SHIMADZU

Application News

Gas Chromatography Mass Spectrometry No.M259

Analysis of Dibutyltin Compounds in Polyvinyl Chloride Products by GC/MS

■ Introduction

Organotin compounds are used widely throughout the world in pesticides, fungicides, wood preservatives, and adhesives. Since organotin compounds are also added to plastics such as polyvinyl chloride (PVC) for thermal stabilization and stabilization against catalytic activity, dibutyltin (DBT) compounds in PVC are now subject to a standard limit established in Japan's Food Sanitation Act. In the material testing[1)] of this material in its food packaging form, the DBT peak elution time and area value in the test solution and standard solution are compared, and the peak area in the test solution must be smaller than that in the standard solution (concentration of 50 µg/g or less in sample; corresponding to a concentration of 1 µg/mL standard solution). In this Application News, we introduce an example of analysis of DBT compounds in a PVC product.

■ Analytical Method

Sample Preparation

Sample preparation was conducted according to that specified in "Section 3: Implements, Containers, and Packaging in the Standards and Criteria for Food and Food Additives, etc."[1)] under Japan's "Food Sanitation Act" as specified in the Ministry of Health, Labour and Welfare notification No. 201. Accordingly, solvent extraction was conducted under acidic conditions (hydrochloric acid), followed by derivatization using sodium tetraethylborate. Analysis was carried out by GC/MS. The sample consisted of a 5 mm piece of a glove made of PVC. The standard solution and test solution were prepared as shown in Fig. 1 and Fig. 2 as specified in the standard, and the GC/MS analytical conditions used are shown in Table 1.

Table 1 Analytical Conditions

Model	: GCMS-QP2010 Plus
-GC-	
Column	: Rtx-5MS (30 mL. × 0.25 mmI.D. df = 0.25 µm)
Col.Temp.	: 45 ˚C (4 min) -15 ˚C/min-300 ˚C (10 min)
Carrier Gas	: He (33 cm/sec, 39.5 kPa)
Carrier Gas Mode	: Constant Linear Velocity Mode
Inj.Temp.	: 250 ˚C
Injection Method	: Splitless Injection
Sampling Time	: 1 min
Injection Volume	: 1 µL
-MS-	
I.F. Temp.	: 250 ˚C
I.S. Temp.	: 200 ˚C
Ionization	: EI
Scan Range	: *m/z* 40-500
Scan Interval	: 0.5 sec
Monitor Ion	: *m/z* 263, 261
SIM Interval	: 0.2 sec

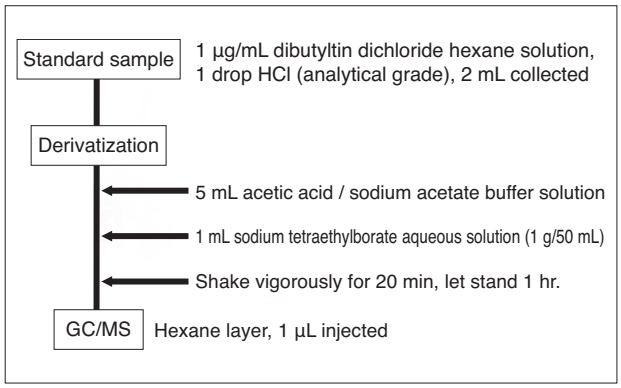

Fig. 1 Preparation of DBT Standard

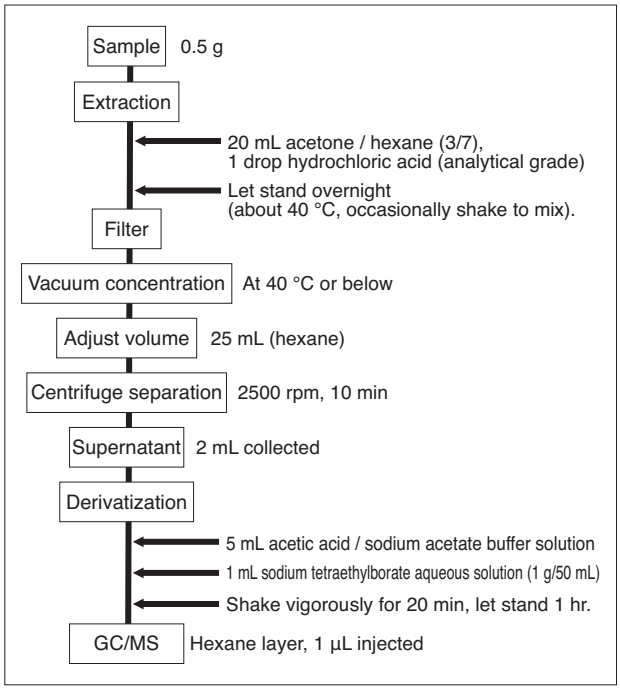

Fig. 2 Preparation of PVC Sample

■ Results and Discussion

Scan

A 1 µg/mL standard sample of DBT (corresponding to 50 µg/g concentration in sample) was prepared and subjected to derivatization.

A 5 mm piece of a glove (0.5 g) made of PVC was subjected to solvent extraction in hydrochloric acid, and the derivatized solution was used as the blank solution. Then, the same solvent extraction solution was spiked with DBT at a concentration of 0.1 µg/mL (1/10 the concentration of that specified in the standard), and the derivatized solution was used as the spiked solution.

Fig. 3 shows the TIC chromatograms obtained from scan measurement of the standard sample, and the blank and spiked samples, and Fig. 4 shows the mass spectra of the derivatized DBT in the standard sample and PVC-spiked sample. From the mass chromatogram of *m/z* 263, the peak is detected in the full-scan analysis even at 1/10 the concentration (0.1 µg/mL) of the specified DBT concentration limit. Furthermore, the mass spectrum also matches that of the standard sample, without any evidence of interference from the matrix.

