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Analytical methods for phenyltin compounds in polychlorinated biphenyl-based transformer oil samples

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Abstract

We present the first study on the analytical methods of phenyltin compounds (PTs) in polychlorinated biphenyl (PCB)-based transformer oil samples. Tetraphenyltin (TePhT) has been used as stabilizer for some kinds of PCBs-based transformer oil formulations. Monophenyltin (MPhT), diphenyltin (DPhT) and triphenyltin (TrPhT) could have been formed from TePhT during long-term use. TePhT was directly measured by gas chromatograph (GC) connected with three types of detectors, a mass spectrometer (MS), a flame photometric detector (FPD) and an atomic emission detector (AED) after dilution with hexane. MPhT, DPhT and TrPhT were propylated with Grignard reagent before measurement. The MS was the most sensitive of the detectors, with detection limits of phenyltin compounds of 30 ng/ml (MPhT), 9.8 ng/ml (DPhT), 5.5 ng/ml (TrPhT) and 0.60 ng/ml (TePhT), respectively. From the viewpoint of selectivity, MS was slightly worse than other detectors, but interference from PCBs matrices was not significant under ordinary analytical conditions. Two used transformer oil samples were analyzed using the analytical methods developed in this study. TePhT and TrPhT were found in both samples.

Keywords: Oils; Detection, GC; Phenyltin compounds; Organotin compounds; Polychlorinated biphenyls

1. Introduction

Several transformer manufacturers have recently announced that some used transformer oils, containing about 60% polychlorinated biphenyls (PCBs), contain tetraphenyltin (TePhT) as a stabilizing agent. The purpose of adding stabilizer was to scavenge the hydrochloric acid generated from PCBs by electrical discharges during use of the transformer. However, records are incomplete as to what type of transformers contain tetraphenyltin, since several transformer manufacturers used different kinds of stabilizers at different times. In Japan, the law concerning special measures on the promotion of appropriate management of waste PCBs requires that waste PCBs be treated within 15 years was enacted on 15 June 2001 [1]. Since the waste containing PCBs from about 50 000 stored transformers must be destroyed without causing new pollution derived from tin compounds, it is an urgent and important task to identify which wastes contain TePhT. It is also necessary to confirm whether and how TePhT is broken down during PCBs

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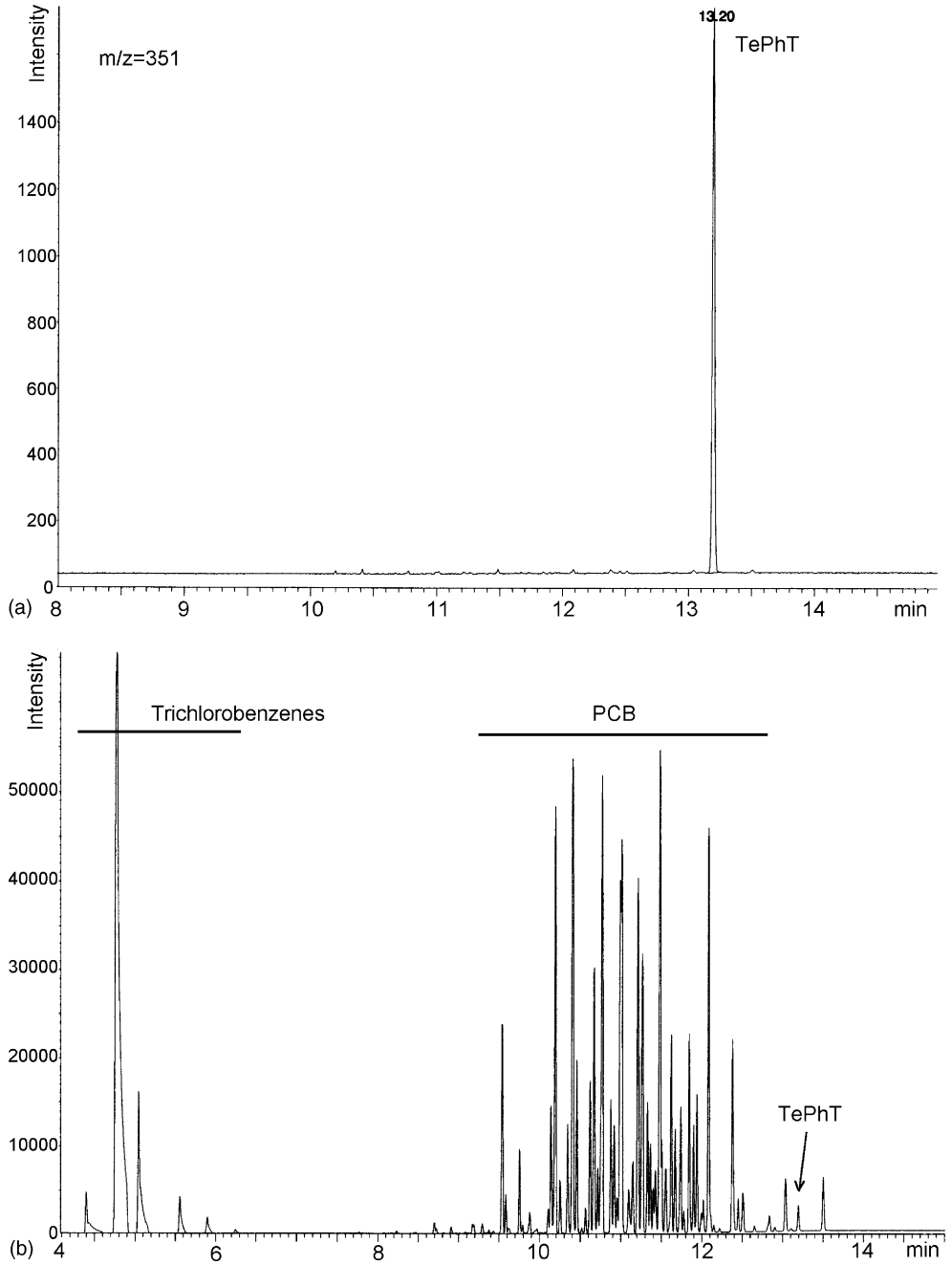

