

Supplementary Information

A novel method to investigate the migration regularity of toxic substances from toys to saliva and sweat

Qing Lv,^{a,b} Zhijuan Wang,^b Qing Zhang,^b Meiling Qi*^a, Hua Bai*^b

^a *Key Laboratory of Cluster Science, Ministry of Education of China, Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials and School of Chemistry, Beijing Institute of Technology, Beijing 100081, China. E-mail: mlqi@bit.edu.cn; Tel.: +86 10 68912668.*

^b *Institute of Industrial and Consumer Product Safety, Chinese Academy of Inspection and Quarantine, Beijing 100176, China. E-mail: baih111@sina.com; Tel.: +86 10 53897466.*

Analytical methods have been conducted mainly to determine styrene in blood ^{S1}, urine ^{S1-S3}, textiles ^{S4}, and foodstuff ^{S5}, but few methods have been applied to determine styrene in plastic products. Extraction approaches, including solid-phase extraction (SPE) ^{S3}, solid-phase microextraction (SPME) ^{S4, S6}, pyrolysis ^{S7}, and other techniques ^{S1, S2, S8}, have been proposed before liquid (HPLC) or gas chromatography (GC-MS) determination is performed. In this study, three extraction methods, namely, dissolution-precipitation, headspace and ultrasound were developed and used to extract styrene from ABS toys; GC-MS was then performed to determine the styrene content of these toys.

Optimization of three extraction methods

The extraction of styrene from ABS toys was investigated by comparing three extraction methods with the same positive toy sample. First, the solubility of ABS toys in various solvents was examined at room temperature. The results showed that the ABS toy (0.4 g) completely dissolved in 10 mL of acetone, DMF,

dichloromethane, or tetrahydrofuran; the same type of sample partially dissolved in 10 mL of ethyl acetate or hexane. By contrast, the ABS toy did not dissolve in 10 mL of methanol.

The specific experimental procedures of dissolution–precipitation and headspace are shown in Fig. S1. In contrast to previous headspace analysis methods, such as solvent extraction/liquid injection, solvent extraction/headspace sampling injection, and direct thermal desorption/headspace sampling injection, the tests were carried out with 0.1 g of sample dissolved in solvent. DMF was selected as the solvent because this substance is characterized by a high boiling point (153 °C) and is able to dissolve ABS (Fig. S1G). The volume of DMF, the extraction temperature and the equilibration time were carefully optimized.

Dissolution–precipitation extraction was modified on the basis of our previous work^{S9}. The improved dosage ratio of the sample and the solvent ensured that styrene can be completely extracted. The specific procedure is shown in Fig. S1. In Figs. S1A to S1D, styrene was extracted in the supernatant; the supernatant was centrifuged and passed through an SPE cartridge for clean-up. SPE was conducted to eliminate matrix co-extractants, such as dyes, in the extract solution. For this purpose, Envi-Carb cartridges, with functional graphitized carbon used as a sorbent, were utilized. Fig. S1F illustrates the capability of SPE to remove dyes. Five solvents, namely, acetone, methanol, hexane, ethyl acetate, and dichloromethane, were evaluated as eluting solvents to achieve optimal recovery because graphitized carbon can also adsorb a portion of styrene. The optimum result was obtained with hexane, which was used in the subsequent experiments.

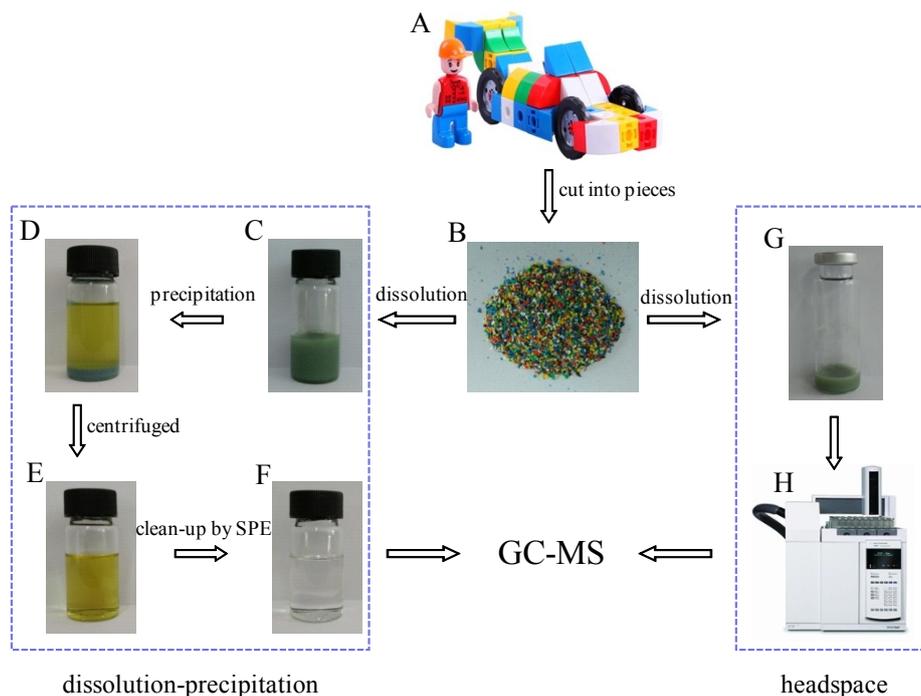


Fig. S1 Dissolution–precipitation extraction and headspace extraction.