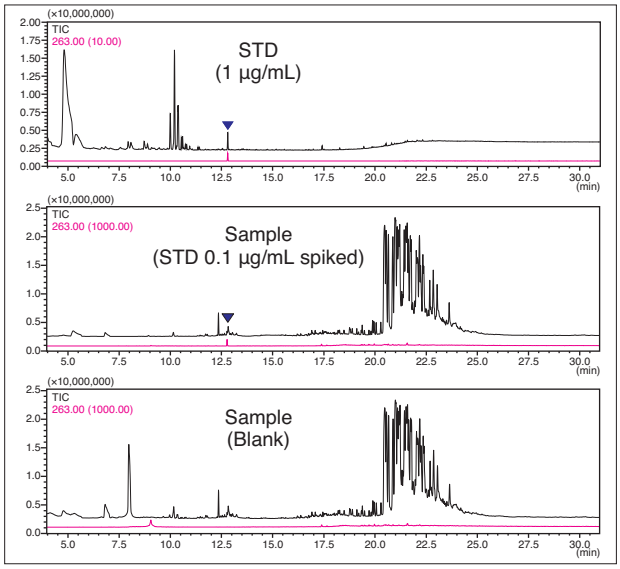

Fig. 3 TIC Chromatograms of Derivatized DBT Standard and PVC Sample (Glove Fragment)

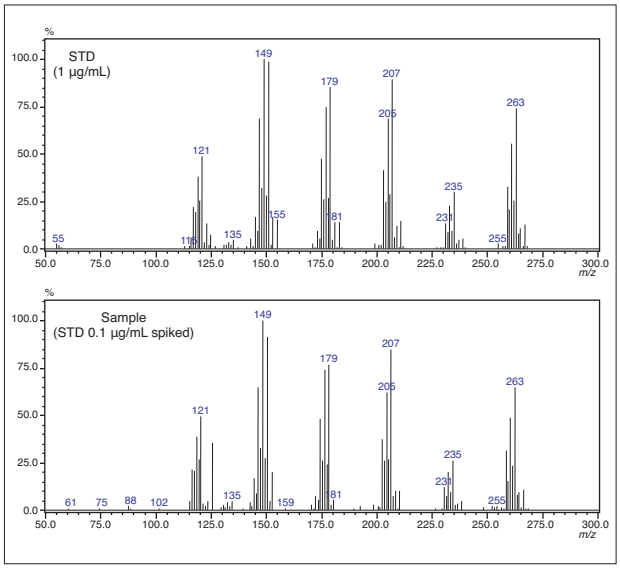

Fig. 4 Mass Spectrum of Derivatized DBT in Standard and in PVC Sample (DBT 0.1 µg/mL spiked)

SIM

The Food Sanitation Act specifies in the testing inspection protocol that assessment be based on a comparison of the sample with the standard substance. However, quantitation was conducted here with respect to an actual sample based on a generated calibration curve. SIM measurements of derivatized samples of DBT using concentrations of 0, 0.01, 0.05, 0.1, 0.5 and 1 µg/mL, respectively, were conducted to generate the calibration curve, and the result of quantitation of an actual sample (blank) confirmed that the level of DBT in the sample was less than 0.01 µg/mL.

The mass chromatogram of the standard sample (0.01 µg/mL) is shown in Fig. 5, and the calibration curve is shown in Fig. 6. The calibration curve shows excellent linearity, with an R^2 value of 0.9999.

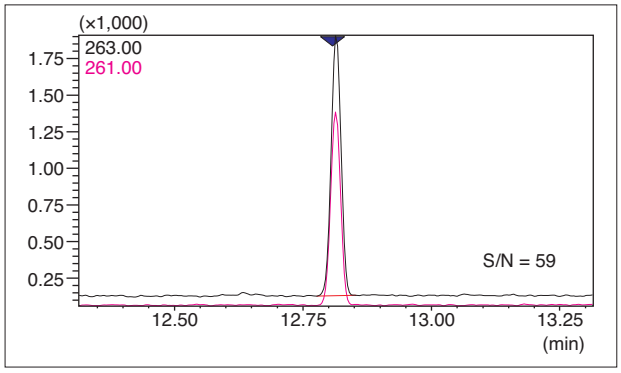

Fig. 5 Mass Chromatogram of Derivatized DBT Standard (0.01µg/mL)

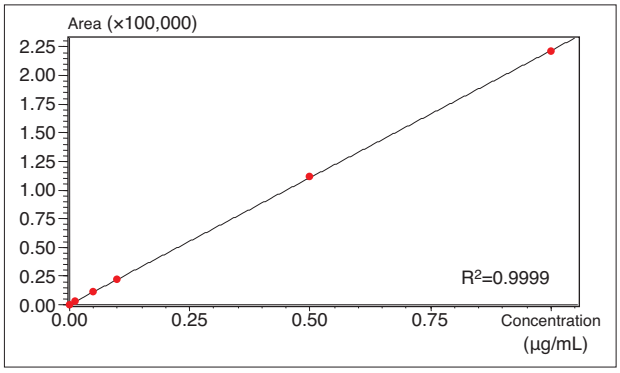

Fig. 6 Calibration Curve of Derivatized DBT

References

1) March 31, 2006 Ministry of Health, Labour and Welfare Notification No. 201
Section 3: Implements, Containers, and Packaging in the Standards and Criteria for Food and Food Additives, etc.

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