Fig. 1. SIM chromatograms of transformer oil simulant spiked with TePhT (TePhT: 0.1 μg/ml, PCBs: 1000 μg/ml). (a) SIM chromatogram ($m/z = 351$); (b) total ion chromatogram ($m/z = 351$, 197, 120).

treatment processes, of which several chemical treatment processes other than incineration are planned. TePhT, a typical organometallic stabilizer [2–4], is a toxic and bioaccumulative compound. Worse, triphenyltin (TrPhT) could have been formed from TePhT. TrPhT is more toxic and, due to its history of use as an agrochemical and antifouling agent, is known to be an endocrine disrupter. Therefore, it is essential to be able to identify phenyltin compounds (PTs) in waste transformer oil.

Analysis of PTs using HPLC [5], SFC [6,7] and gas chromatograph (GC) [8–26] has been reported, but only for environmental samples. Since typical transformer oil comprises about 60% PCBs and 40% trichlorobenzenes, these matrices may interfere with the analysis of PTs. For application to waste oil, it is important to investigate if there are any effects from the matrices.

In this study, we have developed methods for analyzing PTs in PCBs-based transformer oil samples. Analytical procedures of TePhT and other PTs are described and comparisons of GC-MS, GC-flame photometric detection (FPD), and GC-atomic emission detection (AED) are presented, along with quantitative results for PTs in used transformer oil.

2. Experimental

2.1. Materials and samples

Tetraphenyltin (>97%) was purchased from Aldrich. Triphenyltin chloride (>98%), diphenyltin dichloride (>96%), and phenyltin trichloride (>98%) were purchased from Strem Chemicals (Newburyport, MA, USA). Tripentyltin chloride (TrPeT, >95%) used as the internal standard was purchased from Kanto Kagaku (Tokyo, Japan). Separate stock solutions of phenyltin compounds (1000 μg/ml) were prepared by dissolving 20 mg in 20 ml of benzene. Stock solution of TrPeT (1000 μg/ml) was prepared by dissolving 10 mg of TrPeT in 10 ml of hexane. All solutions were stored in a refrigerator (4 °C). A set of TePhT calibration solutions (0.001–10 μg/ml) was prepared by stepwise dilution of stock solution with hexane. A set of mono- to triphenyltin calibration solutions (0.01–100 μg/ml) was prepared by taking each stock solution and stepwise diluting with hexane. TrPeT spike solution (1 μg/ml) was prepared by dilution of stock solution with hexane. A tetrahydrofuran (THF) solution of *n*-propylmagnesium bromide (approximately 2 mol/l) was purchased from Tokyo Kasei Kogyo (Tokyo, Japan). Hexane, benzene, sulfuric acid, and sodium sulfate were of pesticide analysis grade and obtained from Wako (Osaka, Japan). Purified water was prepared using the Millipore EDS-5 water purification system (Billerica, MA, USA). For the examination of the analytical procedure, transformer oil simulants were used. Transformer oil simulants were prepared by spiking phenyltin solutions with hexane solutions of Kanechlor 1000. Kanechlor 1000 is composed of 60% PCBs (Kanechlor 500) and 40% trichlorobenzenes.

Two PCB-based transformer oil waste samples were collected. Sample A was manufactured by Toshiba (Tokyo, Japan) in 1959, used for 33 years and kept for 11 years. Sample B was manufactured by Hitachi (Tokyo, Japan) in 1961, used for 29 years and kept for 13 years. Their type of PCBs formulation was Kanechlor 1000.

2.2. Instruments

Gas chromatographs connected with three types of detection systems—mass spectrometer (MS), FPD and AED were used for measurements.

Table 1
The peak area counts, calibration curves and detection limits of TePhT measured using three detection techniques

	MS	FPD	AED
Area counts (μg/ml)			
0.001	298 (5.0)[a]	N.D.	N.D.
0.01	2470 (12)	8.76 (6.7)	1.43 (24)
0.1	21700 (5.0)	56.7 (10)	4.46 (23)
1	280000 (6.3)	514 (0.90)	34.3 (14)
Intercept	−2130	4.70	0.749
Slope	281000	509	32.4
Correlation coefficient	0.9995	1	0.9987
Detection limits[b] (ng/ml)	0.60	20	30

[a] Average of the peak area counts is presented ($n = 3$). R.S.D. values are also presented in parentheses.
[b] Calculated from $S/N = 3$.

