1 Polymer-coated sample cup for quantitative analysis of semi-volatile

2 phthalates in polymeric materials by thermal desorption-gas

3 chromatography-mass spectrometry

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13 Abstract

14   A new "polymer-coated" sample cup useful for the analysis of phthalates

15 in polymeric materials by thermal desorption (TD)-GC/MS using a temperature

16 programmable furnace type pyrolyzer as a TD device was developed to

17 suppress the emission of semi-volatile phthalates such as dimethyl phthalate

18 (DMP) and diethyl phthalate (DEP) during the measurements. The inner

19 surface of a sample cup was coated by polymers which act as a sorbent for the

20 phthalates. Three polymers, polyvinyl chloride, polystyrene and poly (methyl

21 methacrylate), were chosen as the coating polymers. A mixture of ten

22 phthalates including DMP and DEP was used as the test sample to estimate the

23 performance of the sample cups. When a conventional sample cup without

24 any polymer coating was used, 90 and 50% reductions in the peak areas of

25 DMP and DEP were respectively observed at the waiting time of 200 min. On

26 the contrary, no reduction of peak area of DMP and DEP during the same

27 waiting time was observed with any one of the three coating polymers at the

28 proper polymer film thickness.   These results suggest that the polymer-coated

29 sample cup suppresses the emission of semi-volatile phthalates and is

30 effective for the analysis of phthalates containing DMP and DEP by TD-GC/MS.

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42 1. Introduction

43   Phthalic acid esters, known as phthalates, are used as additives to

44 modify physical properties of polymeric materials.   Some phthalates such as

45 dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP),

46 butyl benzyl phthalate (BBP), di-(2-ethylhexyl) phthalate (DEHP) and di-n-octyl

47 phthalate (DNOP) are widely used as plasticizers to increase flexibility and

48 durability of various polymeric materials such as cellulose esters and polyvinyl

49 chloride (PVC) [1, 2].   Until now, phthalate-containing thermoplastic materials

50 have been widely used in applications ranging from food containers, food

51 wrappers, housewares, toys, electronic devices, and cosmetic products, to

52 medical devices.   Because phthalate additives are not chemically bound to the

53 polymer matrix, some of them are released slowly into the external

54 environment from the materials.   In addition, phthalates have attracted much

55 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

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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 25ºC, 0.26 Pa, is 50 times higher than that of DBP at 25ºC, 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 25ºC [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

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112   Figure 1 shows a cross-sectional view of a sample cup coated with a

113   sorbent polymer film.   The sample cup is made of Pyrex glass (model Eco-cup

114   G, Frontier Laboratories Ltd., Koriyama, Japan) and has the dimensions of:

115   height, 8 mm; outer diameter, 4 mm; inner diameter (i.d.), 3 mm; wall thickness,

116   0.5 mm; and volume, about 50 μL. The sorbent polymers PVC, PS and PMMA

117   were produced industrially.   Additives and semi-volatile compounds (SVOCs)

118   in these polymers were removed by Soxhlet extraction for 12 h using hexane as

119   a solvent prior to the formation of the sorbent polymer film inside the sample

120   cup.   Tetrahydrofuran (THF) was used for PVC, and DCM was used for PS and

121   PMMA as a solvent to make solutions for the film coating.   20 μL of a polymer

122   solution was put in the sample cup using a micro syringe and a polymer film

123   was formed on the inner surface of the sample cup by evaporating the solvent

124   while heating in an electrical furnace at 50ºC for 5 min, and at 200ºC for 10 min

125   as a final preparation procedure.   The polymer film was not formed uniformly

126   and became thicker near the bottom of the sample cup.   The average

127   thickness of the film can be tuned from 0.2 to 4.8 μm by changing the

128   concentration of polymers from 0.5 to 12 μg/μL.

