Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Chromatography A, 1102 (2006) 91–95
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Multiple headspace single-drop microextraction—a new technique for quantitative determination of styrene in polystyrene

Erik Hansson, Minna Hakkarainen *

Department of Fibre- and Polymer Technology, School of Chemical Science and Engineering, Royal Institute of Technology (KTH), Teknikringen 56-58, SE-100 44 Stockholm, Sweden

Received 23 August 2005; received in revised form 19 October 2005; accepted 27 October 2005
Available online 21 November 2005

Abstract

Single-drop microextraction (SDME), an emerging miniaturised extraction technique, was for the first time combined with multiple headspace extraction (MHE) to enable the quantitative determination of volatiles in solid matrixes by SDME technique. The concept of multiple headspace single-drop microextraction (MHS-SDME) was then applied for quantitative determination of styrene in polystyrene (PS) samples. Good linearity for the multiple headspace extraction was obtained when the migration of styrene was facilitated by grinding the samples and incubating them for 1 h at 150 °C prior the first extraction. Two microlitres of butyl acetate was used as the single-drop microextraction solvent and the extraction time was 5 min per cycle. The relative standard deviation (RSD) for single-drop microextraction of styrene standard at $n = 6$ was 7.6%. Linearity was shown for styrene concentrations between 0.005 and 0.75 μg/ml ($R^2 = 0.999$). This corresponds to total amount of styrene between 0.1 and 15 μg. The limit of quantitation for styrene standard at S/N 10 was 0.005 μg/ml. The developed method was validated against and showed good agreement with an earlier reported dissolution–precipitation method.

Keywords: Multiple headspace extraction; SDME; Solvent microextraction; Polymer; Polystyrene; Styrene

1. Introduction

Single-drop microextraction is one of the recent trends in sample preparation. It is a miniaturisation of the traditional liquid–liquid extraction method, where the solvent to aqueous ratio is greatly reduced. The volatiles are extracted by a micro-drop of non water-soluble organic solvent, which is immersed in an aqueous sample [1]. After extracting for a specified amount of time the drop is retracted into the syringe and the micro-drop is transferred to a GC for further analysis. Alternatively the micro syringe needle with the drop can be suspended above the surface of sample phase to perform headspace single-drop microextraction (HS-SDME) [2,3]. HS-SDME is an inexpensive and rapid technique, which uses practically no solvent and eliminates the possible memory effects, because new solvent drop is used every time. SDME has successfully been applied for the extraction of, e.g. dialkyl phthalate in food simulants [4], organophosphorus insecticides in water [5], antifouling agents in water [6], amino acids in urine [7] and iodine pharmaceuticals [8].

In many plastic applications, it is important to identify and quantify the low molecular weight compounds present in the material, because these compounds have a tendency to with time migrate from the plastic product into the surrounding environment. Traditional solvent-based techniques, such as microwave-assisted extraction (MAE) or soxhlet extraction are limited by being rather time, solvent and labour consuming. They also involve the risk of loosing volatiles during sample preparation, extraction and clean-up. To avoid the use of organic solvent, headspace (HS) or headspace solid-phase microextraction (HS-SPME) can be used for the determination of different low molecular weight compounds in polymers [9–12]. Due to various matrix effects internal and external calibration cannot usually be applied for quantitative determination of volatiles in solid matrixes by headspace techniques. To remove these matrix effects and enable the quantitative determination of volatiles in solid matrixes by headspace techniques, multiple headspace extraction (MHE) was developed by Kolb in the 1970s [13–15]. MHE involves several consecutive extractions from the same

* Corresponding author. Tel.: +46 8 790 82 71; fax: +46 8 10 07 75.
E-mail address: minna@polymer.kth.se (M. Hakkarainen).

0021-9673/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2005.10.060

sample vial. The theory considers the extraction to continue until all analyte is removed from the sample, thus resulting in complete recovery and elimination of matrix effects. In practice after linearity of the method has been demonstrated, only two extractions are usually needed to calculate the total peak area. There are only a few studies where MHE [16,17] and more recently multiple headspace-SPME [18,19] were applied for quantitative determination of volatiles in polymer matrixes.

Polystyrene (PS) is one of the most useful plastic materials used in different common consumption products, such as cups, food containers, toys, home furniture, building materials, etc. The main problem with this plastic is the residual styrene, which can migrate from the product during the use. The acute toxicity of styrene has been well studied, being a skin and mucous membrane irritant, having narcotic [20] and genotoxic properties [21]. Recently, both Soxhlet, microwave-assisted extraction, supercritical fluid extraction, headspace extraction and dissolution–precipitation techniques were evaluated and compared to determine the residual styrene content in polystyrene granules [22]. However, only the dissolution–precipitation method gave good results. Methods have also been developed based on, e.g. SPME to determine the amount of styrene emitted during thermal aging [23].