An Agilent Model 6890 gas chromatograph equipped with a Model 7673 automatic liquid sampler and an HP-5MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) was used (Palo Alto, CA, USA). Pure helium was used as the carrier gas at a flow rate of 1 ml/min (MS) or 1.6 ml/min (FPD, AED). Injection mode was splitless and the injection port temperature was maintained at 290 °C. Injection volume was 1 μl. The oven temperature was programmed as follows: 1 min at 80–300 °C at 20 °C/min, and 3 min hold at 300 °C.

For MS detection, an Agilent Model 5973N mass selective detector was used and operated in selected ion monitoring (SIM) mode. Ionization method was electron ionization (70 V). Interface temperature was set at 295 °C. Ionization chamber temperature was maintained at 230 °C. The mass numbers of monitored ions were as follows: 283 and 281 for monophenyltin, 317 and 315 for diphenyltin, 351 and 349 for TrPhT, 351, 197 and 120 for TePhT, 305 and 333 for TrPeT. Dwell time was 50 ms.

For FPD, an Agilent Model G2333A flame photometric detector was used. Detector temperature was set to 250 °C. Makeup gas was He at a flow rate of 60 ml/min. H_2 flow rate was 125 ml/min. Flow rate of air was 100 ml/min. A Sn filter (610 nm) was used.

For AED, an Agilent Model G2350A atomic emission detector was used. Interface temperature was

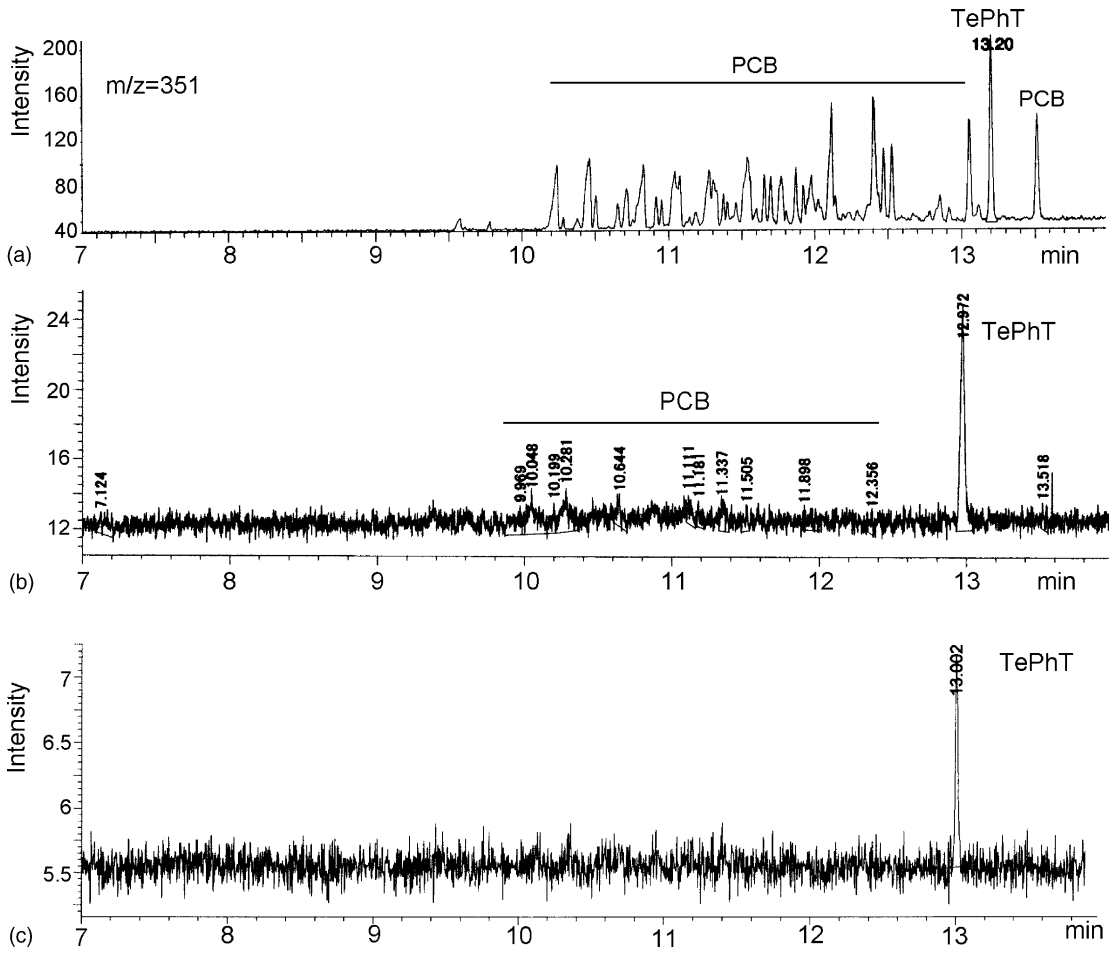

Fig. 2. Interference in detecting TePhT by MS from PCB congeners at 1% level of concentration (TePhT: 0.01 μg/ml, PCBs: 10 000 μg/ml). (a) Measured by MS; (b) measured by FPD; (c) measured by AED.

