Survey on the Presence of Butyltin Compounds in Chinese Alcoholic Beverages, Determined by Using Headspace Solid-Phase Microextraction Coupled with Gas Chromatography–Flame Photometric Detection

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The use of butyltin compounds in some food packaging leads to the contamination of liquid food and may result in subsequent adverse effects on people’s health through the food chain. A survey of butyltin compounds in Chinese alcoholic beverages purchased from retail markets was carried out by using solid-phase microextraction (SPME) followed by gas chromatography coupled with flame photometric detection. Forty-four samples including wine, liquor, and champagne were studied. The levels of monobutyltin and dibutyltin ranged from \(<0.016\) to \(5.687\) and from \(<0.0022\) to \(33.257\) \(\mu\)g of Sn/L, respectively. Low levels of tributyltin were detected. The presence of dibutyltin in wine samples was further confirmed by GC–MS. The result indicated that dry wines generally contained more dibutyltin than sweet wines. The concentrations of butyltin compounds in liquor samples were lower than those in wine samples.

KEYWORDS: SPME; GC–FPD; butyltins; wine

INTRODUCTION

Organotin compounds have been used extensively as poly-(vinyl chloride) (PVC) stabilizers, wood preservers, agrichemicals, catalysts, and antifouling agents since the 1970s. Dialkyltin compounds are common PVC stabilizers, and monoalkyltin analogues are frequently added to enhance their performance. About 23 000 tons of PVC stabilizers are used annually at present, which constitutes about 40% of the world usage of organotin compounds (1).

The level of organotin compounds necessary to stabilize PVC ranges from 0.5 to 3.0 parts per hundred of resin (2). The migration of organotin stabilizers from PVC food containers into liquid foods was studied in the early 1970s (3–5). It was reported that the concentration of organotin leached from PVC bottles was up to 0.01 \(\mu\)g/L in beer and juice. High butyltin levels were also found in some Canadian wines and other imported wines which were sampled directly from PVC-lined storage tanks (6–8). As wine is a popular beverage and the organotin contamination may affect people’s health, it is important to carry out a survey of butyltin occurrence in wine, especially for Chinese wine.

Conventional extraction techniques such as solid-phase extraction (SPE) and liquid–liquid extraction were time-consuming and employed a large amount of toxic organic solvent. In 1994, a solvent-free method, solid-phase microextraction (SPME), was reported for the analysis of a variety of volatile and semivolatile organic analytes (9–12). Besides trace analysis of volatile organic pollutants in different matrices, SPME has also been successfully used in the extraction of organomercury, organoleads, and organotins from various environmental samples (13, 14). Speciation of organotin compounds was commonly performed by GC with selective detection of tin by such methods as flame photometric detection (FPD), atomic absorption spectrometry (AAS) (15), or microwave-induced plasma atomic emission spectrometry (MIP AES) (16).

In this paper, determination of butyltin compounds in wine was carried out by the method of headspace SPME after in situ hydride derivatization. Gas chromatography coupled with QSIL-FPD was used because of its high selectivity and sensitivity in tin determination (17).

EXPERIMENTAL PROCEDURES

Apparatus. A Shimadzu (Kyoto, Japan) GC-9A gas chromatograph equipped with a laboratory-modified flame photometric detector (FPD) was used throughout the experiment. The GC conditions were set as follows: HP-1 fused silica capillary column of 25 m \(\times\) 0.32 mm i.d. coated with 0.17 \(\mu\)m film thickness of methylsilicone (Hewlett-Packard, Palo Alto, CA); carrier gas, high-purity nitrogen with 250 kPa of column head pressure; oven temperature program, 55 °C (1 min hold) to 150 °C (3 min hold) at 10 °C/min; injector temperature, 220 °C; injection mode, splitless. The specific detector used for quantitative analysis was a laboratory-modified FPD using quartz surface-induced tin emission (QSIL-FPD). The configuration and analytical figures of merit of the detector were described previously (18, 19). Its temperature was maintained at 140 °C. The hydrogen-rich flame was created by

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controlling hydrogen and air at flow rates of 260 and 90 mL/min, respectively, which resulted in high sensitivity to tin.

