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Polymer-coated sample cup for quantitative analysis of semi-volatile phthalates in polymeric materials by thermal desorption-gas chromatography-mass spectrometry

Akihiko Hosaka\textsuperscript{a}, Atsushi Watanabe\textsuperscript{a}, Chuichi Watanabe\textsuperscript{a}, Norio Teramae\textsuperscript{a,b}, Hajime Ohtani\textsuperscript{c}

\textsuperscript{a} Frontier Laboratories Ltd. 1-8-14, Saikon, Koriyama, Fukushima 963-8862, Japan
\textsuperscript{b} Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan
\textsuperscript{c} Department of Materials Sciences and Engineering, Graduate School of Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan

Abstract

A new "polymer-coated" sample cup useful for the analysis of phthalates in polymeric materials by thermal desorption (TD)-GC/MS using a temperature programmable furnace type pyrolyzer as a TD device was developed to suppress the emission of semi-volatile phthalates such as dimethyl phthalate (DMP) and diethyl phthalate (DEP) during the measurements. The inner surface of a sample cup was coated by polymers which act as a sorbent for the phthalates. Three polymers, polyvinyl chloride, polystyrene and poly (methyl methacrylate), were chosen as the coating polymers. A mixture of ten phthalates including DMP and DEP was used as the test sample to estimate the performance of the sample cups. When a conventional sample cup without any polymer coating was used, 90 and 50% reductions in the peak areas of DMP and DEP were respectively observed at the waiting time of 200 min. On the contrary, no reduction of peak area of DMP and DEP during the same
waiting time was observed with any one of the three coating polymers at the proper polymer film thickness. These results suggest that the polymer-coated sample cup suppresses the emission of semi-volatile phthalates and is effective for the analysis of phthalates containing DMP and DEP by TD-GC/MS.

Keywords

dimethyl phthalate, diethyl phthalate, thermal desorption-GC/MS, pyrolyzer, polymer-coated sample cup

Corresponding author: Akihiko Hosaka

TEL: +81-24-935-5100
FAX: +81-24-935-5102
E-mail: hosaka@frontier-lab.com

1. Introduction

Phthalic acid esters, known as phthalates, are used as additives to modify physical properties of polymeric materials. Some phthalates such as dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), butyl benzyl phthalate (BBP), di-(2-ethylhexyl) phthalate (DEHP) and di-n-octyl phthalate (DNOP) are widely used as plasticizers to increase flexibility and durability of various polymeric materials such as cellulose esters and polyvinyl chloride (PVC) [1, 2]. Until now, phthalate-containing thermoplastic materials have been widely used in applications ranging from food containers, food wrappers, housewares, toys, electronic devices, and cosmetic products, to medical devices. Because phthalate additives are not chemically bound to the polymer matrix, some of them are released slowly into the external environment from the materials. In addition, phthalates have attracted much public attention because of their carcinogenic and estrogenic properties [3]. As
a result, they ubiquitously exist as hazardous chemicals in a variety of substances including aerosols, indoor and outdoor air, dust, food, and even in human urine and blood [4-6]. In this context, some regulations on the use of phthalates have been announced by several government agencies [7-9].

Determination of phthalates is mostly carried out by gas chromatography coupled with mass spectrometry (GC/MS). In the case of phthalates in water, air, and particulates, isolation and/or enrichment of the phthalates from a sample material has usually been done by using liquid-liquid extraction [10] and solid-phase microextraction [11, 12], prior to the GC/MS measurements. On the other hand, for the determination of phthalates in solid samples such as polymer materials, sample pretreatment using solvent extraction has been generally carried out prior to the GC/MS measurements [13-15]. However, solvent extraction requires tedious and time-consuming procedures along with use of large amounts of harmful organic solvents. In contrast, phthalates in polymer materials can be directly analyzed in the solid state by thermal desorption (TD)-GC/MS without any pretreatment of samples as described previously [16]. In brief, a several hundred µg of a solid sample is simply placed in a sample cup which falls freely into the pre-heated micro-furnace of the pyrolyzer, and then the sample is heated under the computer-programmed temperature conditions. Since this technique requires minimal sample pre-treatment procedures, Accordingly, TD-GC/MS has been recently adopted as an official method of analysis for phthalates in polymeric materials [17].

