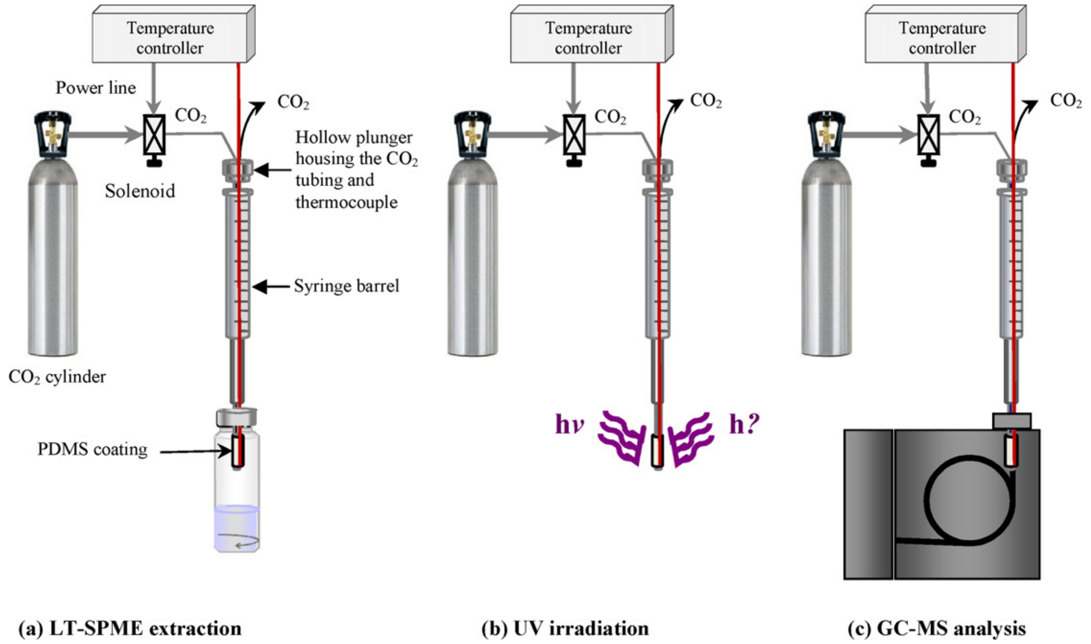

Fig. 1. General experimental procedure followed during the LT-SPME aided photo-studies. (a) Sorption of target analytes into the PDMS reaction medium of the LT-SPME, (b) exposure to UV irradiation and (c) simultaneous analysis of HCB and its photoproducts.

solutions. Deionized water was prepared on an EASYpure RF water purification system supplied by Barnstead/Thermolyne (Dubuque, IA, USA).

2.2. SPME extraction procedure

Based on previous reports the 100 μm polydimethylsiloxane (PDMS) SPME fibre (Supelco, Bellefonte, PA, USA) was used for all experiments [3,4]. In the case of conventional SPME, the PDMS fibre was housed in a manual SPME holder which is commercially available from Supelco (Bellefonte, PA, USA). The LT-SPME fibre device was constructed based on recent published procedures and the barrel of a gastight syringe was used for accommodating a 100 μm PDMS SPME fibre [2(d)–(f)].

The general SPME extraction procedure was as follows: 10 ml of an aqueous solution spiked at 5 $\mu g\, l^{-1}$ with HCB (unless otherwise stated within the text) was placed in a closed 22 ml vial and was let to equilibrate for 5 min at 100 °C in a thermostatized bath. Magnetic stirring (1000 rpm) was applied at all times. The fibre of either the conventional or LT-SPME was then exposed to the headspace above the sample for 45 min. The temperature of the LT-SPME fibre was set for this extraction step at 50 °C (±8 °C) to enhance extraction.

2.3. Photodegradation experiments

For the photodegradation experiments, following extraction the fibre of either conventional or LT-SPME was exposed to UV radiation for a preset period of time and then analysed using a Gas Chromatographer–Mass Spectrometer (GC–MS). A home-made laboratory photoreactor model equipped with two 8 W low-pressure mercury lamps (254 nm) was used in all cases. PDMS does not absorb well at the wavelength used here [5]. A negligible effect of UV irradiation on the performance and lifetime of the SPME fibre due to polymer decomposition is thus expected. The general experimental procedure followed during the LT-SPME aided photo-studies is depicted in Fig. 1. The temperature of the LT-SPME fibre was set at 0 °C (±3 °C) whereas conventional SPME photo-studies were performed at room temperature. For every set of experiments a control experiment (0 min of UV irradiation) was carried out. Dark tests were also run by placing the fibre inside the photoreactor with the lamps switched off for a pre-determined period of time, ensuring thus that any recorded changes were due to the action of photons. All experiments were run at least in duplicates.