An Agilent GC 6890 gas chromatograph coupled with a MS5973 Network mass-selective detector was used for further confirmation of the presence of butyltin compounds. The system was operated in the full scale monitoring with electron impact ionization. GC operating parameters were as follows: injection mode, splitless; injection temperature, 220 °C; HP19091S-433 capillary column (HP-5 MS 5% phenyl methyl siloxan, 30.0 m × 0.25 mm × 0.25 mm nominal); carrier gas, high-purity helium (9.99 psi); oven temperature program, 40 °C (1 min hold) followed by a linear increase of 10 °C/min to 200 °C (1 min hold); detector temperature, 280 °C.

The SPME manual device with 100 μm poly(dimethylsiloxane) (PDMS)-coated fibers was obtained from Supelco Inc. (Bellefonte, PA). Reagents. Monobutyltin trichloride (MBT, 97%), dibutyltin dichloride (DBT, 97%), tributyltin chloride (TBT, 90%), and tetrabutyltin (TeBT, 96%) were obtained from Acros Organics (NJ). TeBT was used as internal standard (IS). The stock standards of butyltin compounds at 1 mg/mL as Sn were prepared in methanol. Working solutions of 1 % (TeBT, 96%) were obtained from Acros Organics (NJ). DBT, 0.434 μg of Sn/L; TBT, 0.547 μg of Sn/L.

<table>
<thead>
<tr>
<th>wine type</th>
<th>MBT (μg of Sn/L) Method I</th>
<th>MBT (μg of Sn/L) Method II</th>
<th>DBT (μg of Sn/L) Method I</th>
<th>DBT (μg of Sn/L) Method II</th>
<th>TBT (μg of Sn/L) Method I</th>
<th>TBT (μg of Sn/L) Method II</th>
</tr>
</thead>
<tbody>
<tr>
<td>dry red</td>
<td>0.092 ± 0.010^a</td>
<td>nd^c</td>
<td>0.599 ± 0.038</td>
<td>0.689 ± 0.056</td>
<td>0.008 ± 0.0002</td>
<td>nd</td>
</tr>
<tr>
<td>white</td>
<td>0.637 ± 0.048</td>
<td>0.756 ± 0.091</td>
<td>5.170 ± 0.419</td>
<td>4.384 ± 0.329</td>
<td>0.135 ± 0.011</td>
<td>nd</td>
</tr>
<tr>
<td>champagne</td>
<td>0.135 ± 0.008</td>
<td>nd</td>
<td>0.845 ± 0.094</td>
<td>0.704 ± 0.077</td>
<td>0.105 ± 0.0001</td>
<td>nd</td>
</tr>
</tbody>
</table>

^a Mean of five repeated determinations. ^b Standard deviation. ^c Not detected. The concentrations were lower than the detection limits (liquid–liquid extraction method): MBT, 0.301 μg of Sn/L; DBT, 0.434 μg of Sn/L; TBT, 0.547 μg of Sn/L.

Evaluation of Extraction Method. To confirm the results obtained by SPME, we analyzed three typical samples, including a dry red wine, a white wine, and a champagne, by the traditional process of Grignard derivatization coupled with liquid–liquid extraction. Detailed results are listed in Table 1. A satisfactory agreement of the results obtained by the two methods was observed, which clearly showed the accuracy of quantitative analysis in this work. Additionally, the detection limits of the headspace SPME method, based on signal/noise for mono-, di-, and tributyltin, were 0.016, 0.0022, and 0.0015 μg/L as Sn, respectively, which proved the high sensitivity of this proposed method.

Qualitative Analysis of Butyltin Compounds in Wine Samples. Butyltin compounds in the wine and liquor samples were separated and identified by GC–QSIIL–FPD after in situ hydride derivatization and headspace SPME procedures. A typical GC–FPD chromatogram of a wine sample including mono-, di-, and tri-butylin compounds is shown in Figure 1. Qualitative identification could be definitely realized by the GC–FPD retention time, and it was further confirmed by GC–MS determination.

