



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



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## 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.

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## 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

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**Table 1**  
Phthalate compounds and their physical properties.

Peak no.	Compound name	Abbreviation	MW	BP <sup>a</sup> (°C)	VP <sup>b</sup> (Pa)
1	Dimethyl phthalate	DMP	194	282	$2.63 \times 10^{-1}$
2	Diethyl phthalate	DEP	222	298	$6.48 \times 10^{-2}$
3	Di-n-propyl phthalate	DPRP	250	317	$1.75 \times 10^{-2}$
4	Diisobutyl phthalate	DIBP	278	327	$4.73 \times 10^{-3}$
5	Di-n-butyl phthalate	DBP	278	340	$4.73 \times 10^{-3}$
6	Di-n-pentyl phthalate	DPP	306	342	$1.28 \times 10^{-3}$
7	Di-n-hexyl phthalate	DHP	334	–	$3.45 \times 10^{-4}$
8	Butyl benzyl phthalate	BBP	312	370	$2.49 \times 10^{-3}$
9	Di (2-ethylhexyl) phthalate	DEHP	390	386	$2.52 \times 10^{-5}$
10	Di (n-octyl) phthalate	DNOP	390	380	$2.52 \times 10^{-5}$

<sup>a</sup> Boiling point.<sup>b</sup> Vapor pressure at 25 °C.

previously [16]. In brief, a several hundred microgram 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, 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,  $4.7 \times 10^{-3}$  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.

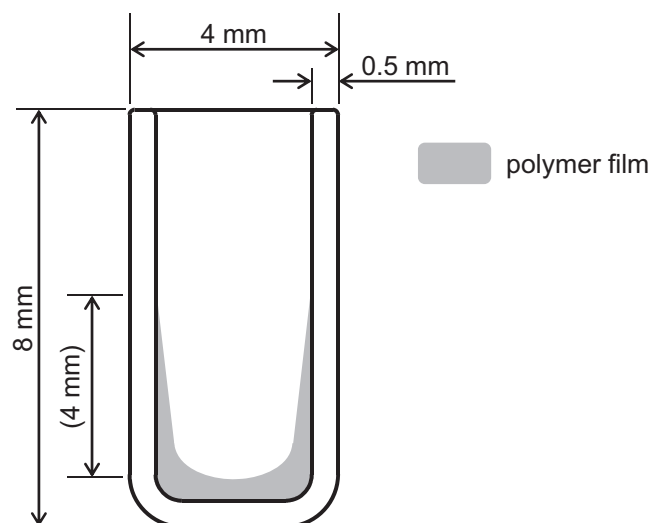
## 2. Experimental

### 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

Fig. 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

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

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 50 °C for 5 min, and at 200 °C 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

Fig. 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<sup>+</sup>-5, 30 m × 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. 25 °C) 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) [20] of phthalates in PVC [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

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