



Simultaneous screening of 33 restricted substances in polymer materials using pyrolysis/thermal desorption gas chromatography–mass spectrometry

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Abstract

The purpose of this study was to offer a quick and efficient method to screen for multiple restricted additives in polymer materials. A solvent-free pyrolysis gas chromatography–mass spectrometry method was developed to simultaneously screen 33 restricted substances, comprising 7 phthalates, 15 bromine flame retardants, 4 phosphorus flame retardants, 4 ultraviolet stabilizers, and 3 bisphenols. The pyrolysis technique and temperatures affecting additive desorption were studied. Under optimized conditions, the instrument sensitivity was confirmed using in-house reference materials at concentrations of 100 mg/kg and 300 mg/kg. The linear range was between 100 and 1000 mg/kg in 26 compounds, and in the other compounds it was between 300 and 1000 mg/kg. In this study, in-house reference materials, certified reference materials, and proficiency testing samples were used for method verification. The relative standard deviation of this method was less than 15%, and recoveries ranged from 75.9 to 107.1% for most of the compounds, with a few exceeding 120%. Furthermore, the screening method was verified with 20 plastic products used in daily life and 170 recycled plastic particle samples from imports. The experimental results showed that phthalates were the main additives in plastic products, and among 170 recycled plastic particle samples, 14 samples were found to contain restricted additives. The main additives in recycled plastics were bis(2-ethylhexyl) phthalate, di-iso-nonyl phthalate, hexabromocyclododecane, and 2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether at concentrations between 374 and 34785 mg/kg, except for some results that exceeded the maximum measured value of the instrument. Compared with traditional methods, an important advantage is that this method simultaneously tests for 33 additives without sample pretreatment, covering a variety of additives limited by laws and regulations, and therefore can provide more comprehensive and thorough inspections.

Keywords Polymer materials · Additive · Pyrolysis/thermal desorption gas chromatography–mass spectrometry · Simultaneous screening

Introduction

Plastic polymers are widely used consumer products found in synthetic fibers, foams, and other materials. However, various additives are added to polymers during the production process to improve the physical chemical properties. These additives are usually not decomposable and release

continuously during product usage and recycling process, which causes a significant threat to the environment and human health [1–5]. In fact, certain additives are restricted by regulations as hazardous substances in the complete life-cycle of polymer products; for example, the most typical regulation, EU RoHS, covers heavy metals, phthalates, and bromine flame retardants [6]. Similar regulations include those from Japan (J-Moss) [7], Korea (the Resource Recirculation law) [8], China (RoHS) [9], and the EU (REACH [10] and POPs [11]).

To date, wet chemical techniques have been widely used for the analysis of additives, such as liquid chromatography coupled with mass spectrometry (LC/MS) or gas chromatography (GC/MS) analysis with solvent extraction, but these methods require complicated, costly, time-consuming

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steps [12–16]. In recent years, an increasing number of studies have been showing interest in screening analysis methods, which are simple, quick, and reliable analytical techniques [17–23]. Numerous researchers began to focus on pyrolysis gas chromatography–mass spectrometry methods for analyzing additives from plastic polymers, which is the oldest approach for studying the structure of polymeric systems [24]. However, one problem is that current pyrolysis techniques generally apply to specific families of additives, mainly involving phthalates and bromine flame retardants. For example, many studies have reported methods for analyzing phthalates [25, 26]. The International Electrotechnical Commission (IEC) has published a series of relevant standards, IEC-62321, to analyze phthalates and bromine flame retardants by pyrolysis/thermal desorption GC-MS (Py/TD- GC-MS) [27, 28]. Yangisawa et al. investigated eight relevant representatives as examples, including tris(2-chloroethyl) phosphate [23]. Although IEC62321 standards and the abovementioned studies have analyzed two to four types of additives, existing pyrolysis methods still cannot cover as many compounds as possible that are restricted by regulations. As a screening method and to analyze a large number of samples, it is necessary to increase the screening capacity. Another limitation of this method is the lack of appropriate test samples, such as certified reference material (CRM) or actual samples, were difficult to source for method verification [22, 23]. To date, in-house reference materials (RMs) are the only alternative to CRMs for the empirical assessment of screening methods.

Considering that other additives are also subject to international chemical regulation [6–11], this research is intended to develop a rapid, green, and sensitive method that can screen multiple additives simultaneously in different plastic polymers by Py/TD-GC-MS while also solving the problem of previous studies, in that their methods could not be verified with actual samples. During method development, the effects of the thermal extraction temperature and pyrolysis technique were studied. It should be noted that the scope of this study was widened to screen 33 additives, comprising 7 phthalates, 15 bromine flame retardants, 4 phosphorus flame retardants, 4 ultraviolet (UV) stabilizers, and 3 bisphenols. In-house RMs, a CRM of polybrominated diphenyl ether in acrylonitrile butadiene (ABS), and a proficiency testing sample of phthalate in polyvinyl chloride (PVC) were used for method verification. Furthermore, the screening method was also verified with plastic polymer products (computers, printers and sports equipment used in daily life) and 170 recycled plastic particle samples from imports (including PVC, ABS, polycarbonate [PC], polystyrene [PS], polymethyl methacrylate [PMMA], poly[ethylene terephthalate] [PET], polypropylene [PP], and polyethylene [PE]). Finally, we found that our proposed method was effective in screening additives in different polymers using Py/

TD-GC-MS, and the detection limit fully met the requirements of the regulations.