The butyltin standards and the wine samples were determined by full-scale monitoring with electron impact ionization to
produce MS spectra of butyltin compounds. The MS spectra of standard butyltin hydrides were characterized with clusters of isotope ions at each fragment. The isotope patterns created by tin abundance contributions of $m/z$ 120 were particularly useful for recognition of organotin compounds. The molecular ion $[M+\text{Sn}]^+$ was usually not observed for butyltin hydrides because of their instability. The characteristic fragmentation pattern of MBT and DBT hydrides was dominated by preferential cleavage of their instability. The characteristic fragmentation pattern of MBT was accompanied by the formation of $[M - 2\text{Sn}]^+$ ions, followed by successive cleavage of an alkyl group. Monobutyltin hydride was identified with the characteristic fragments of $m/z$ 179 (SnBuH$_2^+$) and 149 (SnEt$^+$). The ion fragments of $m/z$ 234 (SnBu$_2^+$) and 177 (SnBu$^+$) were characteristic for dibutyltin hydride. For TBT hydride, however, instability of SnBu$^+$ resulted in preferential cleavage of the largest alkyl groups from $[M]^+$ accompanied by the formation of $[M - \text{R}]^+$ or $[M - \text{R} \pm 2]^+$ ions. Here, tributyltin hydride was characterized with the fragments of $m/z$ 235 (SnBu$_2^+$) and 177 (SnBu$^+$).

The compound in the selected wine sample detectable by GC–MS was DBT, because the concentrations of MBT and TBT were relatively low and the sensitivity of the MS detector was 10$^2$ lower than that of the laboratory-modified FPD. According to the comparison of the mass spectrum of the sample with that of the standard dibutyltin hydride, excellent matches were found. Figure 2 gives the mass spectra of a typical sample (winery 12, province Tianjin) and the standard. A few small differences exist because of the complex sample matrix. Accordingly, the results obtained from GC–MS analysis proved the presence of butyltin compounds in samples.

**Analysis of Butyltin Compounds in Wine Samples.** Quantitative analysis of samples was performed by GC–FPD after headspace SPME. The results listed in Table 2 showed the universal occurrence of butyltin compounds in the Chinese wine samples tested. Monobutyltin concentration ranged from 0.016 to 5.595 µg of Sn/L, and dibutyltin ranged from <0.0022 to 8.553 µg of Sn/L. Tributyltin levels were much lower than either di- or monobutyltins, with the highest level at 0.269 µg/L as Sn. Five wine samples contained relatively high levels (>1 µg of Sn/L) of butyltins. Most of the wine samples contained butyltins lower than 1 µg of Sn/L, wherein mono- and dibutyltin accounted for 49% and 45% (mean value), respectively, of the total butyltin concentration. Tributyltin had the lowest concentration, accounting for 6% (mean value) of the total butyltin concentration. Wines produced in Shanghai were contaminated with relatively high concentrations of butyltin compounds. For overall domestic samples, especially those produced by the same winery, dry wine generally contained more DBT than other wines.

The highest butyltin concentration (MBT, 5.687 µg of Sn/L) in wine samples was found in a wine sample that was imported from Spain and bottled in Shanghai, China. Other imported wine samples (Table 3) had low levels of butyltins contamination, wherein monobutyltin was the dominant compound whose concentration accounted for 96% (mean value) of the total butyltin concentration, and dibutyltin accounted for only 4% (mean value).

Comparing the data in Table 2 with those in Table 4, the mean value of total butyltin concentration (0.397 µg of Sn/L) in wine samples, excluding the exceptionally high concentration (>1 µg of Sn/L), was higher than that in liquor samples (0.172 µg of Sn/L). That may be the result of different production technology or varied containers used for production, preservation, and transportation. However, no significant differences in butyltin concentrations were found between the liquor samples preserved in plastic and in glass bottles.

**Study of Change Trend of Butyltins in Wine Samples.** To show the change trend of butyltin contamination in alcoholic beverages with the time, a liquor sample stored in a plastic bottle...
was studied periodically for 110 days. The opened liquor bottle was sealed with its original plastic cap and held at room temperature between analyses. As dibutyltin was the main contaminant in this sample, the focus was mainly on the change of this typical compound. The results in Figure 3 show that the level of DBT decreased with time. After 110 days of storage,
the concentration of DBT was 27% of the original concentration. It was presumed that butyltin compounds could degrade during the storage period.

**Conclusion.** Simultaneous determination of mono-, di-, and tributyltin from domestic and imported alcoholic beverage samples was carried out by SPME–GC–FPD. The levels of monobutyltin and dibutyltin were measured in the range of $<0.016-5.687$ and $<0.0022-33.257 \mu g$ of Sn/L, respectively. Low levels of tributyltin were detected. The experimental results indicated that dry wines generally contained more dibutyltin than sweet wines. The concentrations of butyltin compounds in liquor samples were lower than those in wine samples. The source of butyltin contamination in alcoholic beverages has not been clearly identified; this will be the subject of our further studies.

**LITERATURE CITED**