

# Determination of residual styrene monomer in polystyrene granules by gas chromatography–mass spectrometry<sup>☆</sup>

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## Abstract

Polystyrene is widely used in formulations intended for children use. The main problem with this plastic is the residual styrene, which can migrate from the product, and therefore, be in contact with children. The acute toxicity of styrene is well known, raising the need of an efficient and fast method of analysis for this compound. Several extraction methods have been evaluated and compared for the determination of residual styrene monomer in polystyrene granules used in toys: supercritical fluid extraction (SFE), microwave-assisted extraction (MAE), Soxhlet extraction, headspace emission and dissolution–precipitation. The analyte was subsequently detected by gas chromatography (GC) with MS detection. The results indicated that the most efficient method was dissolution–precipitation giving even higher extraction efficiency than SFE. For validating the method, PS samples spiked with known quantities of styrene at three concentration levels were prepared to calculate the extraction recovery. The founded validation data proved the suitability of the proposed method.

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*Keywords:* Styrene; Polystyrene; Extraction methods

## 1. Introduction

Polystyrene is a thermoplastic with a lot of desirable properties like transparency, easily colouring and is easy to manufacture. For these reasons, it is one of the most useful plastic used in different common consumption products 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, and therefore, can be in contact with the user. The acute toxicity of styrene has been well studied, being a skin and mucous membranes irritant and having narcotic properties [1–4].

As a result of the toxicity of styrene, some requirements for “chemical toys (sets) other than experimental sets” are willing

to be set by the European Normalisation Committee (CEN) in reference to the safety of toys. Therefore, the development of a fast, reproducible and efficient analytical method for the determination of residual styrene content in polystyrene is necessary.

Several new approaches for the extraction of organic analytes from different matrices have been proposed, including supercritical fluid extraction (SFE), microwave-assisted extraction (MAE) and others [5–14]. The use of these techniques improved recoveries in the determination of most organic additives, as well as permitted considerable reductions in solvent volume and extraction time [15,16]. In the case of styrene, several analytical methods for its determination have been described in the literature. These methods were applied to the determination of styrene in specific matrices, such as urine [17–19] and blood [20,21]; but most of them were applied to foodstuffs [22–26]. The level of styrene migration in food contact polystyrene has also been studied [27–31]. The general process consists of solid-phase microextraction or purge and trap methodology as sample preparation for liquid

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Table 1  
General properties of the polystyrene resins used in this work

Property	Styron 485	Styron 678E	Edistir N1841
Colour	White	Transparent	Transparent
Density (g/cm <sup>3</sup> )	1.050	1.050	1.050
Tensile strength (5 mm/min) (MPa)	43	16	39
Elongation at break (5 mm/min) (%)	2.0	50.0	1.8
Young modulus (1 mm/min) (MPa)	3500	2000	3250
Flexion strength (2 mm/min) (MPa)	80	50	69
Hardness Rockwell (R)	105	55	80
Vicat (VST/A/5010 N) (°C)	93	96	92
Dielectric rigidity (kV/mm)	135	150	70

matrices or headspace analysis for solid samples, followed by determination of styrene by liquid (HPLC) or gas chromatography (GC–MS). The determination of residual styrene in polystyrene, however, has been quite limited. In this sense, electrochemical methods [32] or headspace gas chromatography have been reported [33].

In the present study, the following extraction methods were used to extract residual styrene monomer in polystyrene used in toys: supercritical fluid extraction (SFE), microwave-assisted extraction (MAE), Soxhlet extraction, headspace emission and dissolution–precipitation. GC–MS was used for the quantitative determination of such compound. Styrene extraction efficiency of the different methods was compared, and the final method obtained was validated.

## 2. Experimental

### 2.1. Chemicals and samples

Analytical grade styrene monomer was obtained from Sigma Chemical Co. (St. Louis, MO, USA). The styrene monomer must be stored at 0–4 °C. Stock solution of styrene (100 µg/g) was prepared in methylene chloride. Methylene chloride (GC grade) and methanol (LC gradient grade) were obtained from Merck (Darmstadt, Germany).