129   2.3 TD-GC/MS measurements

130   Figure 2 shows a schematic diagram of the TD-GC/MS system used in

131   this study.   A temperature-programmable furnace type pyrolyzer (Multi-Shot

132   Pyrolyzer, EGA/PY-3030D, Frontier Laboratories Ltd.) was directly coupled

133   with a quadrupole GC/MS (Shimadzu QP-2010 Plus or Agilent 5975) equipped

134   with a metal capillary separation column (Ultra ALLOY[+]-5, 30 m × 0.25 mm i.d.,

135   coated with 5% diphenyl 95% dimethylpolysiloxane in 0.25 μm film thickness,

136   Frontier Laboratories Ltd.).   The pyrolyzer was also coupled with an

137   automated sample introduction system (Auto-Shot Sampler, AS-1020E,

138   Frontier Laboratories Ltd.).   Sample cups were placed at the waiting position

139   on the top of the Auto-Shot Sampler and were held at room temperature (ca.

140   25ºC) before TD-GC/MS measurements. Then, the sample cup was dropped to

141 the heating position at the center of the pyrolyzer furnace which was
142 temperature-controlled. The furnace temperature was increased from 100 to
143 320ºC at a rate of 20ºC/min, and held at 320ºC for 5 min. According to the
144 authors' previous study on evolved gas analysis (EGA) [20] of phthalates in
145 PVC [16], these experimental conditions are sufficient to attain thermal
146 desorption of phthalates from the sample. Gases evolved from the sample
147 were transported to the GC injection port under a 24 mL/min He carrier gas flow
148 that was introduced into the metal capillary separation column with a split ratio
149 of 1:20. The column temperature was programmed from 50ºC to 200ºC at a
150 rate of 40ºC/min and then to 280ºC at a rate of 5ºC/min. The components
151 separated by the column were finally detected by MS with an electron
152 ionization source and identified by their retention times and mass spectra
153 followed by a mass spectral library search.

154

155 3. Results and discussion

156 3.1 Applicability of a conventional sample cup without polymer coating

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

167 Figure 4 shows the dependency of the peak areas of phthalates on the

168 waiting time at 25ºC.   It is seen that the peak areas of DMP and DEP decrease

169 remarkably as the waiting time increases, and 90 and 50% reductions in the

170 peak areas are respectively seen for DMP and DEP at the waiting time of 200

171 min.   These results suggest that DMP and DEP were emitted to the ambient

172 atmosphere during the waiting time; therefore, a reliable calibration curve for

173 the quantitative analysis of semi-volatile phthalates having high vapor

174 pressures cannot be obtained by TD-GC/MS using the conventional sample cup

175 without any polymer coating.   Accordingly, it can be said that additional

176 procedures are necessary to determine semi-volatile phthalates by TD-GC/MS.

177

178 3.2 Analysis of semi-volatile phthalates using a polymer-coated sample cup

179   To reduce the emission of semi-volatile phthalates during the waiting

180 period before TD-GC/MS measurements, the effect from coating the inner

181 surface of a sample cup with polymers was examined, with the expectation that

182 the coated polymer functions as a sorbent for semi-volatile phthalates.   PVC,

183 PS and PMMA were separately used as the coating polymer in this study for the

184 following reasons.   PVC is the most popular polymer containing large amount

185 of phthalates as plasticizers.   When heated at high temperatures, PS and

186 PMMA degrade to a few kinds of pyrolyzates which might interfere with the

187 measurements of phthalates, according to their reported pyrograms [21].

188 Furthermore, all these polymers are soluble in a variety of suitable solvents

189 and readily form a film by the solvent casting method.

190   Polymer coating was first carried out using 120 µg of PVC in THF to form

191 a 2.4 µm thick coated film. The TD-GC/MS measurements for 5 µL of the

192 phthalate stock mixture solution were then performed using the polymer-coated

193 sample cup with changing the waiting time.   The observed results are shown

194 in Fig .5 for waiting times of zero (a) and 200 min (b).   The peak intensities in

195 both chromatograms are comparable for all phthalates.   This result suggests

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196 that the PVC-coated sample cup works well to reduce the emission of

197 semi-volatile phthalates such as DMP and DEP. The reduction of emission

198 can be ascribed to the fast diffusion of the phthalate mixture solution into the

199 coated PVC film.