The aim of the present study was to develop a new technique for quantitative assessment of volatiles in solid polymer matrixes by combining multiple headspace extraction with single-drop microextraction. The new multiple headspace single-drop microextraction (MHS-SDME) technique was then evaluated and validated for the extraction and quantitative determination of styrene in polystyrene. Single-drop microextraction has not yet been applied for extraction of volatiles from solid matrixes, such as polymers. The combination with multiple headspace extraction would broaden its applicability from analysis of aqueous matrixes to even quantitative determination of volatiles in solid matrixes.

2. Experimental

2.1. Chemicals and materials

The syringe used for single-drop microextraction (SDME) was a 1701 Hamilton (Reno, Nevada, USA) gastight syringe with needle tip #2. Twenty millilitres headspace vials with aluminium crimp seal (Supelco, Belafonte, PA, USA) and PTFE septa from Perkin-Elmer (Boston, MA, USA) were used. Methanol 99.8%, dichloromethane 99.8% and styrene 99% were obtained from LabScan (Dublin, Ireland) Butyl acetate 99.7% and acetone 99.8% were purchased from Aldrich (Steinheim, Germany). The studied polystyrene materials included extruded polystyrene stripes and polystyrene cup's manufactured by Duni (Malmö, Sweden).

2.2. Multiple headspace single-drop microextraction

To decrease the diffusion distance the polystyrene stripes and polystyrene mugs were manually grinded to fine powder by scratching with a scalper. A larger amount of polystyrene powder was made and properly mixed before samples were taken for extraction as the polystyrene content inside the stripes may vary from the outer layers. 0.010 g of polystyrene powder was then placed in each 20 ml headspace vial. The vials were incubated for 1 h at 150 °C prior the first extraction and thermostatted for 30 min at 150 °C between each extraction. Before each extraction the vials were cooled by room-tempered water to prevent the drop evaporation. SDME was performed with a 2 μl butyl acetate drop for 5 min. The extraction solvent, i.e. butyl acetate, contained 0.2 μl/ml of ethyl ester of heptanoic acid as internal standard. After sampling the drop was completely retracted into the syringe. When the syringe had been withdrawn from the vial, the plunger was pressed down until 1 μl of the solvent remained in the syringe. The remaining solvent was subsequently analysed with GC–MS. To determine the amount of styrene in the polystyrene samples multiple headspace single-drop microextraction of styrene standard were performed. The standard samples were prepared by injecting into the headspace vial 0.1 ml of a 75 μg/ml styrene acetone solution, making the actual weight of the styrene in the vial equal to 7.5 μg. The vials were sealed and the same SDME parameters than for the PS samples were used. Six parallel extractions were performed to determine also the reproducibility of the method. To determine the linear range and limit of quantitation different styrene amounts varying from 0.05 to 15 μg were extracted and analysed. The extractions were analysed by gas chromatography–mass spectrometry.

2.3. Dissolution–precipitation method

The styrene content in the polystyrene stripes was also determined by a dissolution–precipitation according to Garrigós et al. [22]. 1.5 g of PS was placed in a sealed glass container and 10 ml of dichloromethane was added for dissolving the polymer. The solution was shaken and ultrasonicated to completely dissolve the PS specimen. Finally, 5 ml of methanol were added and the solution was vigorously shaken and ultrasonificated in order to re-precipitate PS. The solution was let to rest until two clear phases were observed: one clear and one precipitate. A small amount of the clear liquid was extracted with a pipette and 1 μl of this liquid was then injected into GC/FID. The mean peak area was calculated from the two sets of solutions with two runs on each in total four GC/FID runs. A calibration curve was made by running different concentrations (10, 20, 50, 80 and 100 μg/ml) of styrene standard dissolved in 2:1 (v/v) dichloromethane:methanol solution. The dichloromethane:methanol solutions were analysed by gas chromatography.

2.4. Gas chromatography

The single-drop microextractions of the samples thermostatted at 80 °C or 120 °C and the dissolution–precipitation samples were analysed by a Perkin-Elmer 8400 GC/FID gas chromatograph (Boston, MA, USA) equipped with a split/splitless injector. Nitrogen (AGA, laboratory grade) was employed as a carrier gas. A DB-225 ((50%-trifluoropropyl)methylsiloxane) capillary column (30 m × 0.25 mm × 0.25 μm) from J&W Scientific (DB,