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Comparative study of thermal desorption and solvent extraction-gas chromatography–mass spectrometric analysis for the quantification of phthalates in polymers

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ABSTRACT

For the quantitative analysis of phthalates in polymers, a thermal desorption (TD)-GC–MS method was compared with solvent extraction (SE)-GC–MS methods which require the long pretreatment procedures using large amount of harmful organic solvents. Calibration curves of TD-GC–MS showed good linearity ($r^2 > 0.9997$) and low method detection limit (<30 mg/kg with 9.0% RSD). Quantification results for three kinds of test phthalate polymer samples (test PTPSs) showed an RSD below 7.4% and acceptable recoveries (78.3–117.4%) as in the standard method of International Electrotechnical Commission. Even in a sample with a high concentration of phthalates (PTPS #3), the method also showed good recovery with low RSD values. The TD-GC–MS results were comparable with those results by SE-GC–MS methods, indicating that TD-GC–MS method also can be used for the quantification of phthalates in polymers. The average recovery (92–103%) and RSD (<20%) values obtained from international inter-laboratory study for TD-GC–MS performed in six laboratories also indicated that TD-GC–MS can be used as an international standard method for the quantification of phthalates in polymers.

1. Introduction

Regulations for hazardous substances in electrotechnical products put the emphasis on the need for the protection of human and environmental health and the native economy to consumers, companies, and governments. These regulations influence every step from production to disposal and even recycling of electronic equipment. One of the most typical regulations for hazardous substances is the EU RoHS I (Restriction of the use of certain Hazardous Substances in electrical and electronic equipment) which took effect in 2006 [1]. Similar regulations were enacted by many countries, for example, Japan, J-Moss [2]; Korea, Resource Recirculation law [3]; and China, RoHS [4]. The hazardous substances enforced by RoHS I were lead (Pb), mercury (Hg), Cadmium (Cd), Chromium VI (Cr^{6+}), polybrominated biphenyls (PBBs), and polybrominated diphenyl ethers (PBDEs), and the RoHS directive nominated hexabromocyclododecane (HBCDD) and three kinds of phthalate, dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), and diethylhexyl phthalate (DEHP), as priority substances of RoHS revision II [1].

Among these substances, phthalates are commonly used as the plasticizers in polymer materials [5] due to their powerful ability to increase the flexibility, transparency, durability, and longevity of plastics. However, phthalates in polymer materials, which are used not only for electrotechnical products but also for textiles, toys, and industrial products, are being strongly regulated in many countries because they can affect human health [6,7] and cause diseases such as breast cancer [8] or endocrine disruption [9].

Many standard methods for phthalate analysis in polymer materials have been published worldwide (Table 1) and make the most

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Table 1
Standard methods for the analysis of phthalate in polymer materials [10–17].

Standard	Title of standard	Application scope
BS EN 14372:2004	Child use and care articles- Cutlery and feeding utensils-Safety requirements and tests	Thermoplastic components of cutlery and feeding utensils
ASTM D 7083:04 (2010) e1	Standard practice for determination of monomeric plasticizers in poly(vinyl chloride) (PVC) by Gas Chromatography	PVC compounds
MHLW 0906-4 (2010)	Test method for determination of 6 phthalic acid esters in plasticized materials of toys	Apparatus, container wrapping and toys(baby)
Health Canada Method C-34 (2006)	Determination of phthalates in polyvinyl chloride consumer products	Consumer products made of PVC
CPSC-CH-C1001-09.3 (2010)	Standard operating procedure for determination of phthalates by Gas Chromatography	Plasticized component parts of children's toys & child care articles
BS EN 15777:2009	Textiles, Test methods for phthalates	Textiles
GB/T 22048:2008	Toys and children's products-Determination of phthalate plasticizers in polyvinyl chloride plastic	Toys and children's products-PVC
KS M 1991:2011	Determination of phthalates content in polymer materials	Polymer materials

use of GC–MS analysis after solvent extraction (SE) techniques such as Soxhlet extraction [10–14,17] or THF dissolution [15–17].

