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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 μg 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.

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 μg/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 matrixes, 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 × 0.32 mm i.d. coated with 0.17 μm 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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Table 1. Comparison of the Results Obtained by Two Extraction Methods: Method I, SPME and Method II, Liquid–Liquid Extraction

	MBT (μg of Sn/L)		DBT (μg of Sn/L)		TBT (μg of Sn/L)	
wine type	Method I	Method II	Method I	Method II	Method I	Method II
dry red	0.092[a] ± 0.010[b]	nd[c]	0.599 ± 0.038	0.689 ± 0.056	0.008 ± 0.0002	nd
white	0.637 ± 0.048	0.756 ± 0.091	5.170 ± 0.419	4.384 ± 0.329	0.135 ± 0.011	nd
champagne	0.135 ± 0.008	nd	0.845 ± 0.094	0.704 ± 0.077	0.015 ± 0.0001	nd

[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.

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; injector 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 μg of Sn/mL were prepared by diluting the stock solution with deionized water just before use. The acidity of the stock and the working solution was adjusted to pH 2 with concentrated HCl to ensure the standards' stability. All the solutions were stored at 4 °C in the dark.

Potassium tetrahydroborate (KBH$_4$, 99.7%), acting as the hydride derivatization agent, was bought from Shanghai Chemical Reagent Co. A 3% (w/v) fresh solution was prepared daily with deionized water.

The Grignard reagent, *n*-propylmagnesium bromide (*n*-PrMgBr, 2.0 M), was laboratory-prepared according to the method of Zhou et al. (*20*). All the other solvents and reagents used in the experiment were of analytical reagent grade or better.

Glassware was rinsed with deionized water, decontaminated overnight in 1:1 nitric acid solution, and then rinsed three times with deionized water.

Sample Collection. Forty-four samples were purchased from supermarkets: there were 30 wine samples and 6 liquor samples produced in 10 provinces in China, and 8 wine samples imported from Italy, Spain, France, and the United States. The imported wine involved two types. One was wine produced and bottled in the country of origin, and the other was wine produced in the country of origin and bottled in China. All of the samples were kept unopened at room temperature until analysis. Samples of champagne were degassed by sonication before extraction.

Sample Pretreatment. *Method I: Headspace SPME after in Situ Hydride Derivatization.* For liquid wine samples, headspace solid-phase microextraction (SPME), used for quantitative analysis, was similar to our previous work analyzing butyltin compounds in seawater (*21, 22*). The optimum SPME conditions were the same. Volumes of 50 mL of sample and 0.3 mL of concentrated acetic acid were poured into a 150 mL glass vial and mixed well with a magnetic stirrer. Suitable dilution was required before pretreatment for those samples with extremely high levels of contaminants. The vial was sealed with a septum cap. The fiber coated with 100 μm PDMS was inserted into the vial and exposed to the headspace above the solution. A volume of 1 mL of 3% (w/v) potassium tetrahydroborate solution was subsequently injected to convert butyltin chlorides and other butyltin forms into butyltin hydrides, which increases the extraction efficiency of SPME and allows GC separation. The reaction was performed at 25 °C with constant stirring for a period of 15 min. During the reaction period, volatile butyltin hydrides were extracted by the fiber. The fiber was then

withdrawn into the needle and directly inserted into the GC injector for 3 min of thermal desorption. The depth of the fiber in the injection port was kept the same for each time. The analytes were finally separated in the capillary column and detected by the QSIL-FPD detector.

Calibration standards were analyzed by the process described above, except that 50 mL of deionized water and a series of working solutions of MBT, DBT, and TBT were used instead of wine samples.