However, the adopted official method was established targeting only six less-volatile phthalates, DBP, BBP, DEHP, diisodecyl phthalate (DIDP), diisononyl phthalate (DINP) and DNOP, that are restricted by the Consumer Product Safety Improvement Act and other similar legislation [7-9], although other phthalates such as DMP, DEP, di-n-propyl phthalate (DPRP) and diisobutyl phthalate (DIBP) are also environmental contaminants and human
health hazards. When applying TD-GC/MS to the analysis of semi-volatile phthalates with a high vapor pressure such as DMP and DEP, accurate determination becomes difficult because of evaporation of such phthalates from the sample cup during the sample preparation procedures. For example, the vapor pressure of DMP at 25°C, 0.26 Pa, is 50 times higher than that of DBP at 25°C, 4.7×10^{-3} Pa [18], and reliable quantitative analysis of such high vapor pressure phthalates is almost impossible.

In the present study, the inner surface of a sample cup was coated with polymers which act as a sorbent for phthalates including DMP and DEP to reduce the effect of evaporation of phthalates on their quantitative analysis by TD-GC/MS. PVC, polystyrene (PS) and poly (methyl methacrylate) (PMMA) were examined as the sorbent polymer coating, and attention was paid to their effects on the evaporation reduction for phthalates and on background signals in chromatograms caused by the thermal decomposition of sorbent polymers at elevated temperature.

2. Experimental

2.1 Samples

Phthalate compounds used in this work were analytical grade supplied by Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) and are listed in Table 1 together with their abbreviations, boiling point [19], and vapor pressure at 25°C [18]. 200 µg of each phthalate was added into 10 mL dichloromethane (DCM) and thoroughly dissolved. This was used as the stock mixture for the analysis experiment. An aliquot (5 µL) of the dichloromethane solution that contained 20 ppm (100 ng) of each phthalate was put in a sample cup using a micro syringe and subjected to the TD-GC/MS analysis.

2.2 Polymer-coated sample cup
Figure 1 shows a cross-sectional view of a sample cup coated with a sorbent polymer film. The sample cup is made of Pyrex glass (model Eco-cup G, Frontier Laboratories Ltd., Koriyama, Japan) and has the dimensions of: height, 8 mm; outer diameter, 4 mm; inner diameter (i.d.), 3 mm; wall thickness, 0.5 mm; and volume, about 50 µL. The sorbent polymers PVC, PS and PMMA were produced industrially. Additives and semi-volatile compounds (SVOCs) in these polymers were removed by Soxhlet extraction for 12 h using hexane as a solvent prior to the formation of the sorbent polymer film inside the sample cup. Tetrahydrofuran (THF) was used for PVC, and DCM was used for PS and PMMA as a solvent to make solutions for the film coating. 20 µL of a polymer solution was put in the sample cup using a micro syringe and a polymer film was formed on the inner surface of the sample cup by evaporating the solvent while heating in an electrical furnace at 50ºC for 5 min, and at 200ºC for 10 min as a final preparation procedure. The polymer film was not formed uniformly and became thicker near the bottom of the sample cup. The average thickness of the film can be tuned from 0.2 to 4.8 µm by changing the concentration of polymers from 0.5 to 12 µg/µL.

2.3 TD-GC/MS measurements

Figure 2 shows a schematic diagram of the TD-GC/MS system used in this study. A temperature-programmable furnace type pyrolyzer (Multi-Shot Pyrolyzer, EGA/PY-3030D, Frontier Laboratories Ltd.) was directly coupled with a quadrupole GC/MS (Shimadzu QP-2010 Plus or Agilent 5975) equipped with a metal capillary separation column (Ultra ALLOY*-5, 30 m x 0.25 mm i.d., coated with 5% diphenyl 95% dimethylpolysiloxane in 0.25 µm film thickness, Frontier Laboratories Ltd.). The pyrolyzer was also coupled with an automated sample introduction system (Auto-Shot Sampler, AS-1020E, Frontier Laboratories Ltd.). Sample cups were placed at the waiting position on the top of the Auto-Shot Sampler and were held at room temperature (ca. 25ºC) before TD-GC/MS measurements. Then, the sample cup was dropped to
the heating position at the center of the pyrolyzer furnace which was temperature-controlled. The furnace temperature was increased from 100 to 320°C at a rate of 20°C/min, and held at 320°C for 5 min. According to the authors’ previous study on evolved gas analysis (EGA) \cite{20} of phthalates in PVC \cite{16}, these experimental conditions are sufficient to attain thermal desorption of phthalates from the sample. Gases evolved from the sample were transported to the GC injection port under a 24 mL/min He carrier gas flow that was introduced into the metal capillary separation column with a split ratio of 1:20. The column temperature was programmed from 50°C to 200°C at a rate of 40°C/min and then to 280°C at a rate of 5°C/min. The components separated by the column were finally detected by MS with an electron ionization source and identified by their retention times and mass spectra followed by a mass spectral library search.

