Study on Primary Screening Method of Phthalic Esters for RoHS 2 Directive

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In the revised RoHS Directive (RoHS 2) that will become effective on 22nd July 2019, 4 phthalic esters are added as restricted substances, so it is urgent to construct an acceptance inspection system at the manufacturing bases. The pyrolysis/thermal desorption -GC/MS (Py/TD-GC/MS) official method in IEC 62321-8 determined by IEC, is an excellent method of accuracy and traceability, but it is not suitable for acceptance inspection at manufacturing bases because of its high equipment introduction cost and necessary of expertise for device management. Therefore, we investigated thin layer chromatography (TLC) and direct injection - mass spectrometry (DI-MS) for primary screening. In the study, enough detection sensitivity was gained in both methods. But it was found that some problems in these methods to use at manufacturing bases. To select the screening method, it is necessary to consider cost, accuracy, operability, and so on.

1. Introduction

In the EU, the RoHS Directive was revised on July 22, 2019 [1)], and most electronic and electrical equipment is regulated by a new regulation. As the revise adds 4 phthalic esters (DIBP, DBP, BBP, and DEHP), the restricted substances have been expanded from 6 to 10. The threshold for all phthalic esters is 1000 mg·kg^{-1}.

The molecular structures of these phthalic esters are shown in Figure 1. These phthalic esters are mainly used as plasticizers for polyvinyl chloride (PVC), which is material for wire coating and insulation tapes. So electric wire companies, electronic/electrical component manufacturers, and set manufacturers are urgently required to comply with the RoHS 2.

A screening method using at manufacturing bases that can easily detect restricted substances in raw materials or products was required. Elemental analysis by X-ray fluorescence (XRF) has been used for screening of preceding 6 restricted substances of RoHS. However, since the phthalic esters do not have characteristic elements, screening by XRF cannot be applied, and it is necessary to introduce a new method.

IEC 62321-8, the international standard for IEC, shows the official analysis method, solvent extraction-GC/MS for precision analysis, and Py/TD-GC / MS for screening. [2)]. However, it is difficult to introduce Py/TD-GC/MS equipment for screening at all domestic and overseas manufacturing bases. In this study, we first described the outline of the official method, and then focused on the TLC and DI-MS which are not official but inexpensive and simple analysis methods. Finally, by comparing each method, the recommended method was selected as the most suitable for screening.

2. Official screening method, Py/TD-GC/MS

The appearance and outline of the Py/TD-GC/MS were shown in Figure 2. In this method, sample is

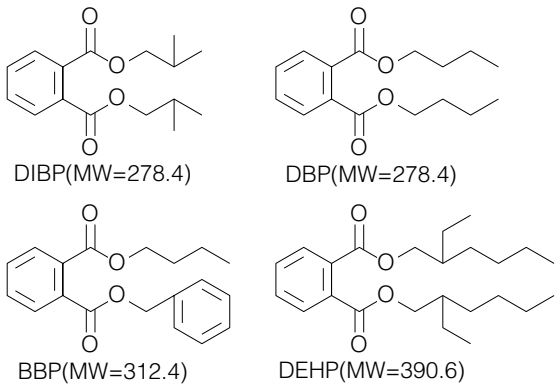

Fig. 1. Structure of phthalic esters.

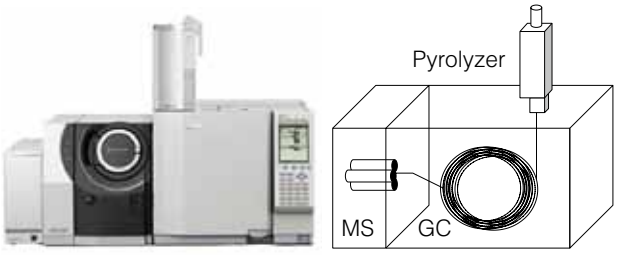

Fig. 2. Appearance and schematic diagram of Py/TD-GC/MS.

1 Advanced Material Technology & Analysis Center

Panel 1. Abbreviations, Acronyms, and Terms.

IEC—International Electrotechnical Commission
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GC/MS—Gas Chromatograph / Mass Spectrometer
RoHS Directive
Directive on the Restriction of the Use of Certain Hazardous Substances in Electrical Equipment

instantaneously pyrolyzed in a pyrolyzer. And volatile components are introduced into GC / MS for qualitative and quantitative analysis.

According to IEC62321-8, semi-quantitative values obtained by Py/TD-GC/MS are judged as follows. Less than 500 $mg \cdot kg^{-1}$; less than RoHS 2 threshold, 500-1500 $mg \cdot kg^{-1}$; gray zone, sample should be analyzed by precision analysis method, and 1500 $mg \cdot kg^{-1}$ or higher; exceeds RoHS 2 threshold.