Experimental

Reagents and materials

Dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), bis(2-ethylhexyl) phthalate (DEHP), di-iso-butyl phthalate (DIBP), di-n-octyl phthalate (DNOP), di-iso-decyl phthalate (DIDP), di-iso-nonyl phthalate (DINP), hexabromocyclododecane (HBCDD), tris(2-chloroethyl) phosphate (TCEP), tris(1-chloro-2-propyl) phosphate (TCPP), tris(1,3-dichloro-2-propyl) phosphate (TDCPP), tri-o-cresyl phosphate (TOCP), tetrabromobisphenol A (TBBPA), bisphenol A (BPA), bisphenol F (BPF), and bisphenol AF (BPAF) were all purchased from Dr. Ehrenstorfer (Augsburg, Germany). 2,4,4'-Tribromodiphenyl ether (PBDE-28), 2,2',4,4'-tetrabromodiphenyl ether (PBDE-47), 2,2',4,4',5-pentabromodiphenyl ether (PBDE-99), 2,2',4,4',6-pentabromodiphenyl ether (PBDE-100), 2,2',4,4',5,5'-hexabromodiphenyl ether (PBDE-153), 2,2',4,4',5,6'-hexabromodiphenyl ether (PBDE-154), 2,2',3,4,4',5',6'-heptabromodiphenyl ether (PBDE-183), 2,2',3,3',4,4',5,6'-octabromodiphenyl ether (PBDE-196), 2,2',3,3',4,4',6,6'-octabromodiphenyl ether (PBDE-197), 2,2',3,4,4',5,5',6-octabromodiphenyl ether (PBDE-203), 2,2',3,3',4,4',5,5',6-nonabromodiphenyl ether (PBDE-206), 2,2',3,3',4,4',5,6,6'-nonabromodiphenyl ether (PBDE-207), and 2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether (PBDE-209) were all purchased from AccuStandard (New Haven, Connecticut, USA). 2-(2H-Benzotriazol-2-yl)-4,6-bis(2-methyl-2-propanyl)phenol (UV-320), 2-(5-chloro-2H-benzotriazol-2-yl)-4,6-bis(2-methyl-2-propanyl)phenol (UV-327), 2-(2H-benzotriazol-2-yl)-4,6-bis(2-methyl-2-butanyl)phenol (UV-328), and 2-(2H-benzotriazol-2-yl)-6-s-butyl-4-(2-methyl-2-propanyl)phenol (UV-350) were purchased from the Shanghai Macklin Company (Shanghai, China), and the purities of all standards were greater than 98%.

Blank polymer materials (no target compounds were included) were purchased on the market (raw materials from a plastic factory), including PVC, ABS, PET, PC, PS, PMMA, PP, and PE particles with a diameter of about 0.5 cm. Methanol, tetrahydrofuran, acetone, dichloromethane, xylene, phenol, and tetrachloroethane were of high-performance liquid chromatography grade and were purchased from CNW Technologies GmbH (Shanghai, China).

Preparation of stock solutions and in-house reference materials

Individual stock solutions were prepared at 1000 mg/L in methanol. A composite mixture of the 33 additives (mixed

standard solution) was prepared at 15 mg/L (PBDE-206, PBDE-207, PBDE-209, HBCDD, TBBPA, DINP, and DIDP) and 5 mg/L (remaining additive compounds) in methanol based on the different sensitivities of compounds. All of the standard solutions were stored in a freezer at $-18\text{ }^{\circ}\text{C}$ for 3 months.

In-house RMs were prepared according to the following procedure [23]. Plastic particles were dissolved using a suitable solvent to prepare the polymer solutions at a concentration of 50 mg/mL (organic solvents suitable for dissolving polymers are listed in Supplementary Material Table S1). Next, 10 μL of the polymer solution (50 mg/mL) and 10 μL of the mixed standard solution (the above-mentioned) were injected into a sample cup (Eco-Cup LF, Frontier Lab) using a microliter syringe. The mixed solutions were then dried at room temperature in the sample cup to produce in-house RMs (300 mg/kg (PBDE-206, PBDE-207, PBDE-209, HBCDD, TBBPA, DINP, and DIDP) and 100 mg/kg (remaining additive compounds)) for Py/TD-GC-MS analysis. Similarly, reference polymer materials (5000 mg/kg) were prepared referring to the same method.

Collection of polymer samples

Twenty plastic products used in daily life and 170 recycled plastic particle samples from import were collected for analysis. Of the plastic products, 18 samples were mainly from computers, printers, and sports equipment used in daily life, and the other two samples were positive as analyzed by the standard methods. Recycled plastic particles were imported from different countries, including industrial and consumer sources, such as electrical and electronic equipment waste, and plastic products and production waste materials containing PVC, PC, ABS, PS, PMMA, PET, PP, and PE polymers.

Sample preparation

Samples were cut into small pieces or powders using a cutter or freeze grinder. Samples weighing approximately 0.5 mg were placed in sample cups, and then were introduced into the furnace by an Auto-Shot sampler. At least three parallel measurements were made for each sample.

Evolved gas analysis–mass spectrometry (EGA-MS) measurements

EGA-MS is one of four pyrolysis techniques, and can provide complementary information on the thermal features of compounds. The specific gases from thermal

pyrolysis were detected to obtain thermal degradation profiles. Pyrolysis temperature ranges of compounds were identified through specific ions based on the EGA profiles.

For EGA-MS measurements, samples were analyzed by a microfurnace pyrolyzer (EGA/PY-3030D, Frontier Lab) coupled with a GC-MS (5890N/5975C, Agilent) through a deactivated metal capillary tube (Frontier, UADTM 2.5 m \times 0.15 mm i.d.). The microfurnace temperature program was increased from 100 $^{\circ}\text{C}$ to 700 $^{\circ}\text{C}$ at 20 $^{\circ}\text{C}/\text{min}$ under a helium flow at 20 mL/min, and the gas chromatograph oven was kept at 300 $^{\circ}\text{C}$. Ionization in the MS was conducted by electron impact (EI) at 70 eV, with a mass range of 50–960 amu. The inlet temperature was 300 $^{\circ}\text{C}$. The MS transfer line temperature was 280 $^{\circ}\text{C}$. The MS ion source temperature was held at 230 $^{\circ}\text{C}$, and the MS quadrupole temperature was 150 $^{\circ}\text{C}$.

