

Screening of Phthalates in Polymer Materials by Pyrolysis GC/MS

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A study on the rapid identification of phthalates in polymer materials has been conducted by employing gas chromatography-mass spectrometry coupled with a pyrolyzer (Py-GC/MS). Since Py-GC/MS does not require any complex solvent-extraction process, a rapid screening of phthalates should be possible. In this study, polymer samples were directly introduced into the pyrolyzer in order to thermally extract phthalates from the polymer under specific heating conditions. By optimizing the Py-GC/MS parameters, a sequential testing cycle of 35 min per sample was feasible without causing any major decomposition of the base materials. Thus, a rapid screening of over 20 samples per day was achieved without any time constraints by effectively utilizing specifically prepared reference polymer sheets for quality control. Py-GC/MS was found to be suitable and effective for identifying phthalates in polymer materials.

Keywords Phthalates, phthalic acid ester, pyrolyzer, Py-GC/MS, reference material

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Phthalic acid di-esters (phthalates) have been widely used in industry as plasticizers, and can be present in high concentrations in polymer products. However, some of the phthalates are now classified as major hazardous substances, posing threat to the reproductive system, and also are found to be carcinogenic.¹ From this perspective, restrictions on these compounds are under regulation in some areas, such as in medical- and child-care products, and even stricter controls are expected to be enforced.²⁻⁴

The problem with the phthalates is that these compounds are semi-volatile. Further, over the past few decades, phthalates have been widely discharged into the environment as contaminants.⁵ Therefore, an extensive monitoring, besides a ban of the intentional use, should be considered essential to ensure compliance with global regulations on phthalates.

The purpose of this study is to offer a rapid and an efficient method to screen phthalates and to help create an effective measure against phthalate contamination. Gas chromatography-mass spectrometry coupled with a pyrolyzer (Py-GC/MS) was used to detect the presence of di-isobutyl phthalate (DIBP), di-*n*-butyl phthalate (DBP), benzylbutyl phthalate (BBP), di-(2-ethylhexyl) phthalate (DEHP), di-*n*-octyl phthalate (DNOP), di-isononyl phthalate (DINP) and di-iso-decyl phthalate (DIDP) in a polymer material. Figure 1 shows a schematic diagram of a Py-GC/MS system.

A Py-GC/MS system has been employed to yield a solvent-free method that rapidly enables the identification of controlled additives present at regulatory levels. Since Py-GC/MS does not require any complex solvent-extraction process, a rapid

screening of phthalates should become available.⁶ Polymer samples can be directly introduced into the pyrolyzer to thermally extract phthalates from the polymer under specific heat conditions. Thermally desorbed phthalates were transferred to the gas-chromatography instrument, which was separated by a gas chromatographic capillary column, and then detected by a

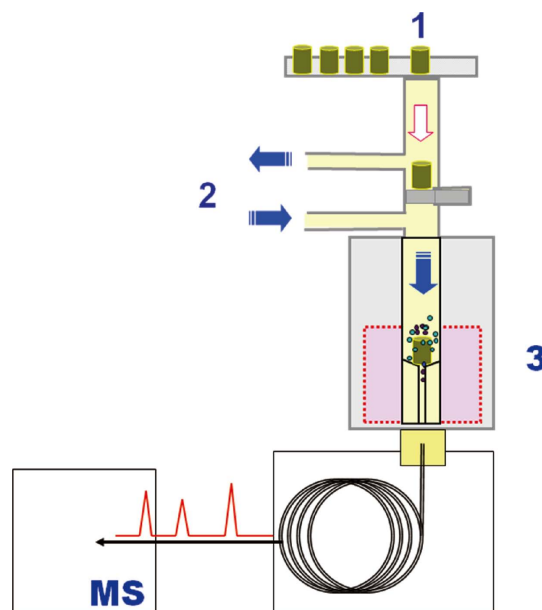


Fig. 1 Schematic diagram of the Py-GC/MS system. 1. Sample cup, 2. Carrier gas, 3. Pyrolyzer.