3. Results and discussion

3.1 Applicability of a conventional sample cup without polymer coating

Figure 3 shows chromatograms of the mixture of phthalates measured by TD-GC/MS using a sample cup without any polymer coating. Figure 3(a) was obtained by the immediate measurement after putting the sample solution into the sample cup, while Fig. 3(b) was obtained after holding the sample cup at the waiting position for 200 min. By comparing both chromatograms in Fig. 3, it can be easily recognized that the intensities of peaks 1 and 2 corresponding to DMP and DEP respectively decrease significantly in Fig. 3(b). On the other hand, peaks 3-10 corresponding to less-volatile phthalates do not show any noticeable decrease in the peak area due to their vapor pressures being sufficiently low at 25°C.

Figure 4 shows the dependency of the peak areas of phthalates on the
waiting time at 25°C. It is seen that the peak areas of DMP and DEP decrease remarkably as the waiting time increases, and 90 and 50% reductions in the peak areas are respectively seen for DMP and DEP at the waiting time of 200 min. These results suggest that DMP and DEP were emitted to the ambient atmosphere during the waiting time; therefore, a reliable calibration curve for the quantitative analysis of semi-volatile phthalates having high vapor pressures cannot be obtained by TD-GC/MS using the conventional sample cup without any polymer coating. Accordingly, it can be said that additional procedures are necessary to determine semi-volatile phthalates by TD-GC/MS.

3.2 Analysis of semi-volatile phthalates using a polymer-coated sample cup

To reduce the emission of semi-volatile phthalates during the waiting period before TD-GC/MS measurements, the effect from coating the inner surface of a sample cup with polymers was examined, with the expectation that the coated polymer functions as a sorbent for semi-volatile phthalates. PVC, PS and PMMA were separately used as the coating polymer in this study for the following reasons. PVC is the most popular polymer containing large amount of phthalates as plasticizers. When heated at high temperatures, PS and PMMA degrade to a few kinds of pyrolyzates which might interfere with the measurements of phthalates, according to their reported pyrograms [21]. Furthermore, all these polymers are soluble in a variety of suitable solvents and readily form a film by the solvent casting method.

Polymer coating was first carried out using 120 µg of PVC in THF to form a 2.4 µm thick coated film. The TD-GC/MS measurements for 5 µL of the phthalate stock mixture solution were then performed using the polymer-coated sample cup with changing the waiting time. The observed results are shown in Fig. 5 for waiting times of zero (a) and 200 min (b). The peak intensities in both chromatograms are comparable for all phthalates. This result suggests
that the PVC-coated sample cup works well to reduce the emission of semi-volatile phthalates such as DMP and DEP. The reduction of emission can be ascribed to the fast diffusion of the phthalate mixture solution into the coated PVC film.

Next, the phthalate mixture was repeatedly measured five times with different waiting times from 0 to 200 min at an interval of 50 min each. As a result, a good reproducibility in the peak area is obtained for all phthalates with RSD of less than 3%. In addition to the peaks related to phthalates, however, new peaks assigned to naphthalene (peak A) and biphenyl (peak B) derived from the PVC film, appear in the retention time ranging from 3 to 5 min as shown in Fig. 5. In addition, it is considered that a large amount of hydrogen chloride may be produced due to dissociation of the side chain of PVC when heated up to 320°C according to the reported thermogram of PVC [11]. However, these compounds originated from PVC do not affect the analytical results on phthalates that show longer retention times than 5 min.