Py/TD-GC-MS measurements

Flash pyrolysis is mainly used to analyze different plastic additives with high pyrolysis temperatures, but its use is limited because polymer pyrolysis occurs along with additive pyrolysis. Temperature-programmed pyrolysis analysis can realize thermal desorption of additives at low temperatures, avoiding the breakdown of polymers [29]. According to the IEC 62321-8 [27] standard, this experimental study employed temperature-programmed pyrolysis. The furnace temperature was increased from 200 $^{\circ}\text{C}$ to 300 $^{\circ}\text{C}$ at 20 $^{\circ}\text{C}/\text{min}$ and maintained at 300 $^{\circ}\text{C}$ for 5 min, and then increased at 5 $^{\circ}\text{C}/\text{min}$ to 340 $^{\circ}\text{C}$ and maintained at 340 $^{\circ}\text{C}$ for 1 min, and the interface temperature was set to 300 $^{\circ}\text{C}$. Gaseous components from thermal desorption were transferred to the GC-MS for analysis.

Studies have shown that unstable HBCDD and PBDEs were likely to occur during thermal decomposition under high temperatures. Based on the experimental results, a DB-5 column (15 m \times 0.25 mm \times 0.1 μm) was selected to analyze 33 additives to shorten the residence time in the chromatographic column. The column temperature was initially held at 70 $^{\circ}\text{C}$ for 2 min, then increased at 20 $^{\circ}\text{C}/\text{min}$ to 210 $^{\circ}\text{C}$, held at 210 $^{\circ}\text{C}$ for 1 min, then increased at 10 $^{\circ}\text{C}/\text{min}$ to 270 $^{\circ}\text{C}$, then further increased at 30 $^{\circ}\text{C}/\text{min}$ to 310 $^{\circ}\text{C}$, and finally held at 310 $^{\circ}\text{C}$ for 5 min. The injection mode was set to split with a ratio of 1/5, and helium was used as a carrier gas at 1.0 mL/min. The MS conditions were as follows: the ion source temperature was 230 $^{\circ}\text{C}$; the transfer line temperature was 300 $^{\circ}\text{C}$; and EI was employed at 70 eV. MS signals were analyzed by focusing on specific target ions in the selected ion monitoring mode. The retention times and quantitation and confirmation ions are shown in Table 1.

Table 1 Quantitation, confirmation ions, and retention time used for simultaneously screening 33 additives analyzed by the Py/TD-GC-MS study

No	Compound name	CAS no	Retention time (min)	Quantitation ion (m/z)	Confirmation ion (m/z)
1	TCEP	84-74-2	6.981	249	251, 205, 143
2	TCPP	85-68-7	7.151	277	125, 157, 201
3	DIBP	117-81-7	7.537	149	167, 223, 205
4	DBP	84-69-5	8.025	149	150, 205, 223
5	BPAF	117-84-0	8.446	336	267, 197, 317
6	BPF	26761-40-0	8.609	200	107, 183, 199
7	BPA	68515-48-0	9.038	228	213, 119, 281
8	PBDE-28	41318-75-6	9.407	248	246, 406, 408
9	TDCPP	5436-43-1	9.809	381	191, 209, 321
10	BBP	60348-60-9	9.979	149	91, 206, 238
11	UV320	189084-64-8	10.844	308	323, 309, 252
12	UV350	68631-49-2	11.005	294	308, 323, 309
13	PBDE-47	207122-15-4	11.054	326	484, 486, 324
14	DEHP	207122-16-5	11.373	149	167, 279, 113
15	TOCP	117964-21-3	11.546	368	165, 277, 179
16	UV328	337513-72-1	12.059	322	323, 351, 336
17	UV 327	446255-39-6	12.114	342	344, 357, 322
18	PBDE-100	63387-28-0	12.372	406	404, 566, 564
19	HBCDD	437701-79-6	12.661	239	157, 319, 400
20	DNOP	1163-19-5	12.749	279	167, 261, 149
21	PBDE-99	3194-55-6	12.844	406	404, 566, 564
22	DINP	79-94-7	13.046	293	149, 127, 167
23	PBDE-154	115-96-8	13.943	484	482, 644, 646
24	TBBPA	13674-84-5	14.551	529	944, 527, 448
25	PBDE-153	13674-87-8	14.551	484	482, 644, 646
26	DIDP	78-30-8	14.028	307	149, 141, 167
27	PBDE-183	3846-71-7	16.168	562	564, 722, 724
28	PBDE-197	3864-99-1	17.361	642	640, 801, 533
29	PBDE-203	25973-55-1	17.514	642	640, 801, 533
30	PBDE-196	36437-37-3	17.582	642	640, 801, 533
31	PBDE-207	80-05-7	18.768	721	719, 879, 360
32	PBDE-206	620-92-8	19.132	721	719, 879, 360
33	PBDE-209	1478-61-1	21.192	799	719, 879, 959

Results and discussion

Method optimization

Thermal extraction temperature

Two types of samples were analyzed by the EGA-MS method: in-house RMs of different polymers (5000 mg/kg) and the positive polymer samples (sample no. 3, 4, 5, 8, and 11 in Table 5). Quantitation ions were extracted from the EGA profiles in the six in-house reference samples PVC, ABS, PS, PC, PMMA, and PET (Fig. 1). Ions with an m/z of 149 corresponded to DEHP (Fig. 1a), m/z of 239 corresponded to HBCDD, and m/z of 529 corresponded to

TBBPA (Fig. 1b). Fragment ions of other additives were extracted according to Table 1 and the detailed results are shown in the supplementary material (Figure S1). Comparing the extracted ion thermograms, thermal desorption zones of phthalates, phosphorus flame retardants, UV stabilizers, bisphenols, HBCDD, and TBBPA were the same from different polymers in the temperature range of 100–350 °C, and additives were completely released before 350 °C.