200   Next, the phthalate mixture was repeatedly measured five times with

201 different waiting times from 0 to 200 min at an interval of 50 min each. As a

202 result, a good reproducibility in the peak area is obtained for all phthalates with

203 RSD of less than 3%. In addition to the peaks related to phthalates, however,

204 new peaks assigned to naphthalene (peak A) and biphenyl (peak B) derived

205 from the PVC film, appear in the retention time ranging from 3 to 5 min as

206 shown in Fig. 5. In addition, it is considered that a large amount of hydrogen

207 chloride may be produced due to dissociation of the side chain of PVC when

208 heated up to 320ºC according to the reported thermogram of PVC [11].

209 However, these compounds originated from PVC do not affect the analytical

210 results on phthalates that show longer retention times than 5 min.

211   Figures 6 and 7 show chromatograms of the phthalate mixture obtained

212 using PS- and PMMA-coated sample cups, respectively. Polymer coating on

213 the inner surface of the sample cup was done by the same procedure as was

214 used in preparation of the PVC-coated sample cup. In both Figs. 6 and 7, the

215 upper chromatograms (a) were obtained immediately after putting the phthalate

216 mixture into the sample cup, and the lower chromatograms (b) were obtained

217 after holding the sample cup containing the phthalate mixture at the waiting

218 position of the Auto-Shot Sampler for 200 min. Irrespective of the holding

219 time for the sample cup, chromatograms are coincident with each other as

220 shown in Figs. 6 and 7. Besides, additional peaks are observed; peaks C

221 (styrene dimer) and D (styrene trimer) in Fig. 6, peaks E (MMA dimers) and F

222 (MMA trimers) in Figs. 7, which are considered to originate from each polymer

223 film. These peaks, however, do not affect the analytical results of the

224 phthalates, since they are well separated from the phthalate peaks. Thus,

225   both PS- and PMMA-coated sample cups can also be used to reduce the

226   emission of semi-volatile phthalates and they are effective for the TD-GC/MS

227   analysis of phthalates including DMP and DEP, the same as the findings for the

228   PVC-coated sample cup.

229

230   3.3 Effect of the amount of a coating polymer on the chromatographic peak

231   area

232   In the former experiment, 120 µg of polymer was used to prepare

233   polymer-coated sample cups for the analysis of phthalates by TD-GC/MS.

234   Here, dependence of the amount of one of the coated polymers (PVC) on the

235   peak areas of phthalates was examined. The obtained results for the mixed

236   sample of 10 phthalates (100 ng each) with the 200 min waiting time are shown

237   in Fig. 8. The less-volatile phthalates show almost constant peak areas

238   irrespective of the PVC amount as shown in the curves of DPRP, DIBP, and

239   DEHP.

240   On the other hand, peak areas of semi-volatile phthalates such as DMP

241   and DEP increase with an increase in the PVC amount, and then reach an

242   almost constant level when the PVC amount is larger than 60 µg. In addition,

243   a good reproducibility with RSD of 2.23 and 2.37% was obtained for the peak

244   areas of DMP and DEP acquired from five sequential measurements with the 60

245   µg PVC-coated sample cup and different waiting times from 0 to 200 min at an

246   interval of 50 min each. Accordingly, it can be said that the PVC-coated

247   sample cup with 60 µg or more of PVC reduces the emission of semi-volatile

248   phthalates and it is applicable to the analysis of phthalates containing DMP and

249   DEP.

250

251   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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332