Table 2
The peak area ratios, calibration curves, and detection limits of PTs measured using three detection techniques

	MS			FPD			AED		
	MPhT	DPhT	TrPhT	MPhT	DPhT	TrPhT	MPhT	DPhT	TrPhT
Area counts (μg/ml)									
0.01	0.0112 (12)[a]	0.0170 (5.2)	0.429 (6.1)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
0.1	0.0867 (9.3)	1.35 (1.7)	4.85 (1.9)	0.0619 (20)	0.537 (1.3)	0.852 (1.7)	0.156 (4.4)	0.568 (11)	0.842 (14)
1	4.41 (8.1)	19.7 (11)	50.7 (5.1)	2.28 (10)	7.17 (7.6)	7.39 (11)	2.13 (7.6)	6.48 (21)	8.11 (13)
Intercept	−0.195	−0.406	−0.151	−0.0957	−0.130	0.0152	−0.0407	−0.0757	−0.0296
Slope	0.456	2.01	5.08	0.230	0.729	0.739	0.218	0.655	0.815
Correlation coefficient	0.9955	0.9995	1.000	0.9966	0.9998	0.9995	0.9997	1.000	0.9998
Detection limits[b] (ng/ml)	30	9.8	5.5	180	24	16	180	33	21

[a] Average of the peak area ratios is presented ($n = 3$). R.S.D. values are also presented in parentheses.
[b] Calculated from $S/N = 3$.

set at 290 °C. Cavity temperature was set at 290 °C. Makeup gas was He at a flow rate of 200 ml/min. H_2 supply pressure was 207 kPa. O_2 supply pressure was 138 kPa. Wavelength for Sn detection was 301 nm.

2.3. Analytical procedure for TePhT in transformer oil samples

Transformer oil simulant was diluted with hexane. The concentration of PCBs was adjusted to about 1000 μg/ml. The diluted sample was directly injected into the GC. TePhT was quantified using the external standard.

2.4. Analytical procedure for MPhT, DPhT and TrPhT in transformer oil samples

Diluted transformer oil simulant (PCBs: 1000 μg/ml, 1 ml) was taken into a large test tube (50 ml). An aliquot of TrPeT spike solution (100 ng as TrPeT)

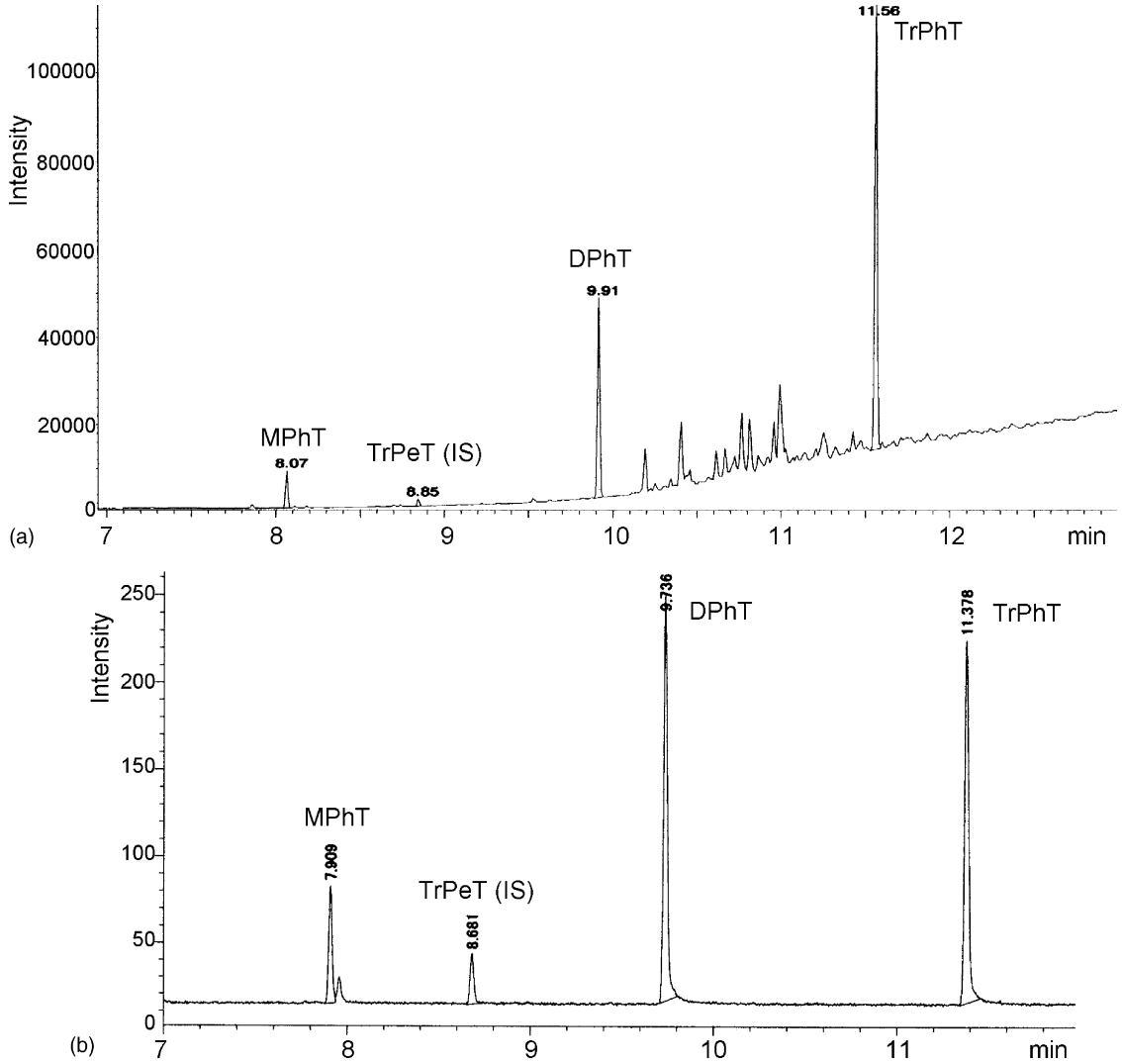

Fig. 3. Chromatograms of transformer oil simulant spiked with PTs (PTs: 1 μg/ml each, TrPeT: 0.1 μg/ml, PCBs: 1000 μg/ml). (a) Measured by MS; (b) measured by FPD; (c) measured by AED.