Positive polymer samples of PVC containing DEHP, and PS containing PBDE-209 produced similar results. The result for phthalate showed a thermal degradation peak in the range of 100–350 °C in PVC, which did not change significantly compared with the RMs shown in Fig. 2a.

Fig. 1 The EGA-MS profile for six polymer samples (PVC, ABS, PS, PC, PMMA, and PET) containing additives at a concentration of 5000 mg/kg: **a** SIM thermogram of phthalates at $m/z = 149$, and **b** SIM thermogram of bromine flame retardants at $m/z = 239$ and 529

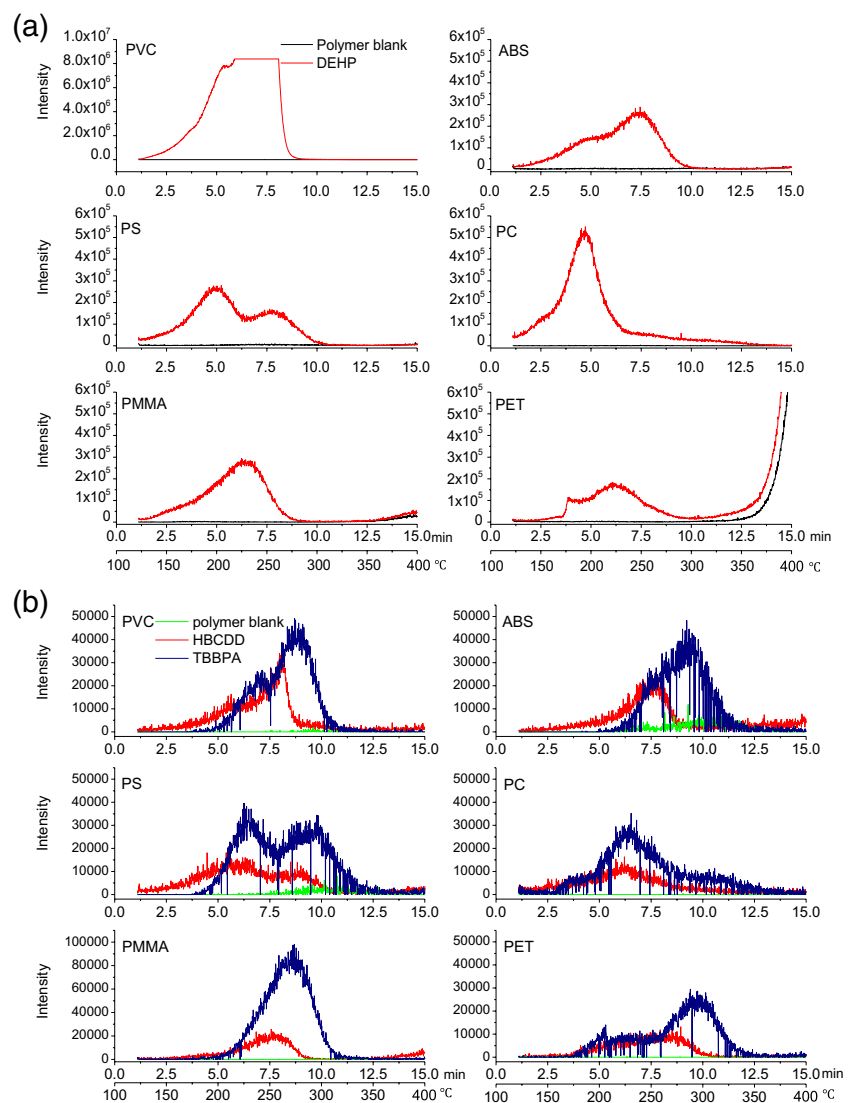


Figure 2b shows the decomposition zone of PBDE-209 from 300 $^{\circ}\text{C}$ to 500 $^{\circ}\text{C}$ with a peak at 370 $^{\circ}\text{C}$ in the PS sample. Previous studies confirmed that flame retardants were stable at temperatures between 300 $^{\circ}\text{C}$ and 370 $^{\circ}\text{C}$, but decomposed at temperature above 380 $^{\circ}\text{C}$ [29]. This was the reason that the response value of PBDE-209 began to reduce at temperatures above 370 $^{\circ}\text{C}$. At 370 $^{\circ}\text{C}$, the simultaneous pyrolysis of PS along with the desorption of PBDE-209 can cause contamination of the column and interference, and PBDE-209 may be overshadowed by the multiple peaks of the polymer fragments. IEC 62321-3-3 suggested that PBDEs and phthalates could be screened simultaneously when the pyrolysis heating temperature was set at 340 $^{\circ}\text{C}$ for PP, PS, and PVC plastics using a Py-GC-MS [28]. Yanagisawa et al. tested pyrolysis heating temperatures of up to 340 $^{\circ}\text{C}$ with respect to all of these analytes (TCEP, DIBP, DBP, BBP, DEHP, TBBPA, PBDE-209, and short-chain chlorinated paraffins) and found that

temperatures up to 340 $^{\circ}\text{C}$ were suitable for ensuring a sufficient MS peak area of PBDE-209 without having any adverse impacts on other analytes [22]. The 300–350 $^{\circ}\text{C}$ temperature range seemed to be the most relevant range in the various studies [29]. Depending on the studies and the EGA-MS experimental results, to minimize the negative effects such as a low pyrolysis temperature and interference effects from matrix decomposition, we set the optimum end temperature to 340 $^{\circ}\text{C}$ for the 33 additives in this method.