The advantage of the Py/TD-GC/MS method is that the data is compelling because it is an official method. And the GC/MS can also be used for precision quantification analysis. On the other hand, its disadvantages are high equipment costs, continuous use of helium which continues to be difficult to supply, and expertise required for measurement and maintenance. The equipment manufacturers explained that even non-experts can easily measure by using dedicated screening software and jigs. However, the introduction of equipment at each manufacturing base requires a lot of cost and human burden, so Py/TD-GC/MS is not introduced very much like XRF in the first RoHS directive.

3. Study of screening method by TLC

3.1 Outline of TLC and experiments

We focused on TLC as a screening method that can be implemented at manufacturing bases. The outline of TLC is shown in Figure 3. The extracted solution obtained from the sample is applied on the reference line of the TLC plate, and the lower part is immersed in the mobile phase. Components in solution are drawn up the plate via capillary action. Because different analytes ascend the TLC plate at different rates, separation is achieved. Since the low cost and simplicity of TLC method in which using only plate and solvents, we have studied its application in primary screening [3) 4)].

Reverse phase type was selected for the TLC plate, and chromatographic grade solvents were used for extraction and mobile phases. A commercially available black light was used to detect the substances. The wire coating PVC with a known formulation and NMIJ SRM 8151-a (polypropylene base material) certified standard material of AIST were selected as resin samples.

3.2 Results and discussion

Separation by TLC of 4 phthalic esters, other plasticizers and other resin additives which could interfere with their detection was attempted.

First, the extraction solvent was investigated. The extraction rates of phthalic esters from resin samples using 4 solvents which have different polarity were shown in Figure 4. When acetone / n-hexane was used as the extraction solvent, a recovery rate was almost 100%. However, in consideration of safety when using at a manufacturing base, we selected ethanol as the extraction solvent in spite of low recovery rate (40%). Next, the mobile phase of TLC was investigated. The phthalic esters were separated using methanol, THF, and acetonitrile, which are known as mobile phases for reverse phase type TLC. With methanol or THF, the separation and elution of each component was insufficient, but acetonitrile was found to be sufficient.

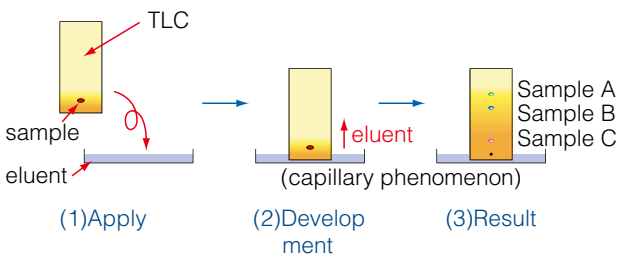

Fig. 3. Outline of TLC method.

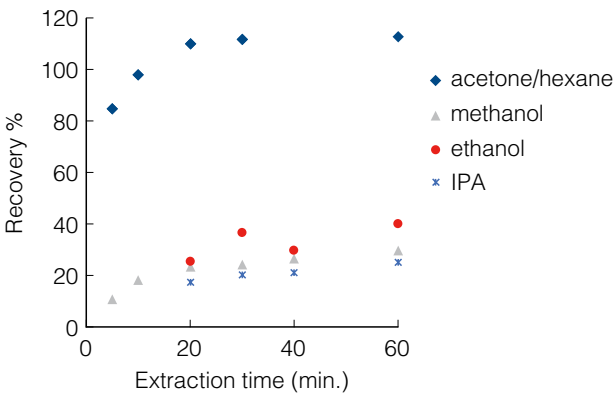

Fig. 4 . DEHP extraction recovery rate with various solvents.

The result of TLC experiment was shown in Figure 5. When in which mobile phase was selected 9 : 1 mixture of acetonitrile and water in order to adjust the dissolubility, phthalic esters were well separated. It was found that phthalic esters in PVC sample were separated and detected with a detection limit of 500 $mg \cdot kg^{-1}$ by TLC screening using obtained conditions.

3.3 Problems and trends of TLC screening

By TLC screening, phthalic esters in PVC samples could be detected with a detection limit of 500 $mg \cdot kg^{-1}$. But the solvent extraction efficiency of phthalate ester in polypropylene, a nonpolar resin, was very low, indicating that the extraction solvent must be changed. Measurement conditions cannot be changed for each sample, resulting in errors in measurement results. So it was difficult to use our TLC method for primary screening at manufacturing bases.

On the other hand, the investigation results of screening method by TLC were recently reported [5]. If the above-mentioned problems can be solved, it may be applicable to screening.