333   Figure Captions

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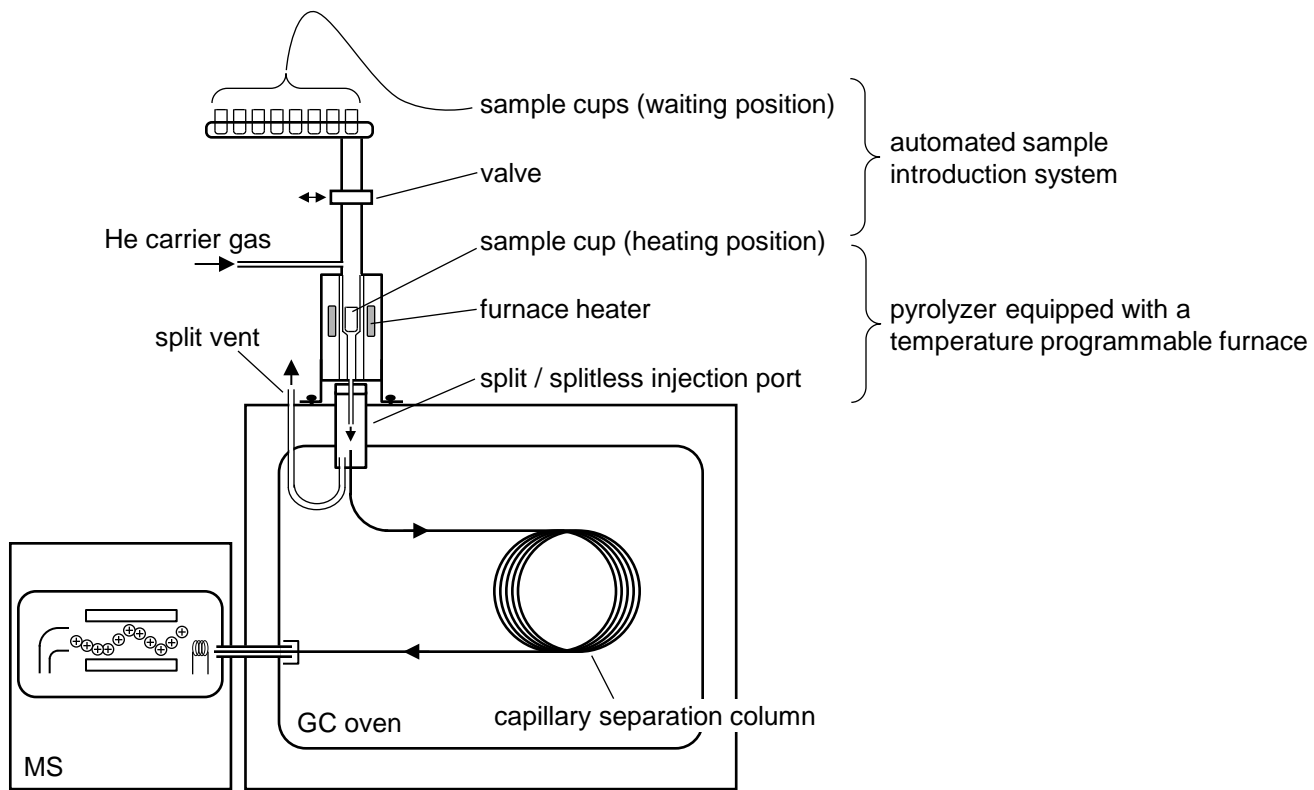
335   film.

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

337   Fig.3   Chromatograms of the phthalate mixture measured by TD-GC/MS at up

338   to 320ºC using a temperature programmable pyrolyzer obtained with plural

339   different waiting times after putting the phthalate mixture into a sample cup

340   without polymer coating (a) 0 min, (b) 200 min. Sample amount was 100 ng for

341   each phthalate (20 ppm×5 µL). For peak assignments, see Table 1.

342   Fig.4   Effect of the waiting time at 25ºC on the peak area of each phthalate

343   obtained by TD-GC/MS using sample cup without polymer coating. ●: DMP, □:

344   DEP, ■: DPRP, ×: DIBP, ○: DEHP.

345   Fig.5   Chromatograms of the phthalate mixture measured by TD-GC/MS at up

346   to 320ºC using a sample cup coated with PVC (average film thickness: 2.4 µm)

347   obtained with plural different waiting times; (a) 0 min, (b) 200 min. A:

348   naphthalene, B: biphenyl. For the other peak assignments, see Table 1.