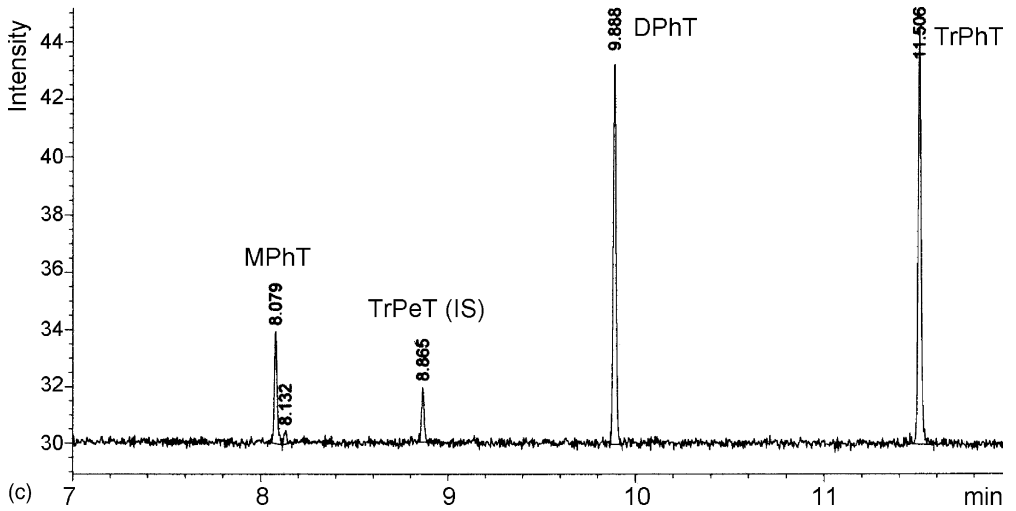

Fig. 3. (*Continued*).

was added to the sample as an internal standard. The sample was then derivatized by addition of *n*-propylmagnesium bromide solution (2 mol/l) and allowed to stand for 60 min at room temperature. After reaction, the excess reagent was quenched by dropwise addition of 10 ml of 0.5 mol/l sulfuric acid while cooling in an ice bath. The derivatized sample was then transferred into a separating funnel containing 50 ml of purified water and 20 ml of 10% (v/v) benzene in hexane. The sample was extracted by shaking for 10 min. The organic layer was separated and dried with anhydrous sodium sulfate, and then concentrated in a rotary evaporator. The concentrated extract was transferred to a test tube and further concentrated to 1 ml with a purified nitrogen stream. PTs were quantified by internal standard.

2.5. Analysis of PTs in transformer oil waste samples

PTs in transformer oil waste samples were analyzed using the analytical method described above. Initially, transformer oil waste sample (1 g) was dissolved in 10 ml of hexane. For the analysis of TePhT, the initial sample solution was diluted 100 times with hexane and then measured by GC-MS. For the analysis of MPhT, DPhT and TrPhT, the initial solution was diluted 10 times with hexane and then propylated and measured by GC-MS. Since interference with TrPhT from PCBs was observed using GC-MS as we discuss below, the levels of TrPhT were confirmed using GC-FPD and AED.

3. Results and discussion

3.1. Examination of the analytical procedure for TePhT in transformer oil samples

TePhT was analyzed by GC without derivatization. A typical TePhT chromatogram measured by GC-MS is presented in Fig. 1. The shape of the TePhT peak was good, with no tailing or leading observed. TePhT eluted after trichlorobenzenes and was separated from PCB congeners using the GC parameters

Table 3
The levels of PTs in the two investigated transformer oil waste samples

Sample	MPhT (μg/g oil)	DPhT (μg/g oil)	TrPhT (μg/g oil)	TePhT (μg/g oil)
A	N.D.[a]	N.D.	36 (3.4)[b]	720 (7.6)
B	N.D.	N.D.	4.9 (8.5)	69 (16)

[a] Detection limits were 3.0 μg/g oil (MPhT), 0.98 μg/g oil (DPhT), 0.55 μg/g oil (TrPhT) and 0.60 μg/g oil (TePhT), respectively.

[b] R.S.D. values are in the parentheses ($n = 3$).

described above. Therefore, no cleanup procedure may be needed if PCBs are the only contaminants observed.