Method II: Liquid−Liquid Extraction Coupled with Grignard Derivatization. A 20 mL sample of wine was used for the analysis of tri-, di-, and monobutyltin compounds. The sample was mixed with 0.3 mL of internal standard TeBT (2 μg/mL) and 10 mL of tetrahydrofuran−hydrochloric acid (11:1) solution. The mixture was then extracted with 25 mL of 0.01% tropolone in hexane solution and again with 10 mL of hexane solution with vigorous shaking for 40 and 10 min, respectively. The combined hexane extracts were concentrated to 2−3 mL by a rotary evaporator at 25 °C, and then Grignard propylation was performed without further treatment. An excess of (*n*-Pr)MgBr was used (1 mL of a 2.0 M solution of (*n*-Pr)MgBr in ether) in the derivatization procedure (*23*). The reaction was complete after 15 min of shaking. Excess Grignard reagent was destroyed by the addition of 5 mL of 0.5 M H$_2$SO$_4$. The propylated butyltin compounds were extracted with 20 mL of hexane, and the organic phase was washed with 40 mL of deionized water by shaking in a separately funnel for 5 min. After phase separation, the organic layer was transferred and concentrated to 1 mL. The analytes were dried and purified on a short Pyrex column packed with anhydrous NaSO$_4$ (2 g) and Florisil (1 g) which was prewashed with 10 mL of hexane. Another 10 mL of hexane was used to fully elute the analytes. The eluted solution was gently concentrated to 1 mL using a stream of nitrogen. A volume of 1 μL of the prepared solution was then injected into a GC for analysis.

RESULT AND DISCUSSION

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−QSIL-FPD after in situ hydride derivatization and headspace SPME procedures. A typical GC−FPD chromatogram of a wine sample including mono-, di-, and tri-butyltin 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
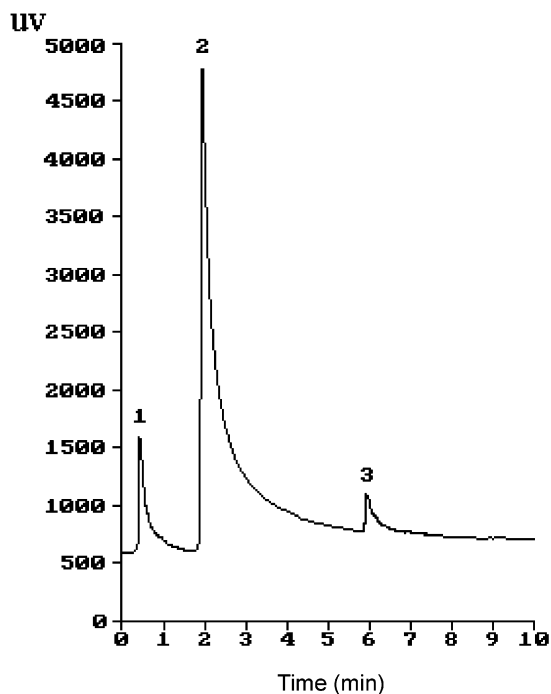
Figure 1. Chromatogram of a typical wine sample. Peaks identified as (1) MBT (t_R = 0.33 min), (2) DBT (t_R = 1.78 min), and (3) TBT (t_R = 5.96 min).

Figure 2. Mass spectra of (a) a dibutyltin hydride of standard and (b) a wine sample.

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 10 tin abundance contributions of m/z 120 were particularly useful for recognition of organotin compounds. The molecular ion $[M]^{+\bullet}$ 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 hydrogen from $[M]^{+\bullet}$ to form $[M - 1]^+$ or $[M - 2]^+$ 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 ($SnEt^{3+}$). The ion fragments of m/z 234 ($SnBu_2^{2+}$) and 177 ($SnBu^{3+}$) were characteristic for dibutyltin hydride. For TBT hydride, however, instability of $SnBu_3^+$ resulted in preferential cleavage of the largest alkyl groups from $[M]^{+\bullet}$ accompanied by the formation of $[M - R]^+$ or $[M - R \pm 2]^+$ ions. Here, tributyltin hydride was characterized with the fragments of m/z 235 ($SnBu_2^{2+}$) and 177 ($SnBu^{3+}$).