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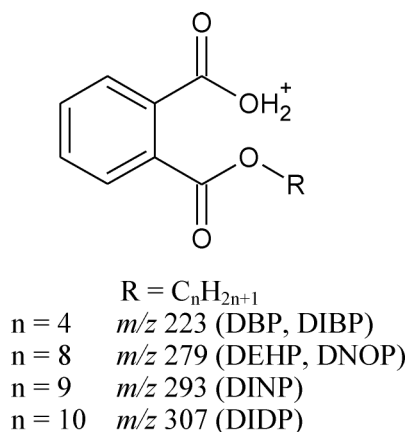


Fig. 2 Quantitative ions.

mass spectrometer. The respective phthalates were identified on the basis of the retention times, m/z (mass to charge ratios of quantitative and confirmation ions), and the ion ratio in comparison with the standard sample analysis. A single-level calibration curve was applied to quantify the presence of any phthalates. Reference polymer materials are recommended for calibration and sensitivity assessment of the instrument to ensure rapid screening in an efficient manner. Stock solutions, prepared with a standard mixture solution, can also be used for calibration. However, to avoid inefficiency in the preparation of the standard, a stock solution should be an alternative measure only if reference polymer materials are not available.

The following instrument parameters have been found to be suitable for the screening of phthalate by Py-GC/MS. A pyrolysis furnace was heated up in the steps described below with a constant pyrolysis-GC interface temperature of 300°C:

200°C → 20°C/min → 300°C → 5°C/min → 340°C (1 min).

As for the GC setting, a GC column with dimensions of 15 m × 0.25 mm i.d., 0.05 µm film thickness (Ultra ALLOY-PBDE, 100% dimethyl polysiloxane) was used for the measurement. The injection-port temperature was set at 320°C and the column oven temperature was set as follows:

80°C → (20°C/min) → 300°C (5 min).

The injection mode was set to split with a ratio of 1/50, and helium was used as carrier gas at a constant linear velocity of 52.1 cm/s.

Mass analysis was performed using both selective ion monitoring (SIM) and scan modes. The ion source was controlled at 230°C with a constant pyrolysis-GC interface temperature of 320°C. For ionization, an energy of 70 eV was supplied to the GC-MS instrument in the electron ionization (EI) mode. Major EI fragmentation of aromatic esters probably proceeds through alpha cleavage. For example, a distinctive ion appeared at m/z 149, resulting from interactions between ortho substituents. In addition, each phthalate can be quantitatively identified with ions characterized by the structures of substituents, as shown in Fig. 2. Here, the substituents are symbolized by $R = C_nH_{2n+1}$, where $n = 4$ for DBP and DIBP (m/z 205), $n = 8$ for DEHP and DNOP (m/z 279), $n = 9$ for DINP (m/z 293) and $n = 10$ for DIDP (m/z 307). Fragment ions of BBP characteristically appeared at m/z 206. Other mass ions,

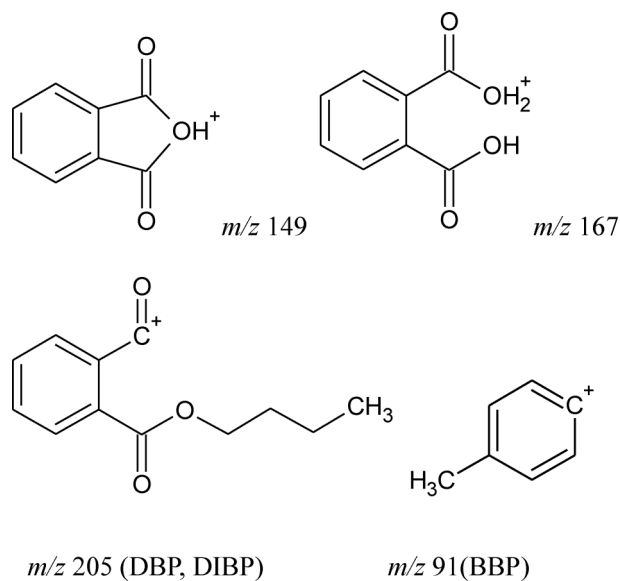


Fig. 3 Confirmation ions.