Many types of GC detection methods, such as MS [8–11], FPD [12–16], AED [17–21], atomic absorption spectrometry (AAS) [22] and inductively coupled plasma (ICP)-MS [23–26] are used for detecting organotin compounds. Though GC-ICP-MS is the most sensitive of these detectors, this type of detector is very expensive and not commonly used. The sensitivity of GC-AAS is comparable to FPD and AED, but commercial GC-AAS systems are not available. In this study, we compared MS, FPD and AED from the viewpoint of sensitivity, reproducibility and

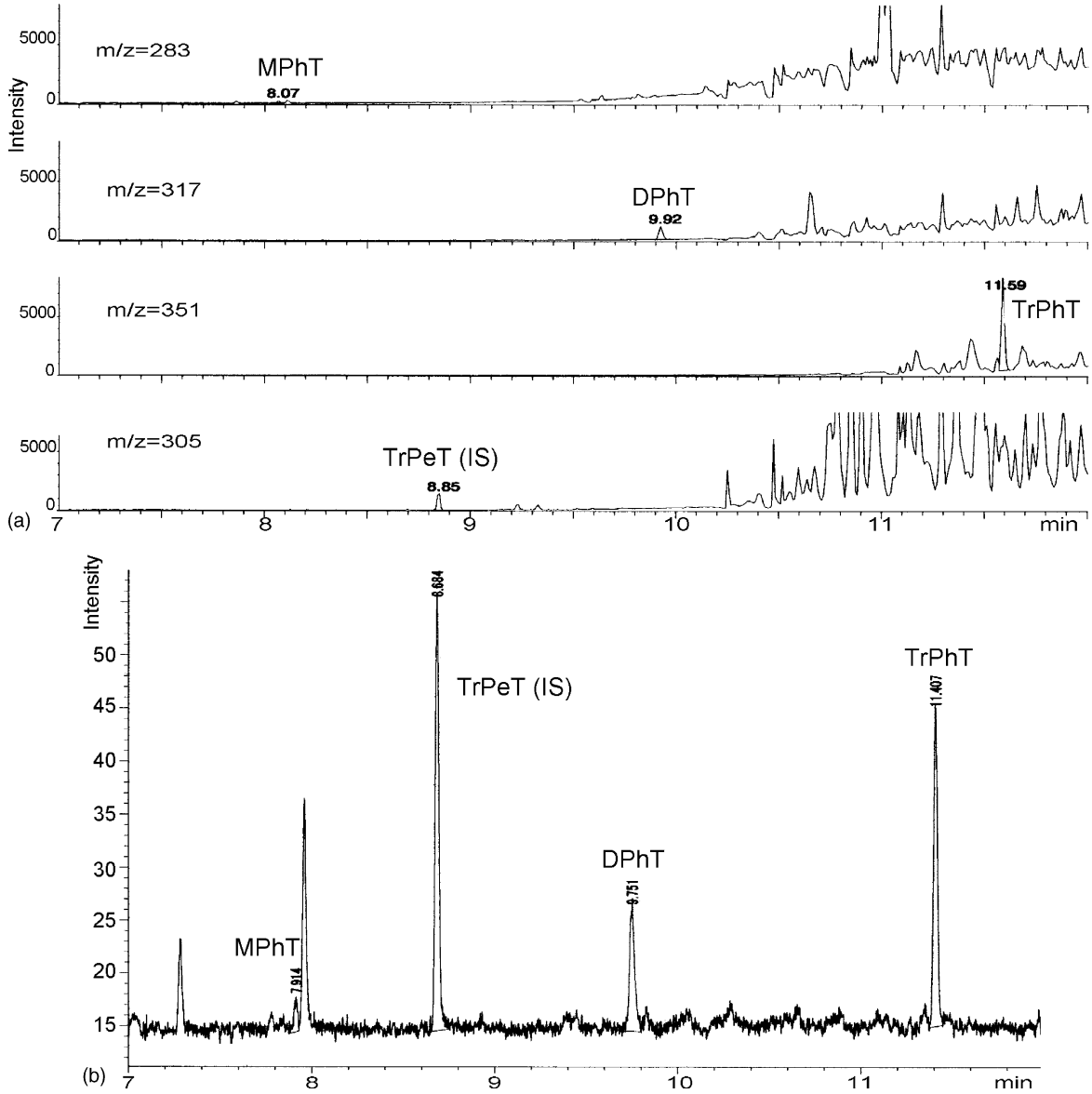

Fig. 4. Interference in detecting PTs caused by PCB congeners at 1% level of concentration (PTs: 0.1 μg/ml each, TrPeT: 0.1 μg/ml, PCBs: 10 000 μg/ml). (a) Measured by MS; (b) measured by FPD; (c) measured by AED.