Figures 6 and 7 show chromatograms of the phthalate mixture obtained using PS- and PMMA-coated sample cups, respectively. Polymer coating on the inner surface of the sample cup was done by the same procedure as was used in preparation of the PVC-coated sample cup. In both Figs. 6 and 7, the upper chromatograms (a) were obtained immediately after putting the phthalate mixture into the sample cup, and the lower chromatograms (b) were obtained after holding the sample cup containing the phthalate mixture at the waiting position of the Auto-Shot Sampler for 200 min. Irrespective of the holding time for the sample cup, chromatograms are coincident with each other as shown in Figs. 6 and 7. Besides, additional peaks are observed; peaks C (styrene dimer) and D (styrene trimer) in Fig. 6, peaks E (MMA dimers) and F (MMA trimers) in Figs. 7, which are considered to originate from each polymer film. These peaks, however, do not affect the analytical results of the phthalates, since they are well separated from the phthalate peaks. Thus,
both PS- and PMMA-coated sample cups can also be used to reduce the emission of semi-volatile phthalates and they are effective for the TD-GC/MS analysis of phthalates including DMP and DEP, the same as the findings for the PVC-coated sample cup.

3.3 Effect of the amount of a coating polymer on the chromatographic peak area

In the former experiment, 120 µg of polymer was used to prepare polymer-coated sample cups for the analysis of phthalates by TD-GC/MS. Here, dependence of the amount of one of the coated polymers (PVC) on the peak areas of phthalates was examined. The obtained results for the mixed sample of 10 phthalates (100 ng each) with the 200 min waiting time are shown in Fig. 8. The less-volatile phthalates show almost constant peak areas irrespective of the PVC amount as shown in the curves of DPRP, DIBP, and DEHP.

On the other hand, peak areas of semi-volatile phthalates such as DMP and DEP increase with an increase in the PVC amount, and then reach an almost constant level when the PVC amount is larger than 60 µg. In addition, a good reproducibility with RSD of 2.23 and 2.37% was obtained for the peak areas of DMP and DEP acquired from five sequential measurements with the 60 µg PVC-coated sample cup and different waiting times from 0 to 200 min at an interval of 50 min each. Accordingly, it can be said that the PVC-coated sample cup with 60 µg or more of PVC reduces the emission of semi-volatile phthalates and it is applicable to the analysis of phthalates containing DMP and DEP.

4. Conclusion
The polymer-coated sample cups with PVC, PS and PMMA coatings were developed, and their basic performance was evaluated by measuring a mixture of phthalates including semi-volatile DMP and DEP. As a result, no reduction of peak areas of DMP and DEP during the waiting time was observed when using PVC-coated sample cups having film thicknesses of 0.6 µm or more. Comparable performances to quench the emission were also observed using PS- and PMMA-coated sample cups. These results suggest that not only less-volatile phthalates but also semi-volatile ones such as DMP and DEP can be measured with high reliability by TD-GC/MS using the polymer-coated sample cups.

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[14] GB/T 22048-2008, Toys and children’s products - Determination of
phthalate plasticizers in polyvinyl chloride plastic (in English),
http://www.codeofchina.com/gb/lightindustry/18893.html (accessed 06.01.15).


Figure Captions

Fig.1  Cross-sectional view of a sample cup coated with a sorbent polymer film.

Fig.2  Schematic diagram of the measurement system for TD-GC/MS analysis.

Fig.3  Chromatograms of the phthalate mixture measured by TD-GC/MS at up to 320ºC using a temperature programmable pyrolyzer obtained with plural different waiting times after putting the phthalate mixture into a sample cup without polymer coating (a) 0 min, (b) 200 min. Sample amount was 100 ng for each phthalate (20 ppm×5 µL). For peak assignments, see Table 1.

Fig.4  Effect of the waiting time at 25ºC on the peak area of each phthalate obtained by TD-GC/MS using sample cup without polymer coating. ●: DMP, □: DEP, ■: DPRP, ×: DIBP, ○: DEHP.

Fig.5  Chromatograms of the phthalate mixture measured by TD-GC/MS at up to 320ºC using a sample cup coated with PVC (average film thickness: 2.4 µm) obtained with plural different waiting times; (a) 0 min, (b) 200 min. A: naphthalene, B: biphenyl. For the other peak assignments, see Table 1.

Fig.6  Chromatograms of the phthalate mixture measured by TD-GC/MS at up to 320ºC using a sample cup coated with PS (average film thickness: 2.4 µm), obtained with plural different waiting times; (a) 0 min, (b) 200 min. C: styrene dimer, D: styrene trimer. For the other peak assignments, see Table 1.

Fig.7  Chromatograms of the phthalate mixture measured by TD-GC/MS at up to 320ºC using a sample cup coated with PMMA (average film thickness: 2.4 µm), obtained with plural different waiting times; (a) 0 min, (b) 200 min. E: MMA dimers, F: MMA trimers. For the other peak assignments, see Table 1.