Pyrolysis techniques

The response of multiple additives was investigated in flash pyrolysis and temperature-programmed pyrolysis methods, and the results are shown in Figs. 3 and 4. The response values of phthalates, phosphorus flame retardants, UV stabilizers, and bisphenols did not show significant differences between the two techniques (Fig. 3).

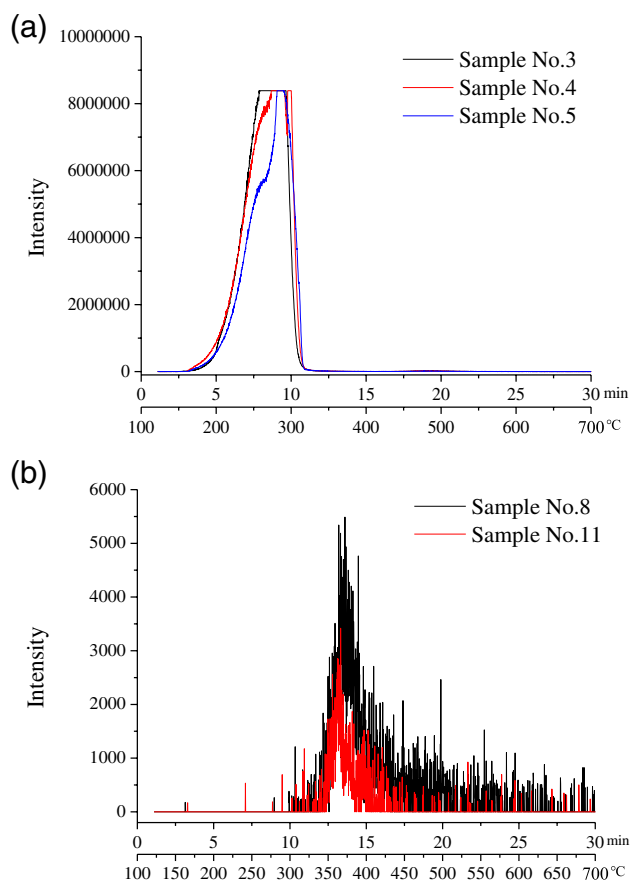


Fig. 2 EGA-MS profile for actual polymer samples (PVC and PS): **a** SIM thermogram of phthalates at $m/z = 149$ in PVC; **b** SIM thermogram of bromine flame retardants at $m/z = 799$ in PS

The temperature-programmed pyrolysis not only ensured the response of most additives but also greatly improved the response value of the low-response PBDE-209 in a

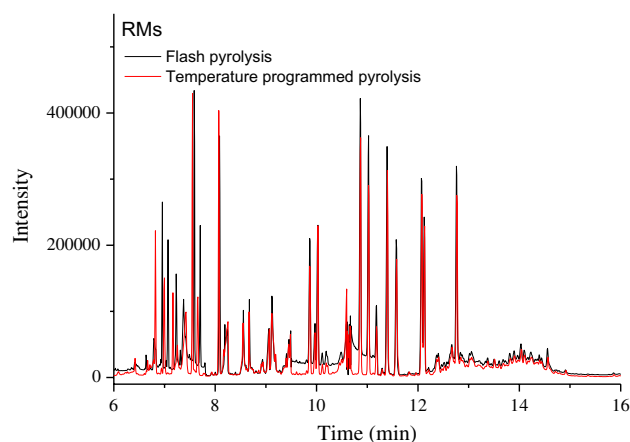


Fig. 3 Total ion chromatogram of phthalates, phosphorus flame retardants, UV stabilizers, and bisphenols at a concentration of 1000 mg/kg using the flash pyrolysis and temperature-programmed pyrolysis methods

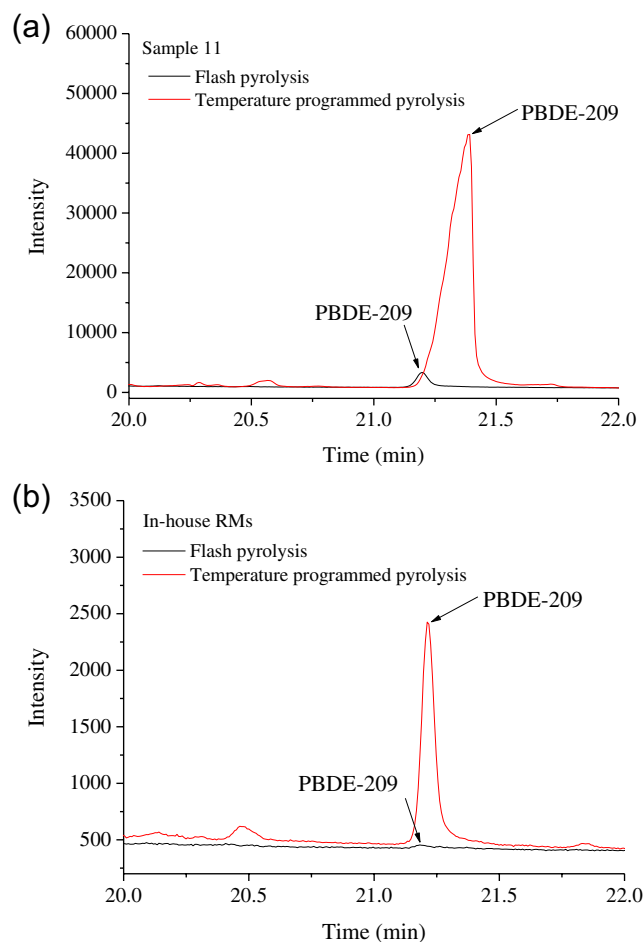


Fig. 4 Total ion chromatogram of PBDE-209 from an actual polymer sample **a** sample no. 11 and **b** in-house RMs using the flash pyrolysis and temperature programmed pyrolysis methods