The PS resins used in this study were Styron 485 and Styron 678E supplied in granules (3 mm diameter and length) by Ashland Chemical Hispania (Barcelona, Spain) (Table 1). For the recovery study, PS samples spiked with known quantities of styrene were prepared. In this case, Edistir N1841 (Ashland Chemical Hispania, Barcelona, Spain) (Table 1) was the PS resin selected for the recovery study. This resin

was supplied in granules (3 mm diameter and length) and is certified as food grade. The fortification procedure included the dissolution of 1.5 g of the polystyrene granules in 10 ml of methylene chloride and the addition of a solution containing a known amount of styrene. Three concentration levels of fortification were tested. In this sense, 208, 840 or 1257 µg of styrene in each case (by adding 165, 665 or 995 µl of a 972 ppm (µg/g) styrene solution in dichloromethane); in order to achieve a final concentration of 125, 500 and 750 ppm (mg/kg sample). After the adequate homogenisation, the mixtures were dried in an oven at 50 °C for 1 h to obtain a solid paste.

### 2.2. Sample extraction

The conditions used for each extraction method are summarised in Table 2. Soxhlet and MAE conditions were chosen based on stated references [10] and previous experience in our laboratory. SFE and headspace were optimised based on previous references [1,34] and some additional experimental work. Finally, dissolution–precipitation conditions were modified based on [35].

SFE was performed using an ISCO Model SFX-220 extraction system (Lincoln, NE, USA) consisting of a SFX-220 extractor, a SFX-200 controller and a 100DX-syringe pump. Supercritical grade CO<sub>2</sub> was supplied by Abelló Linde (Valencia, Spain). Samples (0.5 g) were introduced in stainless steel cartridges (internal volume, 2.5 ml). After equilibration (2 min), extraction was performed in dynamic mode (30 min). Collection was carried out by inserting the restrictor into a graduated dark vial, containing 8 ml of methylene chloride. The capillary restrictor was coaxially heated and the temperature was 105 °C.

Table 2  
Conditions used for SFE, MAE, Soxhlet, headspace and dissolution–precipitation

	SFE	MAE	Soxhlet	Headspace	Dissolution–precipitation
Sample size (g)	0.5	0.5	1	1.5	1.5
Extraction solvent	CO <sub>2</sub>	MeOH	MeOH	CH <sub>2</sub> Cl <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub> /MeOH
Collection solvent	CH <sub>2</sub> Cl <sub>2</sub>	–	–	–	–
Temperature (°C)	105	120	b.p. of solvent	60	Ambient
Pressure (MPa)	48.3	0.5	Ambient	0.045	Ambient
Time	30 min	20 min	5 h	30 min	2 h
Solvent volume (ml)	8	15	70	10	15

MAE was performed using a MSP-1000, 950-W, laboratory microwave extraction system (CEM Corporation, NC, USA) equipped with a 12-vessel position carousel. Samples (0.5 g) were put into the PTFE microwave extraction vessels and mixed with 15 ml of methanol. Extraction was performed with the 50% maximum microwave power, with a constant temperature of 120 °C for an extraction time of 20 min, and 3 min were left to reach the selected extraction temperature. After extraction, vessels were allowed to cool to room temperature before opening, and the final extracts were carefully evaporated to dryness with a weak flow of nitrogen stream. The residue was immediately taken up in 5 ml of methylene chloride.

Soxhlet extraction was performed using 1 g samples filled into a cellulose extraction thimble and inserted into a Soxhlet assembly fitted with a 100 ml flask (containing 70 ml of methanol) in a reflux for 5 h. A Neslab RTE-300 model refrigerated circulator (Thermo NESLAB, Newington, USA) was used as the refrigerator system, set at 3 °C. The final extract was concentrated to a few millilitres in a Kuderna-Danish evaporative flask and concentrator. The remainder of the solvent was carefully evaporated to dryness with a weak flow of nitrogen stream. The residue was immediately taken up in 5 ml of methylene chloride.

Headspace emission was performed using a Perkin-Elmer Turbomatrix 16 automatic sampler (Norwalk, CT, USA) equipped with a 16-vials magazine and a single vial oven, which allows thermostating the sample before injection onto the GC–MS via the heated transfer line. Samples (1.5 g) were used and vials were pressurised with helium (for 4 min) which forces a portion of the headspace gas mixture through the heated transfer line onto the GC column. Tests were carried out at three temperatures (50, 60 and 70 °C) and two thermostating times (30 and 60 min).