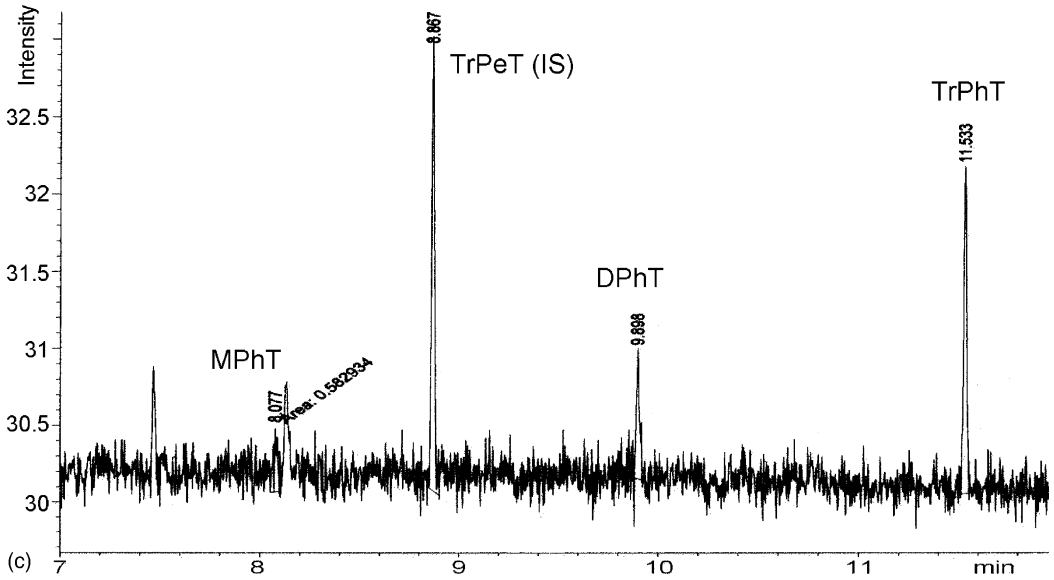

Fig. 4. (*Continued*).

selectivity. In the sensitivity and reproducibility study, simulants containing 0.001–1 μg/ml of TePhT and 1000 μg/ml of PCBs were prepared and analyzed three times at each concentration. The results are shown in Table 1. MS was the most sensitive in detecting TePhT. The detection limits of TePhT by MS, FPD and AED were 0.60, 20 and 30 ng/ml, respectively. All detection techniques showed good correlation between concentrations and responses in the tested range ($r^2 > 0.998$). Relative standard deviations (R.S.D.) of responses at each level were 5.0–12% by MS and 0.90–10% by FPD and 14–24% by AED. MS and FPD were comparable in reproducibility but AED less so. In the selectivity study, simulants containing 0.01 μg/ml of TePhT and 10 000 μg/ml of PCBs were measured. PCB congeners were found in the chromatogram of TePhT measured by MS (Fig. 2a). On the other hand, the peaks of PCB congeners were much smaller in the measurements by FPD and AED (Figs. 2b and c). From the viewpoint of selectivity, MS was slightly worse than the other two detectors. Although the peaks of PCB congeners were found in the chromatogram measured by MS, they did not affect the quantitation result of TePhT since they did not overlap with the TePhT peak. Therefore, MS is better suited for detecting TePhT in transformer samples than FPD or AED.

When the sample solutions are prepared by 1000 times dilution of transformer oil formulations, the expected levels of TePhT in the sample solutions come to around 1 μg/ml, since reported concentration of TePhT is about 0.1% [4]. The analytical procedure examined in this study can detect this level using any detection technique. Interference from PCB congeners may be avoided by increasing the dilution degree of transformer oil samples.

3.2. Examination of the analytical procedure for MPhT, DPhT and TrPhT in transformer oil samples

The analysis of mono- to triphenyltin compounds should be needed in the transformer oil samples containing TePhT, because these mono- to triphenyltin compounds may be formed from TePhT while the transformers are in use. MPhT, DPhT and TrPhT should be derivatized before GC analysis because of their low volatility, low thermal stability and adhesive property to inlets of columns. Generally, they are alkylated by Grignard reagent [8,12,13,17–19,22] or alkylated with sodium tetra-alkylborate [9–11,14–16,20,21,23–26]. The former derivatization reaction proceeds in organic media and the latter takes place in aqueous media. In the analysis of transformer oil samples, derivatization

by Grignard reagent is preferable because derivatization can be completed just adding the reagent to the diluted oil samples. Thus, propylation with *n*-propylmagnesium bromide was adopted. To confirm whether PCBs affect the propylation reaction, transformer oil simulants containing 0.01–1 μg/ml of PTs and 1000 μg/ml of PCBs were propylated and measured using GC/MS. Calibration curves of MPhT, DPhT and TrPhT are shown in Table 2. It appears that PCBs do not affect to the propylation of PTs,