2.4. GC–MS analyses

The conventional SPME fibre was analysed using a GC-17A (Version 3) gas chromatograph coupled to a QP-5050A MS system from Shimadzu (Tokyo, Japan), equipped with a 30 mm × 0.25 mm i.d. DB-5 column (J&W Scientific, Folsom, CA, USA) having a 0.25 μm film thickness. The detector voltage was set at 1.50 kV and the ionization mode was electron impact (70 eV). In the case of LT-SPME fibre, an Agilent 6890A (GC)-Agilent 5973 Network GC–MS equipped with a HR-1 (30 m × 0.25 mm i.d. × 0.25 μm film) column, was used for all analyses. The temperatures of the quadrupole and the ion source were set at 150 and 240 °C, respectively. The rest of the instrumental parameters were the same for both SPME formats and were set as follows: injector operating at 270 °C in the splitless mode with the split closed for 5 min; helium (>99.999% pure) used as the carrier gas at a flow-rate of 1.2 $ml\, min^{-1}$; interface temperature set at 300 °C; full-scan MS detection mode from 45 to 400 amu; oven temperature programme 60 °C, hold 2 min, rate 6 $°C\, min^{-1}$ to 285 °C, hold 2 min. Very good linear behaviours for both SPME procedures were recorded for HCB concentrations ranging between 0.05 and 5 $ng\, ml^{-1}$ (five calibration points).

3. Results and discussion

Preliminary investigations consisted of extracting HCB using the conventional headspace SPME procedure and then the SPME fibre was exposed to UV irradiation (16 W, 254 nm) at room temperature for 0–20 min before GC–MS analysis. Dark tests run in parallel confirmed a considerable amount of HCB was desorbed from the fibre and analyte losses could not be accurately quantified.

Photodegradation studies were then performed using PDMS coating as the photoreaction medium and the LT-SPME fibre support. HCB was extracted under the experimental conditions found in the supporting information and the fibre was then exposed to UV

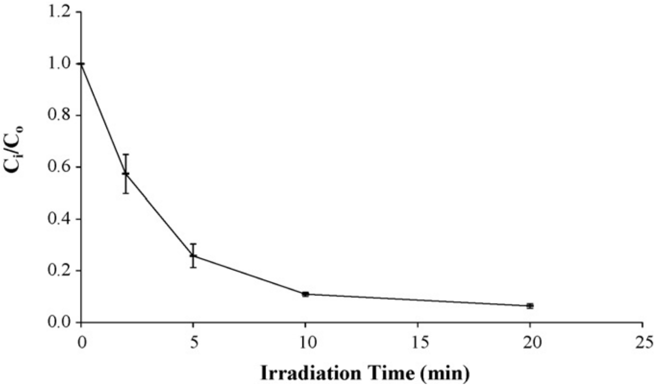

Fig. 2. Normalised peak area–time profiles during photodegradation studies of HCB sorbed in a PDMS coating of LT-SPME fibre.

irradiation for 0–20 min, with the LT-SPME fibre temperature kept constant at 0 °C. Dark tests run in parallel confirmed that no volatilisation losses were taking place. Fig. 2 shows the normalised peak area–time profile for the sorbed analyte subjected to UV irradiation. As seen, nearly complete HCB photoremoval could be achieved within 20 min of irradiation. In general, the photolysis of HCB in distilled water has been repeatedly reported to proceed at very slow rates [6,7] and it has been suggested that at the low HCB aqueous concentrations (limited by solubility), the chance of photochemically produced reactant-new radical is low [7]. Nonetheless, elimination times, comparable to the one recorded here, have been reported in the case of organic solvent solutions [8,9].

Keeping the temperature of the SPME fibre low eliminated analyte losses and facilitated photochemical studies of the more volatile compounds. Under the present experimental conditions and during the course of the HCB photoreaction, four photoproducts could be detected: pentachlorobenzene (PeCB), two tetrachlorobenzene isomers (1,2,3,5-TeCB and 1,2,4,5-TeCB) and small amounts of a trichlorobenzene isomer (1,3,5-TriCB). Identification of isomers was done by comparing elution times with standard analyte solutions.

The photoreduction of aryl halides, resulting specifically in photodechlorination, has been reported in several occasions [8–10]. In the present studies, the identity of the generated photoproducts also pointed toward a reductive dechlorination photodegradation pathway following a successive loss of chlorine atoms (Fig. 3).