Finally, dissolution–precipitation of the polymer was carried out with methylene chloride/methanol. Samples (1.5 g) were placed in a sealed glass container and 10 ml of methylene chloride were added for dissolving the polymer. The solution was slightly shaken to achieve complete dissolution. At this stage, it is necessary to wait until sample is totally dissolved. Finally, 5 ml of methanol were added and the solution was vigorously shaken for a few seconds in order to re-precipitate polystyrene. The solution was let to rest until two clear phases were observed: one precipitate and one clear liquid. After separation of the two phases (1–2 h), an aliquot of the solution was transferred to the GC–MS for analysis of styrene.

### 2.3. Analysis

Analysis of extracts were performed by gas chromatography (GC) with mass spectrometry detection, using a Shimadzu GC14A QP-1100 EX MS detector (Kyoto, Japan) equipped with a Shimadzu AOC-20i auto-injector, a SPB-5 capillary column (30 m long  $\times$  0.32 mm i.d. with 0.5  $\mu$ m film thickness) (Supelco, Bellefonte, PA, USA), a split–splitless

injector and a quadrupole mass spectrometer. Helium was used as the carrier gas, with a head pressure of 153 KPa. Temperatures for injector and detector were 300 °C and 250 °C, respectively, and the column temperature was programmed from 35 °C (hold 10 min) to 150 °C at a 7 °C/min heating rate to 220 °C (hold 6 min) at a 20 °C/min heating rate. Samples (2  $\mu$ l) were injected in the splitless mode (1.5 min splitless-period). Quantitation of styrene was performed in SIM (selected ion monitoring) mode focused on 104 (main) and 78 ions, by comparing chromatographic peak areas for sample extracts with those of standards in the same concentration range. Retention time obtained for styrene was 12.5 min (Fig. 2a).

## 3. Results and discussion

Calibration curves for styrene were run at five concentration levels using appropriately diluted standards. For dissolution–precipitation extraction, calibration standards of styrene were prepared in methylene chloride/methanol (2:1). Each concentration level was injected in triplicate, and chromatographic peak areas were fitted by linear regression. The linearity range was 0.4–20  $\mu$ g/g with correlation coefficients higher than 0.999. No sample clean-up was done on the extracts prior to analysis.

### 3.1. Extraction efficiency

The extraction of styrene monomer from polystyrene was studied by using different extraction techniques with the two resins Styron 485 and Styron 678E. The aim of using these “older” resins was to have an enough styrene monomer concentration presented to be extracted with the different extraction methods used, as we did not know the efficiency of the methods in advance. For headspace emission, some tests were carried out in triplicate at different temperatures (50, 60 and 70 °C) and thermostating times (30 and 60 min) with the solid PS sample in the headspace vial. The transfer line and injection needle temperatures were set 10 °C above oven temperature. No styrene detected was obtained in any case. Other tests were performed varying the same conditions but dissolving the polymer in a sealed glass container with 10 ml of methylene chloride. After dissolution of the polymer, a portion (1 or 2 ml) was transferred to the headspace vial. Very irreproducible results were obtained between replicates, with the most efficient conditions being 2 ml of sample, 60 °C (70 °C for transfer line and injection needle temperatures) and 30 min. Obtained results are shown in Table 3. We suppose that as this is an emission method and styrene must be kept in the polystyrene matrix, the diffusion of styrene monomer will not be so reproducible as in an extraction method, such as MAE or SFE.

For supercritical fluid extraction, some experiments were carried out in triplicate at 48.3 MPa and two different extraction temperatures: 50 and 105 °C. Obtained results are

Table 3  
Mean concentrations (mg/kg) of styrene extracted from polystyrene by different methods

Polystyrene	Styrene in sample <sup>a</sup> (%R.S.D.) (mg/kg)				
	SFE	MAE	Soxhlet	Headspace	Dissolution–precipitation
Styron 485	2301 (2)	229 (3)	28 (4)	1757 (7)	4550 (1)
Styron 678E	3451 (2)	182 (2)	27 (5)	453 (10)	6304 (1)

Conditions used for extraction methods as indicated in Table 2.