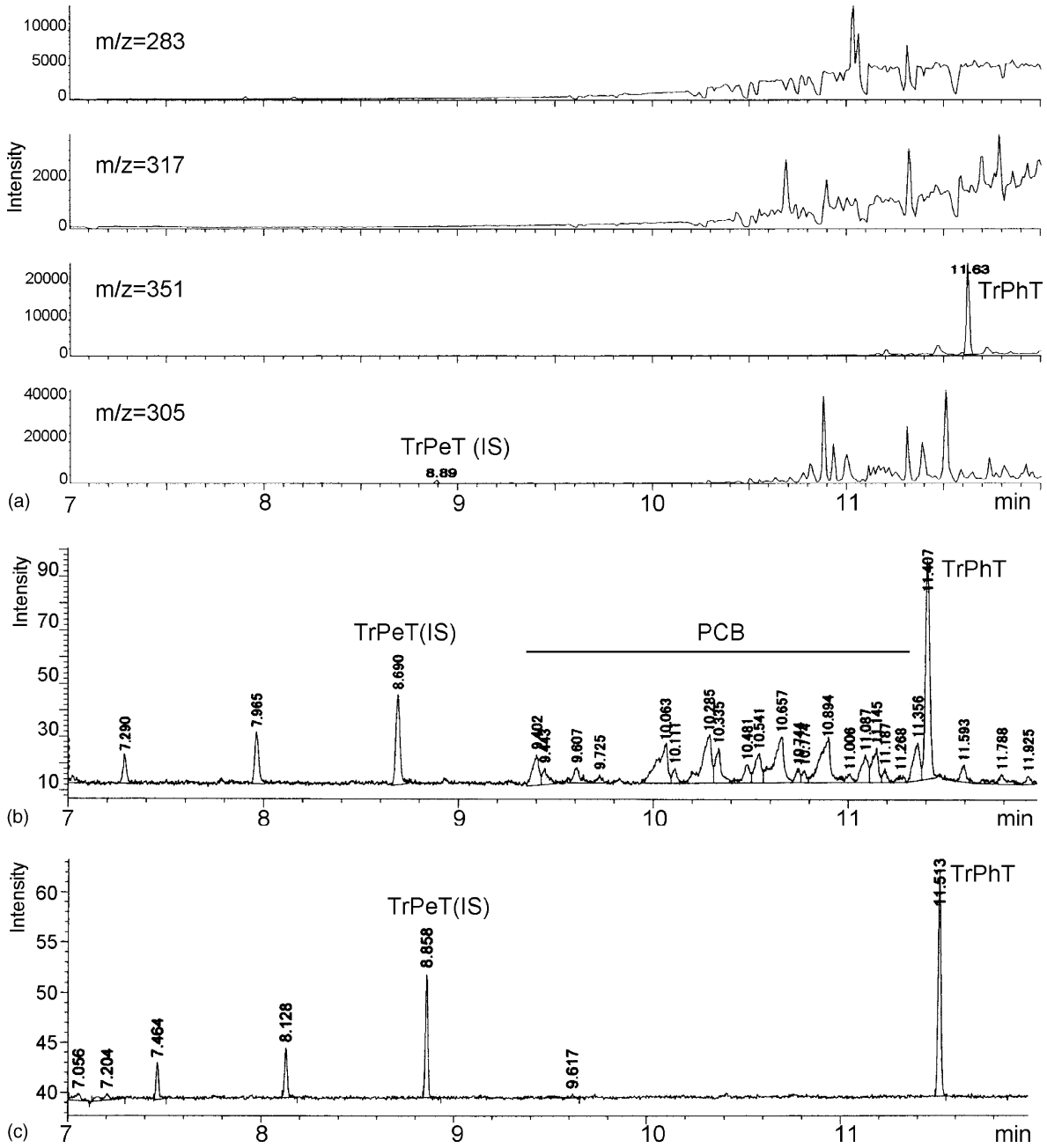

Fig. 5. Chromatograms of TrPhT in transformer oil waste Sample A. (a) Measured by MS; (b) measured by FPD; (c) measured by AED.

since the calibration curves of PTs are quite linear ($R^2 > 0.995$). Thus, PTs in transformer oil samples can be analyzed by GC following propylation without separating them from PCBs matrices.

Detection techniques were also compared. Simulants containing 0.01–1 μg/ml of each PTs and 1000 μg/ml of PCBs were prepared and measured for the sensitivity and reproducibility study. The results are shown in Table 2. Detection limits of MPhT, DPhT and TrPhT by MS were 30, 9.8 and 5.5 ng/ml, respectively. Detection limits of PTs by FPD and AED were several times higher than by MS. Relative standard deviations of response ratios were 1.7–11% by MS, 1.3–20% by FPD and 4.4–21% by AED. These results indicate that MS is superior to other detection methods from the viewpoints of both sensitivity and reproducibility (Fig. 3a–c). To confirm the selectivity of these detection techniques, simulants containing 0.1 μg/ml of PTs and 10 000 μg/ml of PCBs were analyzed. Chromatograms of PTs are shown in Fig. 4. In using MS for detection, TrPhT was interfered with by PCBs matrices, though interference by matrices with MPhT and DPhT detection was negligible (Fig. 4a). On the other hand, interference by PCBs was not significant in FPD and AED detection (Figs. 4b and c). Stäb et al. compared MS and AED for detecting organotin compounds in environmental samples and concluded that MS was more sensitive but less selective than AED [9]. The same pattern was confirmed in our study. However, when a sample preparation is used such that PCBs concentration is below 1000 μg/ml, interference from PCBs matrices is not significant to detect TrPhT by MS.

The levels of mono- to triphenyltin in transformer oil formulations may be lower than the initial levels of TePhT, since these compounds are formed from TePhT. Thus, when the sample solutions are prepared as described above, the levels of these PTs should be below 1 μg/ml. Dilution degrees of transformer oil samples should be reduced, when detection limits described here are insufficient for detecting these PTs in the sample solution.

3.3. Analysis of PTs in transformer oil waste samples

PTs in transformer oil waste samples were analyzed using the methods examined above. The levels of phenyltin compounds are listed in Table 3. TePhT was found in both samples. The level of TePhT in Sample A was 720 μg/g oil, close to the reported composition stated by the manufacturer. The level of TePhT in Sample B was 69 μg/g oil and about one-tenth of the level in Sample A. In the analysis of other PTs, only TrPhT was found in both samples. Chromatograms of PTs are shown in Fig. 5. As we mentioned above, interference by PCB congeners was found in the chromatogram of TrPhT measured by GC/MS (Fig. 5a). The peaks of PCB congeners were also found in the chromatogram measured by FPD (Fig. 5b). Only the chromatogram measured by AED was unaffected by PCBs (Fig. 5c). The levels of TrPhT were 36 and 4.9 μg/g oil, respectively. These results indicate that about 5% of TePhT had changed into TrPhT during the lifetime of the transformer.

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