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 10^3 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
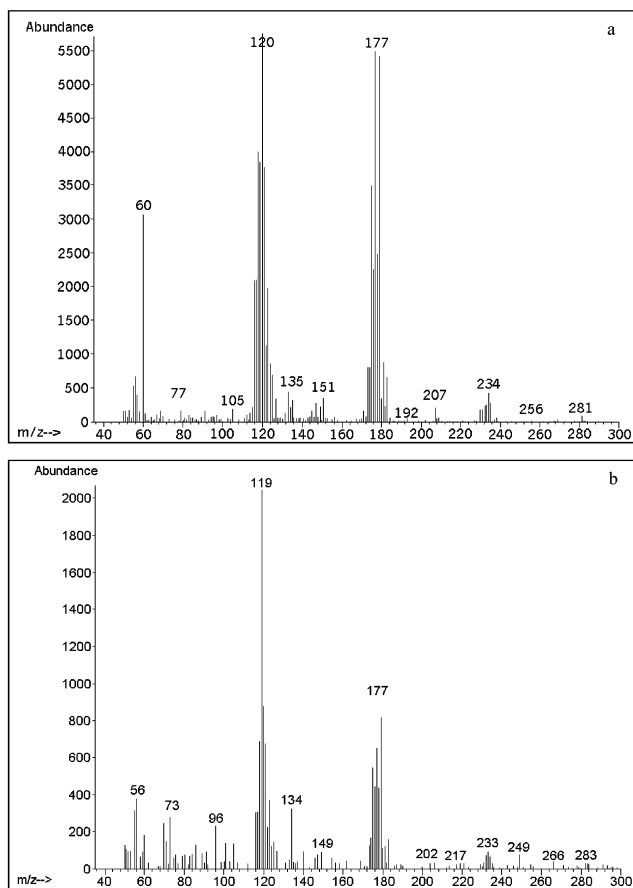
Sn. Five wine samples contained relatively high levels (>1 μg of Sn/L) of butyltins. Most of the wine samples contained butyltins lower than 1 μg of Sn/L, wherein mono- and dibutyltin accounted for 49% and 45% (mean value), respectively, of the total butyltin concentration. Tributyltin had the lowest 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; DBT, 33.257 μg of Sn/L; TBT, 13.567 μg of Sn/L) 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 butyltins 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

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Table 2. Levels of Butyltin Compounds in the Tested Chinese Wines

| province and city | winery | wine type | mean[a] level ± SD[b] (μg of Sn/L) | | |
			MBT	DBT	TBT
Beijing	1	dry red	0.224 ± 0.008	0.070 ± 0.005	nd[c]
Beijing	1	dry white	1.690 ± 0.234	nd	0.020 ± 0.001
Beijing	2	white	0.147 ± 0.016	0.032 ± 0.001	nd
Beijing	2	red	0.195 ± 0.018	0.013 ± 0.001	nd
Beijing	2	dry red	0.170 ± 0.021	0.099 ± 0.008	nd
Beijing	2	dry white	0.152 ± 0.011	0.047 ± 0.004	nd
Beijing	3	dry red	nd	0.629 ± 0.006	0.236 ± 0.023
Beijing	3	white	0.638 ± 0.004	5.171 ± 0.419	0.135 ± 0.012
Beijing	3	champagne	0.135 ± 0.008	0.845 ± 0.133	0.015 ± 0.001
Beijing	4	dry white	0.348 ± 0.044	0.483 ± 0.066	nd
Beijing	4	dry red	0.132 ± 0.016	0.140 ± 0.017	nd
Beijing	5	dry red	0.284 ± 0.019	0.056 ± 0.002	nd
Hebei	6	kiwi wine	0.149 ± 0.016	nd	nd
Hebei	7	red	0.478 ± 0.065	0.013 ± 0.002	nd
Hebei	7	dry red	0.125 ± 0.007	0.219 ± 0.013	0.028 ± 0.001
Jilin	8	red	0.204 ± 0.026	0.009 ± 0.0009	nd
Jilin	9	dry red	0.575 ± 0.054	0.038 ± 0.0007	nd
Shanghai	10	red	1.803 ± 0.086	1.679 ± 0.156	nd
Shanghai	11	dry red	1.691 ± 0.004	8.553 ± 0.913	nd
Tianjin	12	dry red	0.146 ± 0.002	0.621 ± 0.060	0.269 ± 0.029
Tianjin	13	dry red	0.063 ± 0.004	0.386 ± 0.0003	nd
Shanxi	14	kiwi wine	0.106 ± 0.007	0.065 ± 0.008	0.021 ± 0.0003
Shandong	15	dry red	0.092 ± 0.011	0.599 ± 0.053	0.008 ± 0.0002
Shandong	15	champagne	nd	0.012 ± 0.0007	nd
Shandong	16	red	nd	nd	nd
Shandong	16	dry red	0.170 ± 0.016	0.069 ± 0.009	nd
Shandong	16	dry white	0.225 ± 0.031	0.031 ± 0.0004	nd
Shandong	16	brandy	0.446 ± 0.047	0.003 ± 0.0004	nd
Shandong	16	champagne	5.595 ± 0.627	nd	nd
Anhui	17	white	0.308 ± 0.086	nd	nd