<sup>a</sup> Based on three replicates.

shown in Fig. 1. As it can be seen, better extraction performance was accomplished at 105 °C. A higher extraction pressure (55.2 MPa) led to worse results, probably due to losses of styrene for styrene volatility at increasing flow rate. As one of the limiting steps in extraction is diffusion to the surface of the polymer, the particle size is extremely important. In this way, extractions were performed at the most efficient conditions found (48.3 MPa and 105 °C) but with grinding the samples. As it can be seen in Fig. 1, grinding the sample greatly improved the extraction efficiency. These results (Table 3) gave better extraction efficiency when compared with the other extraction methods tested: Soxhlet, MAE and headspace.

Finally, dissolution of the polymer followed by re-precipitation of the polymer by addition of methanol was considered, resulting in the most efficient extraction method for styrene in PS granules compared with all the other tested methods mentioned above (Table 3). Dissolution and re-precipitation, therefore, provides an effective method for the extraction of styrene, although it is more time consuming. The advantage of this extraction method is that there is no possibility of some analyte remaining bound in the polymer network, although inclusion of the analyte in the re-precipitated polymer can occur [10].

In terms of selectivity, some differences in the extract characteristics for the extraction methods tested were found. In Fig. 2, GC–MS chromatograms for these techniques are shown for the extraction of Styron 485. As it can be seen, at the conditions used, SFE showed less additional organic components extracted from the PS granules than the rest of techniques; being the most selective one.

### 3.2. Recovery of extraction process

In order to determine the recovery of the dissolution–precipitation extraction process and to validate the method proposed, PS samples spiked with known quantities of styrene were used. As it is impossible to obtain a PS resin totally free of styrene, the best guarantee was using one resin in accordance with food contact materials Directive 90/128/CEE. So, we decided to apply the proposed method to a certified food grade PS resin, such as Edistir N1841 (with a controlled styrene monomer concentration). Three concentration levels of fortification were tested: 125, 500 and 750 ppm (mg/kg sample). Extraction was accomplished for the sample without styrene spiking (being the styrene content obtained used as a blank corresponding to a zero concentration level) and for the samples spiked. In this sense,

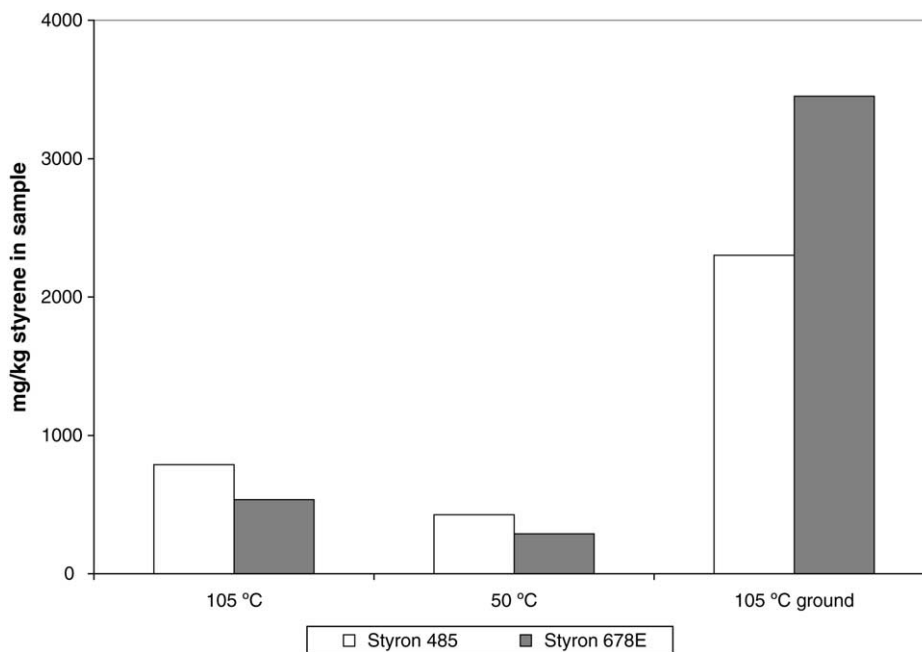


Fig. 1. Results obtained for SFE optimization of styrene from polystyrene (48.3 MPa, 2 min static time, 30 min dynamic time).