4. Study of screening method by DI-MS

4.1 Outline of DI-MS and experiments

Py/TD-GC/MS determined in IEC62321-8 takes about 15 to 30 minutes for one measurement. In addition, if the sample contains high-boiling compound or high concentration components, a blank run must be inserted after measurement to remove them remaining in the device. Therefore, we focused on DI-MS as a screening method that can be measured in a shorter time than Py/TD-GC/MS [6] [7]. Since this method is a configuration in which a DI probe is attached to the GC/MS, it is assumed that the GC/MS is owned. However, compared to Py/TD-GC/MS, the measurement can be expected in a shorter time, and the introduction cost is lower than the pyrolyzer of Py/TD-GC/MS.

For the study of the measurement method, GC/MS (Shimadzu QP-2010ultra) with an optional DI probe (Shimadzu DI-2010) attached was used. DI probe Appearance was shown in Figure 6. In this analysis, a weighed sample is placed in a glass vessel for DI. The vessel is set on a DI probe and inserted into an MS ion source for mass spectrometry. Target substances such as phthalic esters are detected and semi-quantified.

Because the DI method is suitable for the analysis of low-volatile substances, it was found that DBP and DIBP with relatively low molecular weight volatilized before the start of measurement and could not be analyzed accurately. To solve this problem, the resin coating technique in direct mass spectrometry reported by Tsugoshi et al [8] [9]. was applied. In this method, the volatilization of low molecular weight compounds is suppressed by forming a polystyrene (PS) coating film on the surface of the sample.

4.2 Results and discussion

The DI chromatogram of phthalic esters with and without PS coating were shown in Figure 7. Without coating, DBP was vaporized before the start of analysis. On the other hand, with coating, good chromatogram was obtained because DBP volatilization started after PS was heated and softened. The measurement time for one analysis was 5 minutes or less, and it was possible to shorten the measurement time compared to Py/TD-GC/MS.

The relationship between the amount of DEHP loaded to DI probe and the chromatogram peak area

Fig. 5. Results of separation of phthalic esters by TLC.

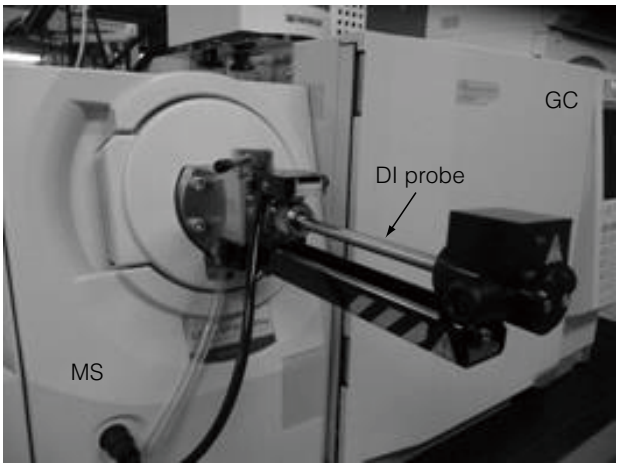

Fig. 6. Appearance of DI probe.

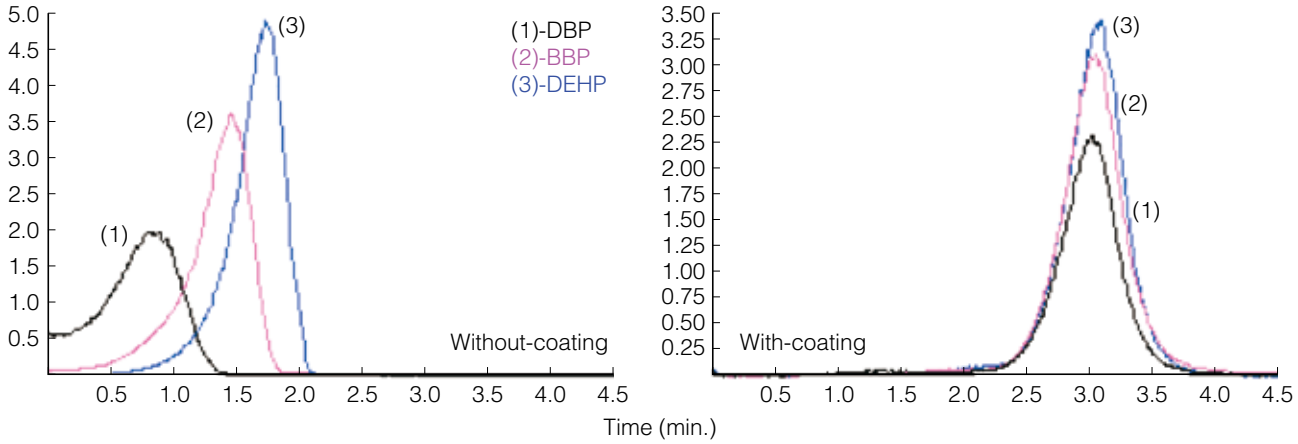

Fig. 7. DI chromatogram of phthalate ester.