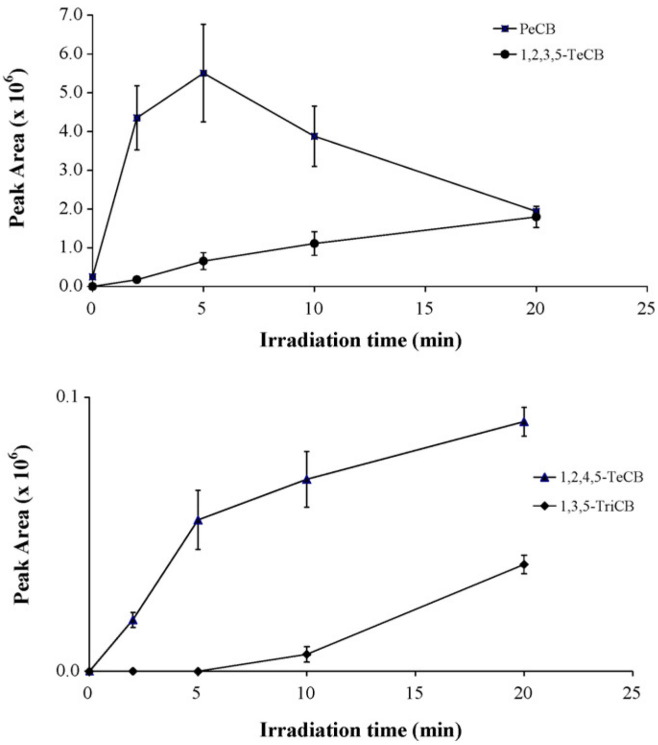

Fig. 4. Peak area–time profiles of the byproducts (namely PeCB, 1,2,3,5-TeCB, 1,2,4,5-TeCB and 1,3,5-TriCB) detected during LT-SPME photo-studies of HCB.

Indeed, close examination of the peak area–time profiles of the detected byproducts (Fig. 4) revealed a sequential byproduct formation was taking place with initial generation of PeCB and then in order of 1,2,3,5-TeCB, 1,2,4,5-TeCB and 1,3,5-TriCB.

Early studies on the photodecomposition of HCB in hexane and in wavelengths greater than 220 nm resulted in measurable amounts of PeCB and TeCB within 5 min and no HCB was detectable after 15 min [9]. The authors concluded that reductive dehalogenation was the main degradation mechanism. In a more recent report, Yamada et al. [8] compared the photodegradation pathways of HCB in hexane, 2-propanol and methanol with those predicted by quantum chemical calculations. In their experimental photo-studies, the authors reported exposing HCB organic solvent solutions (hex-

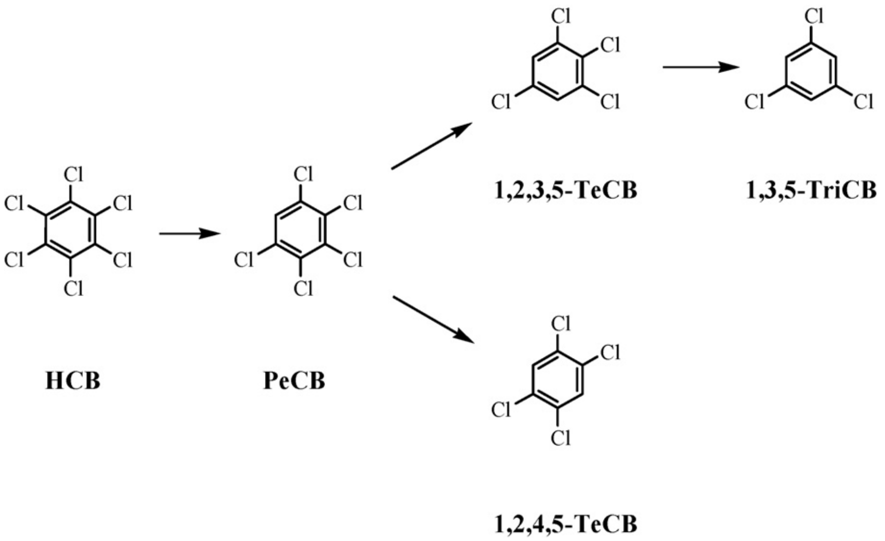

Fig. 3. Photoproducts detected during the LT-SPME photo-studies of HCB.

ane, methanol and 2-propanol) at 254 nm UV irradiation lead to the sequential formation of the chlorinated benzene congeners within the 20 min studied here. The authors assumed dechlorination proceeded via a chlorophenyl radical, produced by UV-induced C–Cl bond dissociation. The main degradation pathways were experimentally determined by identifying the major intermediate products at each stage of dechlorination and then in turn identifying the major products produced by irradiation of those intermediates. In all tested solvents, the main tetrachlorinated products were 1,2,3,5-TeCB and 1,2,4,5-TeCB, the main trichlorinated products were 1,3,5-TriCB and 1,2,4-TriCB and the main dichlorinated compounds were 1,4-dichlorobenzene and 1,3-dichlorobenzene. It should be mentioned here that the preferential formation of 1,2,3,5-TeCB over 1,2,4,5-TeCB has been reported during the photolysis of HCB in organic solvent solutions [8,11].

In conclusion, the use of PDMS as a photoreaction medium and LT-SPME device as the tool to perform the UV exposure and sample introduction into GC enabled for the first time monitoring of the photochemical degradation of HCB, a model volatile compound. Studying photodegradation mechanisms with LT-SPME is fast given photolysis of the parent compound and byproduct formation proceed onto the same LT-SPME fibre subsequently used for analysis. More importantly and for the first time, analyte losses, including those of the photoproducts generated "in situ" are eliminated due to the low temperature of the LT-SPME. Further extension of research in this direction will lead to investigation of different coatings as reaction media and effects of temperature variations during reaction facilitating determination of thermodynamic parameters. Furthermore, since previous studies demonstrated the great potential in automation of traditional LT-SPME procedures, this research can be extended toward testing the performance of automated photo-LT-SPME.

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