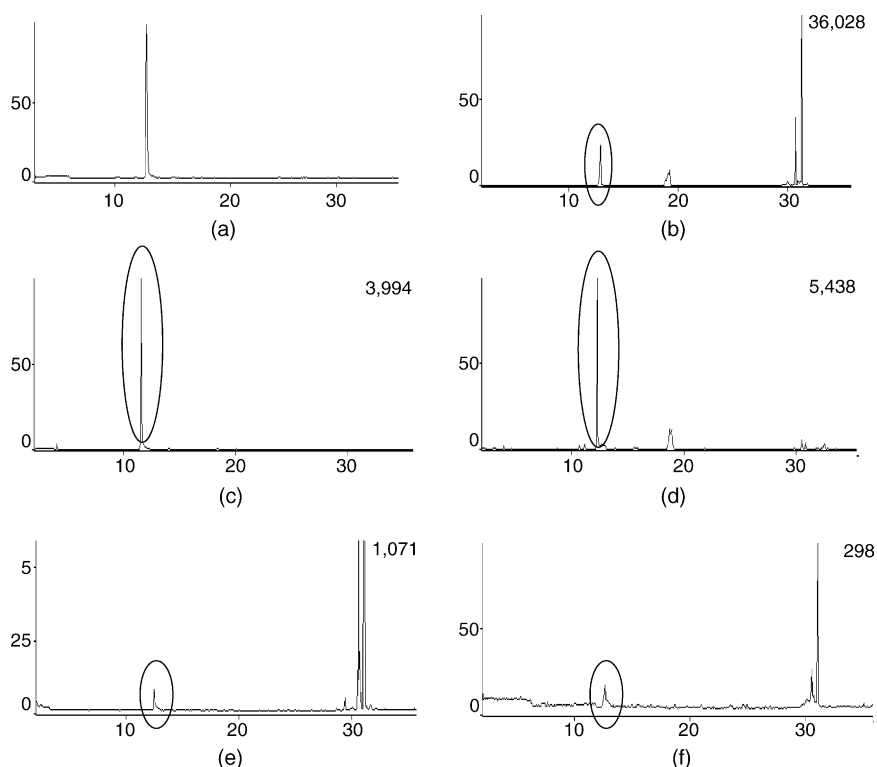


Fig. 2. GC–MS chromatograms of a 20 ppm solution of styrene (a) and dissolution–precipitation (b), SFE (c), headspace (d), Soxhlet (e) and MAE (f) extracts of Styron 485.

Table 4  
Recovery obtained for Edistir N1841 resin spiked at three different concentration levels

Spiked styrene level (ppm)	Mean recovery (%) <sup>a</sup>	R.S.D. (%)
125	98.2	3.2
500	98.9	2.1
750	99.1	3.3

<sup>a</sup> Based on six replicates.

the amount of styrene found in the unspiked sample (blank) was considered as the reference value for the extraction yield calculation. Six replicates from each level were performed. Results are shown in Table 4. The coefficient variation at the different concentration levels varied between 2.1 and 3.3%. The linearity test of the method performed as  $\mu\text{g}$  of styrene spiked versus mean  $\mu\text{g}$  of styrene found in samples after extraction resulted in correlation coefficients varied between 0.9932 and 0.9985. This results in recovery values from 98.2–99.1%, proving the suitability of the proposed method for the determination of styrene in polystyrene granules.

#### 4. Conclusions

An analytical method for the determination of styrene monomer in polystyrene granules has been developed using dissolution–precipitation extraction followed by GC–MS analysis. This extraction method has provided the higher extraction efficiency when compared with other extraction

methods tested as SFE, MAE, Soxhlet and headspace. From all these methods, SFE was found to be the most selective method, with less additional matrix components extracted together with the analyte. The method has been validated using a spiked PS food grade sample at three concentration levels obtaining recovery values from 98.2–99.1%.

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