positive sample and in-house RM sample (Fig. 4). The low response of PBDE-209 was due to its slight volatility and high molecular weight; it may be that the low concentration in the polymer affected its detection. In flash pyrolysis, PBDE-209 showed a low concentration peak, and when the temperature was slowly increased in temperature-programmed pyrolysis, the enrichment of the component resulted in an increase in the response value of PBDE-209. To ensure the maximum sensitivity for low-response PBDE-209, whether due to the influence of chemical properties or concentration, temperature-programmed pyrolysis was chosen as the pyrolysis method of the 33 additives. The furnace temperature was increased from 200 °C to 300 °C at 20 °C/min and maintained at 300 °C for 5 min, after which it was slowly increased from 300 °C to 340 °C at a rate of 5 °C/min, and held for 1 min at 340 °C.

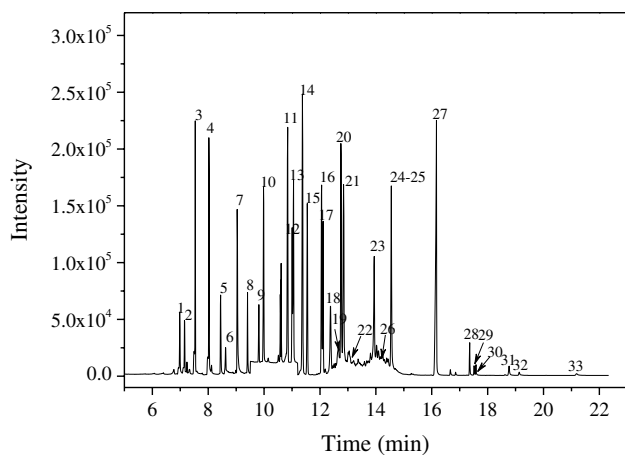


Fig. 5 Total ion chromatogram of a standard solution containing 33 additives at a concentration of 1000 mg/kg (the numbers of the compounds are the same as in Table 1)

GC-MS condition

A standard solution containing 33 additives was prepared to set up a suitable GC-MS method. Then, 5.0 μL of the standard solution at the concentration of 100 $\mu\text{g}/\text{mL}$ was injected into a sample cup for the Py/TD-GC-MS analysis. All additives were successfully registered in the compound table of the GC-MS control system for quantification. For reference, Fig. 5 shows a typical total ion chromatogram of a standard solution containing 33 additives at a concentration of 1000 mg/kg.

Sensitivity and calibration curves

The instrument sensitivity was confirmed using signal-to-noise (S/N) ratio of each compound in the in-house RMs of eight polymers, including ABS, PC, PET, PMMA, PS,

PVC, PP, and PE. The concentration of PBDE-206, PBDE-207, PBDE-209, HBCDD, TBBPA, DINP, and DIDP in the samples was 300 mg/kg, and the concentration of other additives was 100 mg/kg. The S/N ratios of the quantitative ions of the additives in the eight polymers were all greater than three (Table S2). Whether referring to the most typical RoHS Directive 2.0 or China RoHS, EU REACH, EU POPs, or other regulations, most countries set maximum regulatory levels for additives at 0.1% (Table 2) [6–11]. This proposed screening method was designed to meet the requirements of major chemical regulations.

Calibration curves were created by testing the standard solution of 33 additives diluted at different levels, with six compounds at concentrations between 300 and 1000 mg/kg, and others at concentrations between 100 and 1000 mg/kg. The data show that good coefficients of correlation (R^2 values) of more than 0.990 were obtained. More data are shown in Table S3 in the supplemental material.

Verification of screening method

Various studies only focus on in-house RMs and no other appropriate test samples for method verification [22, 23]. In this study, a CRM (CNAS T038, National Institute of Metrology, China, PBDE in ABS, with both low concentration and high concentration samples) and a proficiency testing sample (CNCA-19-B10, Certification and Accreditation Administration of the People's Republic of China, phthalate in PVC) were analyzed to evaluate the developed method. Analyte concentrations of the two samples were quantified to evaluate the method's repeatability and recovery rates ($n=6$). As can be seen in Table 3, a relative standard deviation (RSD) ranging from 3.4 to 14.2% and acceptable recoveries ranging from 87.1 to 123.3% were obtained for all PBDEs. The RSD was less than 10% for most additives, and very few exceeded 10%. A relatively

Table 2 Major regulations and limitations of 33 additives

Compounds	Regulations/Directives	Additives	Limit
Phthalates	RoHS 2.0	DEHP, BBP, DBP, DIBP	0.1%
	Consumer Goods Safety Improvement Act (CPSI)	DEHP, DBP, BBP, DINP, DIDP, DNOP	0.1%
	REACH Annex XVII	DEHP, DBP, BBP, DIBP, DINP, DIDP, DNOP	0.1%
Bromine fluorides	RoHS	PBBs, PBDEs	0.1%
	REACH Annex XVII	PBDE-209	0.1%
	JIS C 0950 [30]	PBBs, PBDEs	0.1%
	REACH SVHC	HBCDD	0.1%
	Prohibition on Certain Hazardous Substances in Consumer Products (PoHS)	HBCDD Tetrabromobisphenol A	0.1% 1%
Phosphorus flame retardant	REACH SVHC	TCEP	0.1%
Bisphenols	REACH SVHC	Bisphenol A	0.1%
UV stabilizers	REACH SVHC	UV320, UV327, UV328, UV350	0.1%

Table 3 Average concentration, repeatability, and recovery rates from the quantitative analysis of PBDE in the CRM (PBDE in ABS) using the Py/TD-GC-MS method ($n=6$)