Fig.8  Relationship between the film thickness of PVC and the peak area of phthalates obtained by TD-GC/MS for 200 min waiting time. ●: DMP, □: DEP, ■: DPRP, ×: DIBP, ○: DEHP.
Table 1 Phthalate compounds and their physical properties

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Compound name</th>
<th>Abbreviation</th>
<th>MW</th>
<th>BP*1 (ºC)</th>
<th>VP*2 (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dimethyl phthalate</td>
<td>DMP</td>
<td>194</td>
<td>282</td>
<td>2.63 x 10^1</td>
</tr>
<tr>
<td>2</td>
<td>Diethyl phthalate</td>
<td>DEP</td>
<td>222</td>
<td>298</td>
<td>6.48 x 10^2</td>
</tr>
<tr>
<td>3</td>
<td>Di-n-propyl phthalate</td>
<td>DPRP</td>
<td>250</td>
<td>317</td>
<td>1.75 x 10^2</td>
</tr>
<tr>
<td>4</td>
<td>Diisobutyl phthalate</td>
<td>DIBP</td>
<td>278</td>
<td>327</td>
<td>4.73 x 10^3</td>
</tr>
<tr>
<td>5</td>
<td>Di-n-butyl phthalate</td>
<td>DBP</td>
<td>278</td>
<td>340</td>
<td>4.73 x 10^3</td>
</tr>
<tr>
<td>6</td>
<td>Di-n-pentyl phthalate</td>
<td>DPP</td>
<td>306</td>
<td>342</td>
<td>1.28 x 10^3</td>
</tr>
<tr>
<td>7</td>
<td>Di-n-hexyl phthalate</td>
<td>DHP</td>
<td>334</td>
<td>-</td>
<td>3.45 x 10^4</td>
</tr>
<tr>
<td>8</td>
<td>Butyl benzyl phthalate</td>
<td>BBP</td>
<td>312</td>
<td>370</td>
<td>2.49 x 10^3</td>
</tr>
<tr>
<td>9</td>
<td>Di (2-ethylhexyl) phthalate</td>
<td>DEHP</td>
<td>390</td>
<td>386</td>
<td>2.52 x 10^5</td>
</tr>
<tr>
<td>10</td>
<td>Di (n-octyl) phthalate</td>
<td>DNOP</td>
<td>390</td>
<td>380</td>
<td>2.52 x 10^5</td>
</tr>
</tbody>
</table>

*1: Boiling point, *2: Vapor pressure at 25ºC

Fig.1 Cross section of a polymer-coated glass sample cup.
Fig. 3 Chromatograms of the phthalate mixture measured by TD-GC/MS at up to 320°C using a temperature programmable pyrolyzer obtained with different waiting times after putting the phthalate mixture into a sample cup without polymer coating (a) 0 min, (b) 200 min. Sample amount was 100 ng for each phthalate (20 ppm × 5 µL). For peak assignments, see Table 1.

Fig. 2 Schematic diagram of the measurement system for TD-GC/MS analysis.
Fig. 4 Effect of the waiting time at 25°C on the peak area of each phthalate obtained by TD-GC/MS using sample cup without polymer coating. ●: DMP, □: DEP, △: DPRP, ×: DIBP, ○: DEHP.

Fig. 5 Chromatograms of the phthalate mixture measured by TD-GC/MS at up to 320°C using a sample cup coated with PVC (average film thickness: 2.4 μm) obtained with different waiting times; (a) 0 min, (b) 200 min. A: naphthalene, B: biphenyl. For the other peak assignments, see Table 1.
Fig. 6 Chromatograms of the phthalate mixture measured by TD-GC/MS at up to 320°C using a sample cup coated with PS (average film thickness: 2.4 µm), obtained with different waiting times; (a) 0 min, (b) 200 min. C: styrene dimer, D: styrene trimer. For the other peak assignments, see Table 1.

Fig. 7 Chromatograms of the phthalate mixture measured by TD-GC/MS at up to 320°C using a sample cup coated with PMMA (average film thickness: 2.4 µm), obtained with different waiting times; (a) 0 min, (b) 200 min. E: MMA dimers, F: MMA trimers. For the other peak assignments, see Table 1.

Fig. 8 Relationship between the film thickness of PVC and the peak area of phthalates obtained by TD-GC/MS for 200 min waiting time. ●: DMP, □: DEP, △ DPRP, ×: DIBP, ○: DEHP.