349   Fig.6   Chromatograms of the phthalate mixture measured by TD-GC/MS at up

350   to 320ºC using a sample cup coated with PS (average film thickness: 2.4 µm),

351   obtained with plural different waiting times; (a) 0 min, (b) 200 min. C: styrene

352   dimer, D: styrene trimer. For the other peak assignments, see Table 1.

353   Fig.7   Chromatograms of the phthalate mixture measured by TD-GC/MS at up

354   to 320ºC using a sample cup coated with PMMA (average film thickness: 2.4

355   µm), obtained with plural different waiting times; (a) 0 min, (b) 200 min. E: MMA

356   dimers, F: MMA trimers. For the other peak assignments, see Table 1.

357   Fig.8   Relationship between the film thickness of PVC and the peak area of

358   phthalates obtained by TD-GC/MS for 200 min waiting time. ●: DMP, □: DEP, ■:

359   DPRP, ×: DIBP, ○: DEHP.

Table 1 Phthalate compounds and their physical properties

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

*1: Boiling point, *2: Vapor pressure at 25ºC
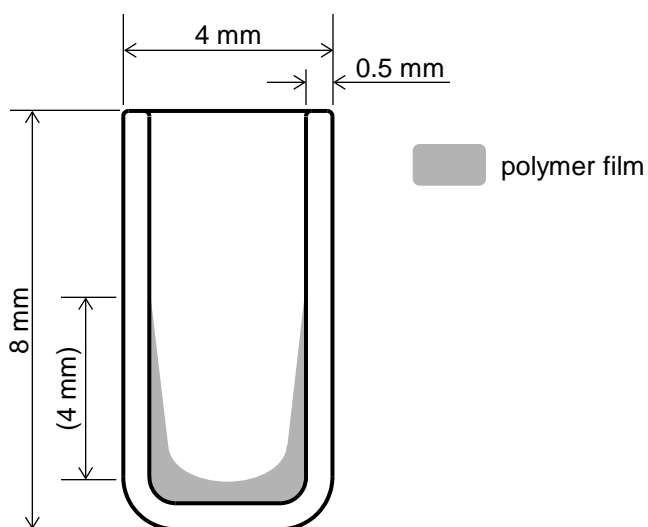
Fig.1 Cross section of a polymer-coated glass sample cup.

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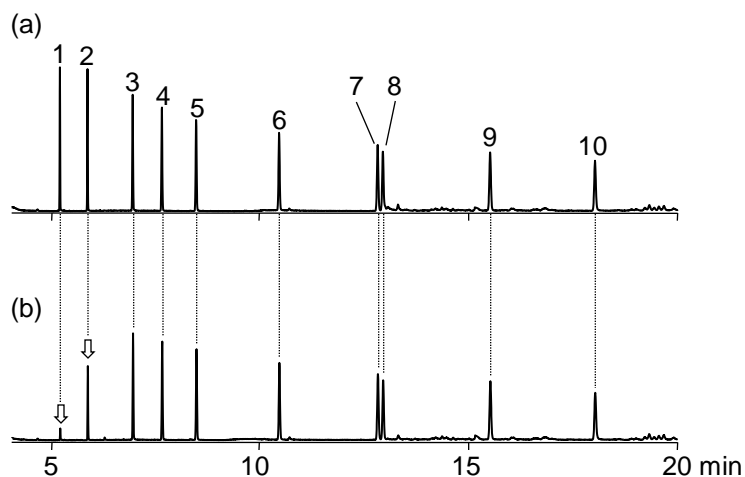