NO	Compounds	Low concentration (mg/kg)		RSD (%)	Recovery (%)	High concentration (mg/kg)		RSD (%)	Recovery (%)
		Average	Reference			Average	Reference		
1	PBDE-47	87.7	92.1	3.6	94.8	364.0	389	4.5	93.6
2	PBDE-99	83.2	95.5	4.1	87.1	347.2	385	4.5	90.2
3	PBDE-100	22.5	25.8	3.4	87.2	89.3	100	4.7	89.3
4	PBDE-183	/	/	/	/	302.5	368	8.9	82.2
5	PBDE-197	45.7	42.7	13.1	107.1	204.7	166	3.9	123.3
6	PBDE-209	/	/	/	/	858.3	974	14.2	88.1

unstable recovery or insufficient repeatability may be attributed to the specific combination of base polymers and additive, such as with PBDE-197 and PBDE-209 in ABS. The RSD value for phthalates was between 8.2% and 12.1%, and with recovery rates between 75.9% and 125% (Table 4), phthalates in PVC showed relatively stable recovery rates and repeatability. As a preventive measure, for the 0.1% regulatory standard, a 50% preset margin was used to screen these additives according to the IEC62321 standards and previous studies [22, 23]. Therefore, the recovery rate of the method was acceptable at 50–150% when values below 500 mg/kg and above 1500 mg/kg were considered below the limit and above the limit, respectively. If the concentration level of the additive is within the range of 500–1500 mg/kg, it is necessary to analyze it using accurate quantitative methods, such as traditional GC-MS or LC-MS. ASTM D7823 introduced the quantitative methods of DBP, BBP, DEHP, DNOP, DIDP, and DIDP in PVC, and the influence of sampling methods on analytical precision was compared. A plastic toy sample was used for precision analysis, including the film method, in which a polymer was dissolved with an organic solvent and part of the solution was used for analysis, and the direct method, in which randomly selected particles of the sample were used for analysis [31]. The repeatability (DEHP, RSD = 1.15% [$n=4$]) of the film method was better than the direct method (DEHP, RSD = 4.79% [$n=4$]). However, the thin film method was not suitable for some polymers, such as PP and PE, because they are minimally soluble in

some solvents. In this experiment, the direct method was adopted to analyze phthalates and PBDEs, which showed acceptable repeatability (< 15%) and recoveries (> 75%). These results indicated that major additives present in polymer materials were simultaneously determined by Py/TD-GC-MS, which is a rapid, environmentally sound, and sensitive method, and can be used on a variety of liquid and solid samples.

Comparison with other methods

Twenty plastic products and 170 recycled plastic particle samples were detected using wet chemical methods with reference to international and national standards or using study methods. Phthalates were detected using the GC-MS method according to IEC 62321-8, 2017 [27], bromine flame retardants were analyzed using the GC-MS method according to IEC 62321-6, 2015 [12], and HBCDD was analyzed using the LC-MS method according to GB/T 38415-2019 [16]. The results are shown in Table 5.

Considering that additives may react with polymers or other additives, the developed method needed to be verified with actual samples before its implementation. Twenty plastic products used in daily life and 170 recycled plastic particle samples were analyzed by the developed methods. In the plastic products, DBP and DEHP were detected in a plastic-dipped dumbbell and DEHP was founded in a PVC plastic coating of steel wire. The experimental results were consistent with wet chemical methods in 170 recycled

Table 4 Average concentration, repeatability, and recovery rates of the quantitative analysis of phthalate in proficiency testing samples (phthalate in PVC) using the Py/TD-GC-MS method ($n=6$)

NO	Compounds	Low concentration (mg/kg)		RSD (%)	Recovery (%)	High concentration (mg/kg)		RSD (%)	Recovery (%)
		Average	Reference			Average	Reference		
1	DBP	887.8	712	10.4	124.7	1812.2	1450	12.1	125.0
2	BBP	888.0	860	11.1	103.3	2002.6	2058	8.4	97.3
3	DEHP	575.5	671	9.0	85.8	1298.6	1711	8.2	75.9

Table 5 Comparison of the test results of 170 recycled plastic and original plastic samples by the wet chemical GC-MS/LC-MS and Py-TD-GC-MS methods, ($n = 3$)

Samples	Polymers	Compounds	Concentration (mg/kg) (GC-MS/LC-MS)	Concentration (mg/kg) (this method)	Compounds	Concentration (mg/kg) (GC-MS/LC-MS)	Concentration (mg/kg) (this method)
1	PP	DEHP	151	404	/	/	/
2	PE	DEHP	242	374	/	/	/
3	PVC	DEHP	68700	> 5000	DINP	101400	> 5000
4	PVC	DEHP	44600	> 5000	DINP	87600	> 5000
5	PVC	DEHP	269400	> 5000	/	/	/
6	PVC	DEHP	88600	> 5000	DINP	856	635
7	PVC	DEHP	4870	4948	DINP	5152	3204
		DNOP	1187	1567	/	/	/
8	PS	PBDE-209	21891	18782	/	/	/
9	PS	PBDE-209	28788	34785	/	/	/
10	PS	PBDE-209	4026	4198	/	/	/
11	PS	PBDE-209	14000	11496	/	/	/
12	ABS	HBCDD	716	642	/	/	/
13	PS	HBCDD	422	439	/	/	/
14	PS	HBCDD	428	619	/	/	/
15*	PVC	DEHP	598	378	DBP	770	783
16*	PVC	DEHP	307000	> 5000	/	/	/

“*”: A representative samples of original polymer products;

“15* - plastic-dipped dumbbell”; “16* - steel wire with plastic coating”

“> 5000”: Signal value saturation

plastic particle samples (Table 5), and 14 samples were found to contain restricted additives. The polymers containing restricted additives in the samples were mainly PVC and PS, and some samples were PP, PE, and ABS. The restricted additives were mainly phthalates and flame retardants: DEHP, DINP, DIDP, HBCDD, and PBDE-209. The large numbers of positive samples in recycled plastics may be because various additives were not restricted in polymer materials more than 10 years ago. These additives did not decompose or transfer for a long time, and were present with the regeneration of the plastics. Positive samples in this study solved the issue that previous studies had with not being able to collect sufficient data on actual samples.