Although SE-GC–MS methods were known as the standardized high precision method, SE requires complicated steps with long extraction times using large amounts of solvent; such steps are considered problematic [18]. Recently, a fast quantification method for the phthalates in polymers, using a thermal desorption (TD)-GC–MS method, was developed [19–22] and approved as a new ASTM method (ASTM D7823-14) [23]. By this method, six kinds of phthalate, DBP, BBP, DEHP, di-*n*-octyl phthalate (DNOP), di-*iso*-nonyl phthalate (DINP), and di-*iso*-decyl phthalate (DIDP), can be directly analyzed using a pyrolyzer without any sample pretreatment such as solvent extraction. This standard method meets many regulations for phthalates: EU, Directive 2005/84/EC; US, Consumer Product Safety Improvement Act of 2008 (section 108); Japan, Health, Labor and Welfare Ministry guideline No. 336 (2010). Although this new ASTM method has already been published and other technical notes using TD-GC–MS method have also been reported, a direct comparison of the TD-GC–MS method with the conventional SE-GC–MS method has not yet been reported.

Recently, the International Electronical Committee (IEC) Technical Committee (TC) 111 Working Group 3 (WG 3) handling the international testing methods for environmental standardization for electrical and electronic products has been preparing a new international standard (IEC 62321-8, Phthalates in polymers by pyrolysis (Py)-GC–MS, Direct Inlet Probe (DIP)-Ion Attachment Mass Spectrometry (IAMS), SE-GC–MS and SE-Liquid Chromatography–Mass Spectrometry (LC–MS) for the analysis of seven phthalates (diisobutyl phthalate (DIBP), DBP, BBP, DEHP, DNOP, DINP, and DIDP) in polymers [24,25]. Possible candidate instrumentations for this standard are divided into two groups, depending on the analytical purposes: (1) fast qualitative and screening analysis, and (2) high precision chemical analysis. IEC TC111 WG3 nominated IAMS or TD-GC–MS as the fast qualitative and screening systems and SE-GC–MS or SE-LC–MS methods for the precise quantification analysis of phthalates. For example, a precise SE-GC–MS or SE-LC–MS method has to be performed if the phthalate concentration ranges from 500 to 1500 mg/kg. Although SE-GC–MS and SE-LC–MS have already been established as the precise system for phthalate analysis, sufficient verification for DIP-IAMS and TD-GC–MS had not been performed. Moreover, international inter-laboratory study (IIS) has never been carried out in IEC TC111 WG3. Therefore, IEC TC111 WG3 undertook the first internal IIS in order to confirm the reliability of the TD-GC–MS method as one of the fast qualitative and screening methods.

Table 2
Target phthalates of this study and their monitoring mass information.

Phthalate	Quantitative ion (*m*/*z*)	Confirmation ions (*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

In this study, the effectiveness of the TD-GC–MS method for the analysis of phthalates in polymers was evaluated using various test samples and the obtained results were compared with those results obtained by SE-GC–MS for the first time. Additionally, IIS results for the TD-GC–MS method, organized by IEC TC 111 WG3, were discussed in this study.

2. Experimental

2.1. Samples

The target phthalates are listed in Table 2, and the polymer forms of standard and test samples are listed in Table 3. The reference materials (RMs), which were provided by Japan National Committee, have three different concentration levels of phthalates in polyethylene (PE) films (blank, 80–125 mg/kg and 850–965 mg/kg), and were used as standard samples for the preparation of the calibration curve. One further PE film sample, in which the concentration was 245–295 mg/kg, was prepared by the same manufacturing process as the RMs and used as phthalate test polymer sample (PTPS #1). PTPS #2, produced by Korea Research Institute of Standards and Science (KRISS), is the certified reference material (CRM) in which phthalate concentration ranged from 962 to 989 mg/kg in poly (vinyl chloride) (PVC) resin. The industrial rubber sample, donated by the Hyundai Motor Company, was also used as a test sample (PTPS #3) to evaluate the possibility of analysis of a high concentration of phthalates (around 2%) in nitrile-butadiene rubber (NBR). The expected concentration values in all RMs and PTPSs, except PTPS #3, were pre-evaluated via the EN 14372 standard method which is based on the solvent extraction method followed by GC–MS (Table 3).