Fig.3 Chromatograms of the phthalate mixture measured by TD-GC/MS at up to 320ºC using a temperature programmable pyrolyzer obtained with different waiting times after putting the phthalate mixture into a sample cup without polymer coating (a) 0 min, (b) 200 min. Sample amount was 100 ng for each phthalate (20 ppm × 5 µL). For peak assignments, see Table 1.
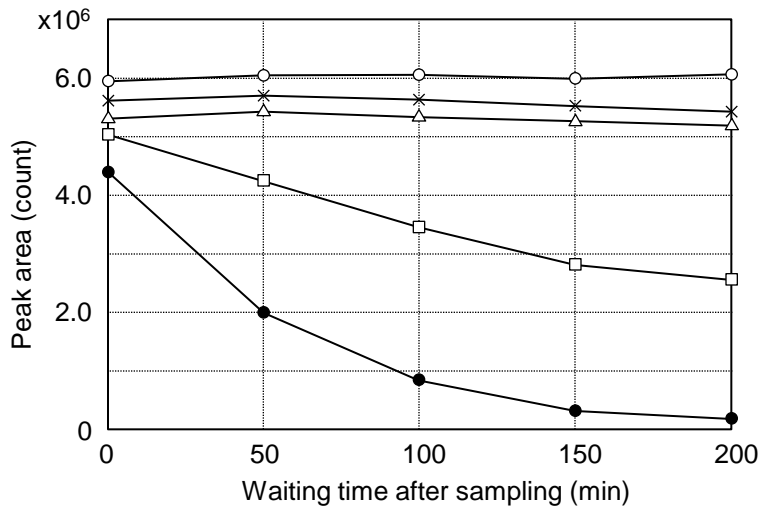
Fig.4 Effect of the waiting time at 25⁰C on the peak area of each phthalate obtained by TD-GC/MS using sample cup without polymer coating. ●: DMP, □ : DEP, △ DPRP, × : DIBP, O: DEHP.
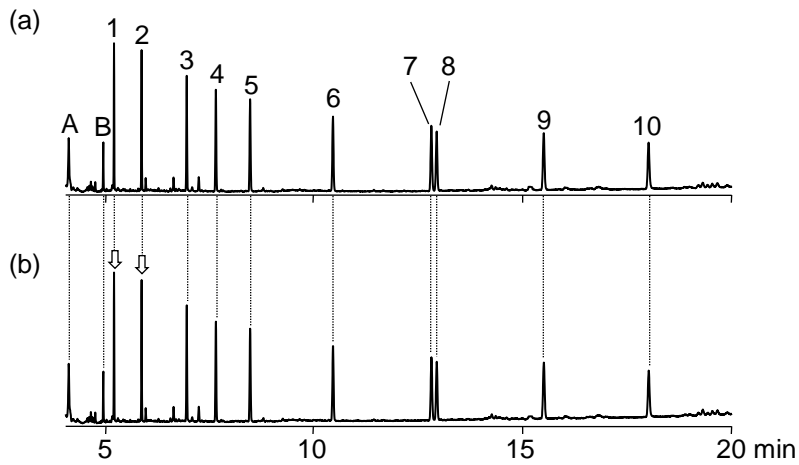
Fig.5 Chromatograms of the phthalate mixture measured by TD-GC/MS at up to 320⁰C using a sample cup coated with PVC (average film thickness: 2.4 µm) obtained with different waiting times; (a) 0 min, (b) 200 min. A: naphthalene, B: biphenyl. For the other peak assignments, see Table 1.
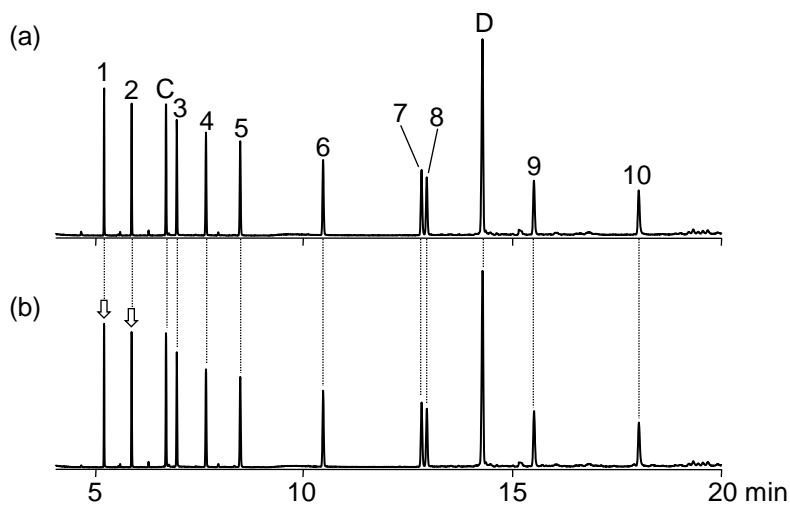
Fig.6 Chromatograms of the phthalate mixture measured by TD-GC/MS at up to 320ºC using a sample cup coated with PS (average film thickness: 2.4 µm), obtained with different waiting times; (a) 0 min, (b) 200 min. C: styrene dimer, D: styrene trimer. For the other peak assignments, see Table 1.
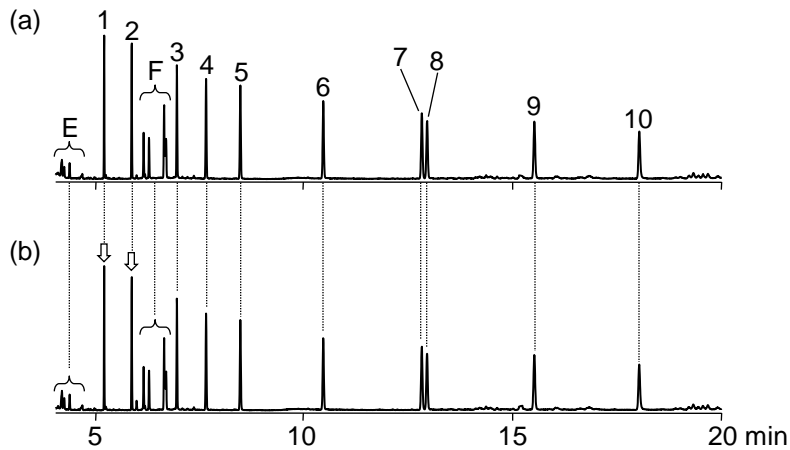