Table 1 Monitoring mass

Phthalate	Quantitative (m/z)	Confirmation 1 (m/z)	Confirmation 2 (m/z)
DIBP	223	205	149
DBP	223	205	149
BBP	206	91	149
DEHP	279	167	149
DNOP	279	167	149
DINP	293	167	149
DIDP	307	167	149

shown in Fig. 3, were also monitored for confirmation. A list of monitoring mass ions for quantification and confirmation is given in Table 1

As mentioned above, Py-GC/MS executes a sequential testing cycle of 35 min per sample. Quality control, *i.e.*, calibration and sensitivity assessments, was also easily performed by using reference polymer materials with phthalates concentrations of approximately 1000 mg/kg (for calibration) and 100 mg/kg (sensitivity assessment). Thinly stretched reference polymer sheets were specifically prepared for convenience of the sampling procedure.⁷ The quality control samples of 1.0 – 2.0 mm in diameter were punched out from a 0.2 mm thick reference polymer sheet using a micro-puncher. Test samples were cut out from the polymer material in less than a few minutes. Samples are required to be cut into small pieces of less than 3 mm length. Approximately 0.5 – 1.0 mg of the cut or powdered samples was put into sample cups of the thermal pyrolysis unit in a short time using a micro-spatula. In this way, a rapid screening of over 20 samples per day was possible, without any time constraints, providing sufficient time for data analysis. By selecting specific heating conditions for pyrolysis, phthalates were monitored and identified without causing any major decomposition of the base materials.⁸

The instrumental sensitivity was confirmed by the S/N ratio of 50 ng phthalates ($S/N > 30$). Reference polymer material (100 mg/kg) was injected as the control sample to assess the sensitivity so as to ensure a calculated detection limit of less

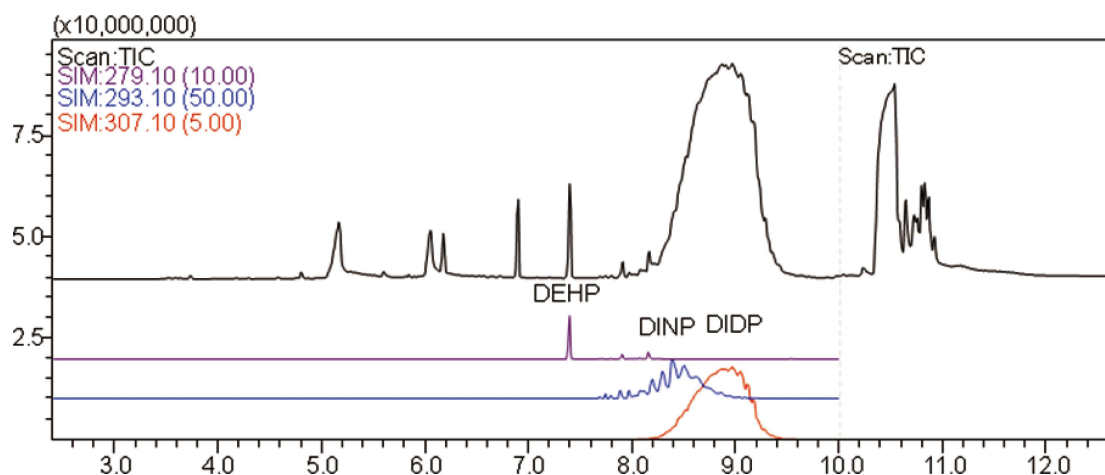


Fig. 4 An example test result of a PVC cable coating.

than or equal to 100 mg/kg. The detection limit of the actual method was within the range of 12 – 17 mg/kg, as determined by repeating the measurement 7 times. In addition, a blank sample was analyzed to check for any carryover. The background level of phthalate was confirmed to be less than 30 mg/kg. Figure 4 shows the test result for a PVC cable coating.

Py-GC/MS screening is subject to some limitations, including interferences or the concentration range of phthalates; however, this method should help to reduce the complexity in verifying the concentrations as per the chemical regulations.

For example, it would be a sensible precaution to set up a criterion for presence, absence or conduct further testing relative to the projected regulatory limit of 1000 mg/kg. If the screening method produces values that are between 500 and 1500 mg/kg, follow-up actions would be recommended to make a final presence/absence decision by applying conventional GC/MS or LC/MS methods. In other words, values less of than 500 mg/kg and exceeding 1500 mg/kg can be regarded as being the “below limit” and “over limit”, respectively, on a regulatory basis.

The conclusions drawn from the study described above can be summarized as follows.

Py-GC/MS was found to be effective for screening phthalates in polymer materials without requiring any complex solvent extraction process. This rapid screening enables an extensive monitoring of phthalates, and should serve to create an effective preventative measure against phthalate contamination.

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