Ultrasonic-assisted extraction, which is easily operated and widely reported, was used for comparison. The samples (0.1 g) were ultrasonically extracted with 10 mL of methanol for 20 min because ABS polymer does not dissolve in methanol. Afterward, 3 mL of methanol was used to wash the residue. The combined solution was then treated through SPE and further analyzed through GC–MS in the same way as that of dissolution–precipitation.

Relative extraction efficiency

For headspace analysis, an external standard calibration curve method was adopted for quantitation. The calibration curves of styrene were run at six concentrations by using 2 mL of DMF diluted standards. The linearity range was 0.4–1000 mg/kg with a correlation coefficient of 0.9995. Dissolution–precipitation and ultrasonic extraction were quantified using an external standard method. The calibration curves of styrene were run at six concentrations by using diluted standards with methanol. Each concentration was also injected in triplicate. The linearity range was 10–2000 mg/kg with a correlation coefficient of 0.9999.

After the same ABS toy sample was subjected to extraction via the three methods,

gas chromatograms were obtained (Fig. S2). The three methods showed good selectivity that styrene was baseline separated with other impurities. The quantitative results (Table S1) indicated that dissolution–precipitation achieved the maximum value of 406.3 mg/kg, headspace analysis attained 403.0 mg/kg, and ultrasonic extraction yielded 177.6 mg/kg. Among the three methods, dissolution–precipitation exhibited the highest extraction efficiency. Dissolution–precipitation was simple to operate at room temperature without depending on other instruments. The high limit of quantification (LOQ, 10 mg/kg) did not hinder detection because the styrene content of ABS toys was relatively large (> 200 mg/kg).

Table S1

Comparison of the three extraction methods in terms of extraction conditions and detection results.

	Headspace	Ultrasound	Dissolution–precipitation
Sample size (g)	0.1	0.1	0.1
Solvent volume (mL)	2	25	25
Temperature (°C)	100	RT	RT
Operation Time (min)	30	20+20	5+20
LOQ (mg/kg)	0.4	10	10
Linear range (mg/kg)	0.4–1000	10–2000	10–2000
Results of styrene in a toy sample ^a (mg/kg)	403.0	177.6	406.3