[a] $n = 5$. [b] Standard deviation. [c] Not detected. The concentrations were lower than the detection limits (headspace SPME method): MBT, 0.016 μg of Sn/L; DBT, 0.0022 μg of Sn/L; TBT, 0.0015 μg of Sn/L.

Table 3. Concentrations of Butyltin Compounds in the Tested Imported Wines

| country of origin | country of bottling | wine type | mean[a] level ± SD[b] (μg of Sn/L) | | |
			MBT	DBT	TBT
Italy	China	dry red	0.649 ± 0.019	nd	nd[c]
Spain	China	dry red	5.687 ± 0.657	33.257 ± 1.881	13.567 ± 0.950
USA	China	dry white	0.146 ± 0.017	0.024 ± 0.001	nd
USA	China	dry red	0.496 ± 0.036	0.022 ± 0.001	nd
USA	China	red	0.248 ± 0.011	nd	nd
France	China	red	0.369 ± 0.019	0.022 ± 0.001	nd
France	France	red	nd	nd	nd
USA	USA	red	nd	nd	nd

[a] $n = 5$. [b] Standard deviation. [c] Not detected. The concentrations were lower than the detection limits (headspace SPME method): MBT, 0.016 μg of Sn/L; DBT, 0.0022 μg of Sn/L; TBT, 0.0015 μg of Sn/L.

Table 4. Concentrations of Butyltin Compounds in the Tested Chinese Liquors

| alcohol type | province | container | mean[a] level ± SD[b] (μg of Sn/L) | | |
			MBT	DBT	TBT
liquor	Beijing	glass bottle	nd	0.016 ± 0.002	nd[c]
liquor	Beijing	glass bottle	nd	0.021 ± 0.001	nd
liquor	Sichuan	plastic bottle	nd	nd	nd
yellow wine	Zhejiang	plastic bottle	0.160 ± 0.004	0.003 ± 0.0001	nd
yellow wine	Shanghai	plastic bottle	0.076 ± 0.004	0.011 ± 0.0001	nd
rice wine	Anhui	glass bottle	0.625 ± 0.018	0.122 ± 0.012	nd

[a] $n = 5$. [b] Standard deviation. [c] Not detected. The concentrations were lower than the detection limits (headspace SPME method): MBT, 0.016 μg of Sn/L; DBT, 0.0022 μg of Sn/L; TBT, 0.0015 μg of Sn/L.

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,
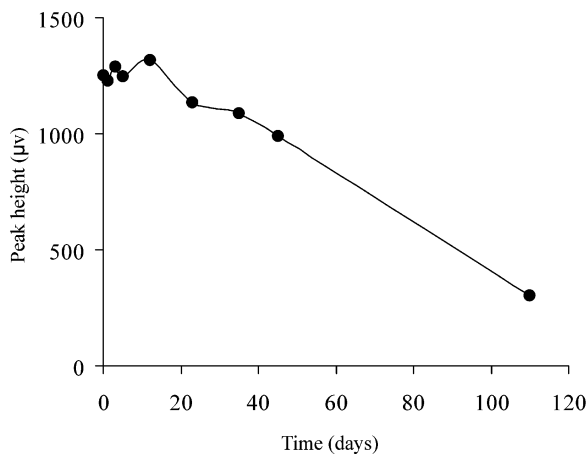
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Figure 3. Variation of dibutyltin concentration (identified as the peak height) with time in a liquor sample stored in a plastic bottle.

the concentration of DBT was 27% of the original concentration. It was presumed that butyltin compounds could degradate 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 μg 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.

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