The results of two methods the developed method and the wet chemical method were analyzed in detail. Except for the samples for which results were expressed as “> 5000” in Table 5, the relative deviations of most sample results were less than 30%, with only a few exceptions. The most likely reason for the large deviation was the homogeneity of samples, including in the production and sampling processes. The simple mixed production process from recycled plastic resulted in high variability of the additive concentration. The standard methods required a relatively large amount of each sample (minimum 100 mg) and complete dissolution with a suitable solvent, which ensured the homogeneity of samples to an extent. However, the random sampling of particles

and a small amount of samples (about 0.5 mg) in the developed method likely caused deviations and inhomogeneity, especially for quantification purposes. Overall, the detection results of the two methods were consistent. This indicated that the developed method is also an appropriate analytical method, especially when the sample quantity and detection time are limited, such as when testing a large number of small parts of mobile phones or computers, and rapid detection is required.

The applicability of a method will generally be evaluated according to its complexity and its energy and time consumption. The developed method did not require sample pretreatment procedures compared with traditional methods (method 3, 4, and 5), and the analysis time only included instrument analysis time, which was shortened to less than 1 h. Even if three parallel analyses were implemented, it would require much less time than the traditional method, and would not need to consume manual labor. From the perspective of environmental protection and human hazards, consumption of organic solvents was also an important factor in the method evaluation. In methods 3, 4, and 5, one sample consumed between 80 and 170 mL of organic solvent. If a large number of samples needed to be detected in the future, the solvent consumption would be a serious security problem. However, the developed method barely consumed any organic solvent, and the energy consumption

was drastically reduced. In addition, methods 2 and 6 did not require organic solvents and had similar time efficiency. Yangisawa et al., investigated eight relevant representatives as examples using the traditional method, covering phthalates and bromine flame retardants [23], while only polybrominated biphenyls, polybrominated diphenyl ethers and phthalates were studied in IEC62321-3-3 [28]. However, a more important advantage of the newly developed method is that the number of additives covered is increased to 33, including a variety of additives limited by laws and regulations to ensure more comprehensive inspections. A detailed comparison between IEC 62321 and other studies in the literature is shown in Fig. 6.

Conclusion

A Py/TD-GC-MS method for analyzing multiple harmful additives in polymers was established. It was found that a pyrolysis temperature of 340 °C and a temperature-programmed mode were suitable pyrolysis parameters for the simultaneous screening of 33 additives in different polymers. The instrument sensitivity was confirmed using the S/N ratio

each component in the in-house RMs of eight polymers at concentrations of 100 mg/kg and 300 mg/kg. Furthermore, the S/N ratios of the quantitative ions of the additives in the eight polymers were all greater than three. With regard to repeatability and recovery rates, RSDs of less than 15% were confirmed by in-house RMs, CRMs, and proficiency testing samples. The analysis of actual samples from recycled plastics and original plastics showed that DEHP, DIDP, DINP, HBCDD, and PBDE-209 were the main additives in PVC and PS polymers. In conclusion, the Py/TD-GC-MS method was shown to be suitable for screening multiple additives simultaneously, ensuring that harmful additives are not omitted to a large extent. Unlike traditional methods, the developed method did not require sample pretreatment procedures and required minimal organic reagents. The analysis time only included instrument analysis time, which was shortened to less than 1 h. Overall, the developed method is simple and environmentally friendly.

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Declarations

Competing interests The authors declare no competing interests.

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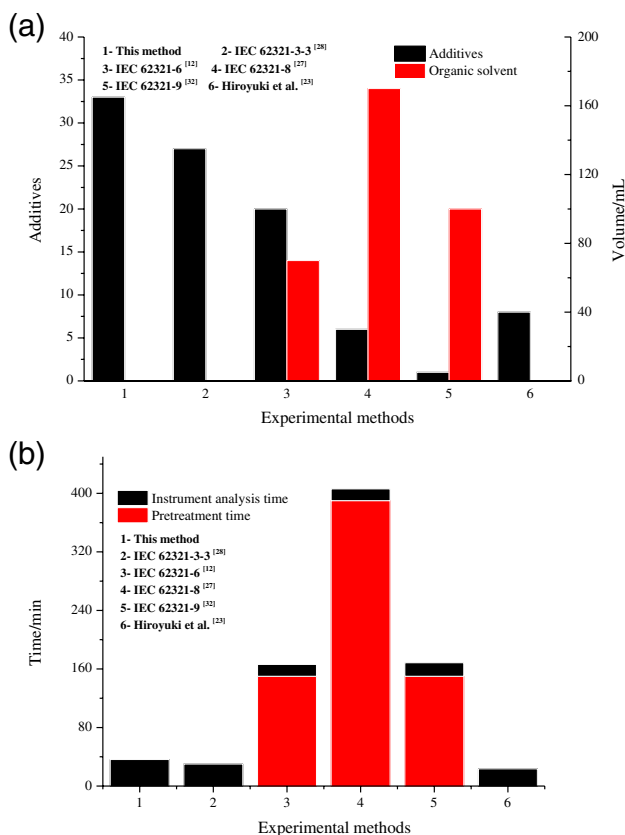


Fig. 6 Comparison of IEC 62321, the developed method, and other studies: **a** additives and organic solvent consumption; and **b** sample analysis time

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