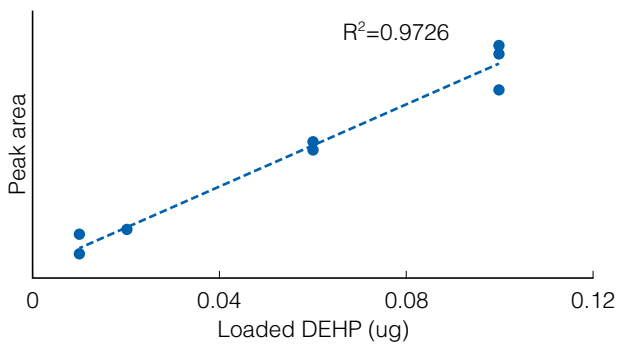

Fig. 8. Relationship between DEHP introduction amount and DI chromatogram peak area.

were shown in Fig. 8. It was found that sufficient sensitivity was obtained for a threshold of 1000 mg·kg^{-1}, and semi-quantitative analysis was possible. Well detection sensitivity and quantitative performance were obtained for other phthalic esters same as DEHP. And it was confirmed that a quantitative value of about ± 20% of the certified value of the certified standard material was obtained by DI-MS measurement.

Furthermore, in the analysis of PVC for electric wires containing about 20 wt% of phthalic ester that is not subject to the RoHS 2, a trace amount of DEHP was detected without interference by the phthalic ester. Thus, this method was found to be useful as a screening method.

4.3 Problems of DI-MS

Although screening by DI-MS is simple and can be performed in a short time, it cannot be applied to manufacturing bases that do not have GC/MS. In addition, since this method cannot be measured automatically at present, continuous measurements of many samples are difficult.

5. Other screening methods

5.1 Infrared spectroscopy (IR)

The IR is suitable for screening because it is easy to operate, inexpensive, and almost maintenance-free. On the other hand, the low sensitivity of IR is a problem for applying to screening (IR is 3 or more orders of magnitude less sensitive than GC/MS). Instrument manufacturers have investigated phthalic esters screening technique by IR, but currently no device or method has been developed that can reliably screen for a threshold of 1000 mg·kg^{-1}.

5.2 Thermal desorption mass spectrometry (TD-MS)

TD-MS is a method in which a sample is heated and the volatilized components are introduced into a mass spectrometer for analysis. An analysis by TD-MS has the advantage that the measurement time is shorter than GC/MS because the components are not separated by chromatography. Conversely, it is difficult to separate the same molecular weight components, for example, DIBP and DBP cannot be distinguished.

Hitachi High-Tech Science launched HM1000, a dedicated TD-MS device for screening phthalic esters [10]. Since this equipment uses nitrogen instead of helium as the carrier gas, it has a lower running cost than GC/MS. And the measurement operation is simple and almost no maintenance work is required by the equipment user. Therefore, HM1000 is a suitable device for the purpose of "screening routinely performed by users at manufacturing bases who do not have expertise of analysis". The current disadvantages of HM1000 are that the equipment price is as high as GC/MS, and it is not the official method determined in IEC62321.

Table 1. Comparison of screening methods.

Analytical method	official method	sensitivity	cost	operability	expertise	multiple measurement	maintenance
Py/TD-GC/MS	Yes	Excellent	Bad	Average	Bad	Good	Bad
TLC	No	Average	Excellent	Good	Average	Average	Good
DI-MS	No	Good	Average	Good	Average	Bad	Average
IR	No	Bad	Good	Excellent	Excellent	Bad	Excellent
TD-MS	No	Good	Average	Excellent	Good	Good	Good
IAMS	Yes	Excellent	Bad	Good	Average	Average	Average

5.3 Ion attachment mass spectrometry

IAMS (ion attachment mass spectrometry) is mentioned in IEC62321-8 as a reference method for screening. IAMS is a method similar to TD-MS and can be measured easily and in a short time. However, the device is expensive because it is made to order. Therefore, it is difficult to introduce as a screening device.

6. Comparison of methods

The results of a comparative study of the methods mentioned in this report were summarized in Table1. The primary screening method at the manufacturing bases must satisfy low cost, operability, measurement sensitivity and so on. But unfortunately, no method has been found that satisfies all of them. Although it is not an official method at present, TLC method with cost merit and TD-MS method with simple operability are relatively recommended methods. For introducing the equipment, it is important to select according to the situation and purpose of each manufacturing base.

7. Conclusion

To comply with RoHS 2, TLC and DI-MS methods for primary screening methods of phthalic esters were studied. And they were compared with other analytical methods. At present, no method has been found that satisfies all the requirements such as cost, operability, and measurement sensitivity required for screening at manufacturing bases. It is important that the screening method is selected according to the situation and purpose of each manufacturing base. And construction of system to compensate for the disadvantages of each screening method is needed.

References

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