Fig.7 Chromatograms of the phthalate mixture measured by TD-GC/MS at up to 320ºC using a sample cup coated with PMMA (average film thickness: 2.4 µm), obtained with different waiting times; (a) 0 min, (b) 200 min. E: MMA dimers, F: MMA trimers. For the other peak assignments, see Table 1.
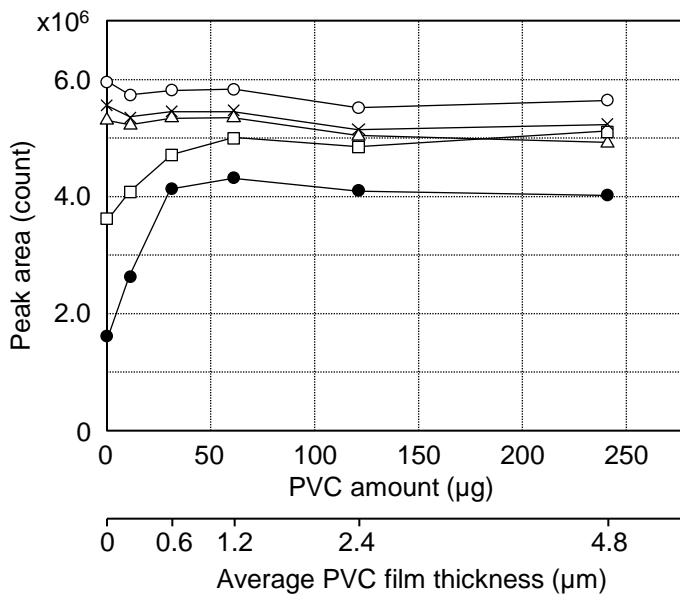

Fig.8 Relationship between the film thickness of PVC and the peak area of phthalates obtained by TD-GC/MS for 200 min waiting time. ●: DMP, □ : DEP, △ DPRP, ×: DIBP, ○: DEHP.