^a Based on three replicates

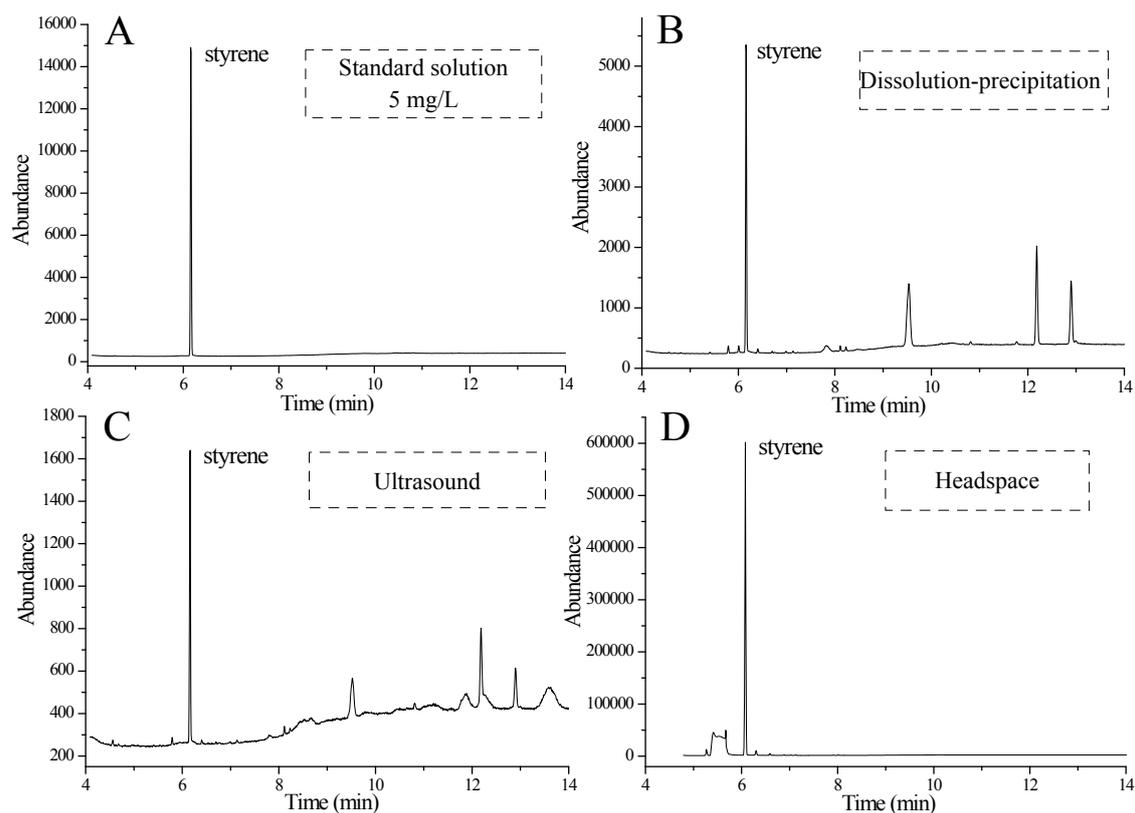


Fig. S2 GC-MS chromatograms (selected ion monitoring mode) of a styrene standard solution and different extracts of an ABS toy.

Absolute extraction efficiency

The relative extraction efficiency indicated that dissolution–precipitation and headspace analysis could extract more styrene contents than ultrasound. To determine the absolute extraction efficiency of dissolution–precipitation extraction and to validate the proposed method, we performed the following tests.

Dissolution–precipitation was conducted to extract a positive sample, and this procedure was repeated several times until styrene was no longer detected. In Fig. S3, the average peak area of styrene was 41,513 after the first extraction; the average peak area of styrene was 683 after the second extraction of residue. Conversely, the average peak area of styrene was not detected after the third and fourth extraction.

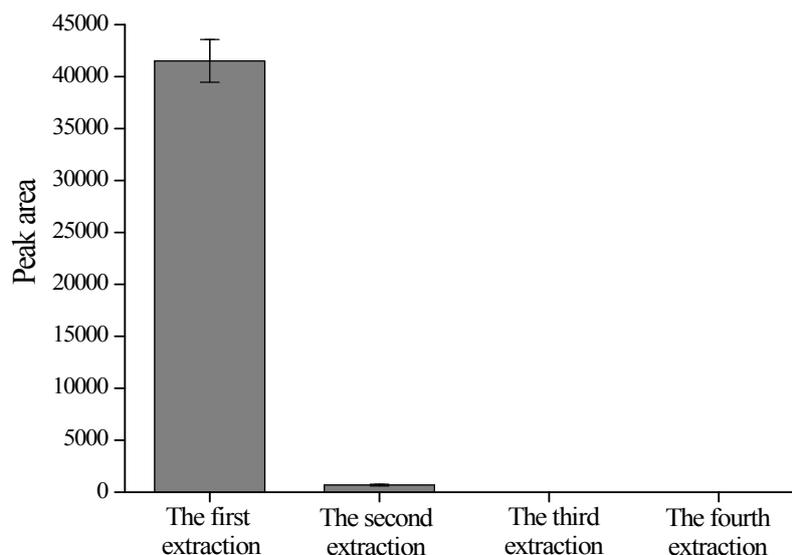


Fig. S3 Styrene peak area obtained through multiple extraction from a toy sample ($n = 4$).

A toy sample containing 406.3 mg/kg of styrene was subjected to recovery studies by applying dissolution–precipitation method. Extraction was performed for a sample without spiked styrene and for a sample with spiked styrene. The amount of styrene found in the unspiked sample was considered as the reference value of the calculated recovery. Two different concentrations of 400 and 800 mg/kg were spiked into the dissolved sample. The results showed that the average recoveries of styrene through dissolution–precipitation analysis ranged from 96.2% to 102.3% ($RSD \leq 6.1\%$, $n=5$). These results confirmed that styrene could be almost completely extracted from ABS toys through the extraction process.

References

- S1 M.J. Prieto, V. Berenguer, D. Marhuenda and A. Cardona, *J. Chromatogr. B*, 2000, 741, 301-306.
- S2 J.F. Periago, C. Prado and A. Luna, *J. Chromatogr. A*, 1996, 719, 53-58.
- S3 C. Prado, P. Marín and P. Simon, *J. Chromatogr. B*, 2006, 830, 18-24.
- S4 H.O. Zhu, Z.G. Lu, J.H. Cai, J.J. Li and L.R. Gao, *Polym. Test.*, 2009, 28, 521-527.
- S5 C. Carrillo-Carrión, R. Lucena, S. Cárdenas and M. Valcárcel, *J. Chromatogr. A*, 2007, 1171, 1-7.
- S6 S. Sungkaew, C. Thammakhet, P. Thavarungkul and P. Kanatharana, *Anal. Chim. Acta.*, 2010, 664, 49-55.
- S7 S.S. Choi and H.M. Kwon, *Polym. Test.*, 2014, 38, 87-90.

- S8 M.D. Geraldo, M.I. Montenegro and D. Pletcher, *Talanta*, 1995, 42, 1725-1729.
- S9 Q. Lv, Q. Zhang, W.T. Li, H.Y. Li, P. Li, Q. Ma, X.S. Meng, M.L. Qi and H. Bai, *J. Sep. Sci.*, 2013, 36, 3534-3549.