Determination of 17 Organotin Compounds in Beverages Using Triple Quadrupole GC-MS/MS System

Application Note

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Abstract

A gas chromatography-triple quadrupole mass spectrometer (GC-MS/MS) method has been developed for the determination of 17 organotin compounds in beverages. The sample was derivatized with $NaBEt_4$, and used liquid-liquid extraction with hexane. Data were acquired in the MRM mode and an external standard was used for quantitative determination. Calibration curves were generated for all of the derivatized compounds with concentrations for most of them ranging from 0.001mg/L to 0.200 mg/L. Samples were concentrated by a factor of 10 during preparation and so the working range for the method was effectively 0.0001mg/L to 0.0200 mg/L. Correlation coefficients for all of the calibration curves were higher than 0.995. Recoveries were determined for three replicate extractions at two spike levels (0.001 mg/L and 0.005 mg/L). The average recovery for the vast majority of the organotins was between 70.0% and 120.0% with the relative standard deviation less than 10.0%. The method was found to be simple, fast and sensitive. It can be used for the trace analysis of multiple organotin compounds in beverages for both qualitative and quantitative analysis.

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Introduction

Organotin compounds (OTCs) have been widely used as polymer stabilizers, insecticides and pesticides. The highest amounts of OTCs are found in coating materials for boats and ships. They are used to prevent crustacean attachment to hulls. OTCs are identified as endocrine disruptive chemicals (EDCs) which may have a negative impact on human health due to exposure through the food chain.

OTCs have been found in ocean water, sediments, textiles and human urine. However, there are fewer studies on OTCs in food. These compounds can be analyzed using GC-PFPD, GC/MS (single quadrupole), ICPMS, or LC-ICPMS. In China, food is referenced against GB method 5009.215-2008 for organotin compounds. This method uses GC-PFPD, and can typically be calibrated down to between 0.5 and 1 µg/kg (depending on target compound). We needed a method that could be calibrated down to 0.1 µg/kg (in the sample) for various beverage samples, and would cover a wider range of compounds (as shown). We wanted to achieve this performance with a sample size no larger than 10 mL (commensurate with what was available) and with a preparation procedure that could be carried out conveniently with small-scale glassware and minimal use of reagents.

An Agilent 7000 Series GC-MS/MS was used in this research work to develop a precise, rapid, and reliable method to study 17 OTCs in beverages. Eleven beverage samples were tested to determine if they contained any of these organotins.

Experimental

Samples and reagents

- **Samples:** Beer, carbonated soft drinks, energy drinks, and drinks containing metabolic stimulants
- **Acetate buffer:** 82 g/L sodium acetate dissolved in water, solution adjusted to pH 4.5 with acetic acid
- **Derivatization reagent:** 2g $NaBEt_4$ dissolved in 10 mL of ethanol. This solution should be freshly prepared.
- Ethanol, hexane, methanol, chromatography grade purity

Standards and derivatization method

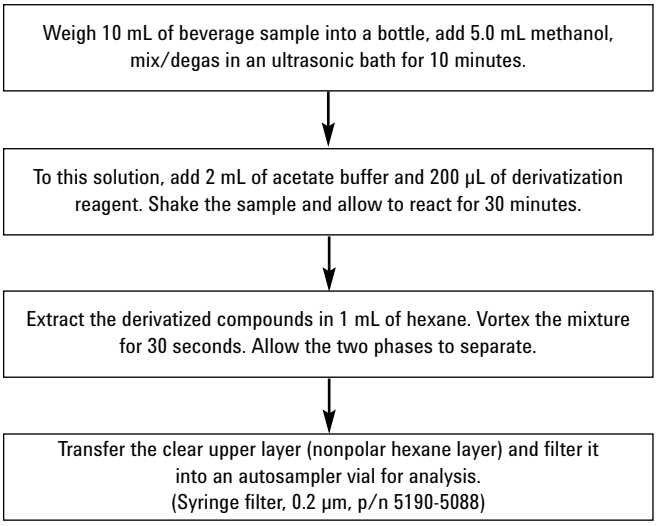
Standards

The standards were dissolved in methanol at 1,000 ppm (1 mg/mL), then further diluted to the required concentration.

Derivatization method

To 1 mL of standard solution, 1 mL of acetate buffer and 50 µL of derivatization reagents were added. The solution was shaken and allowed to react for 30 minutes. After the addition of 5 mL of water, the derivatized compounds were extracted in 1 mL of hexane. The mixture was vortexed for 10 seconds, and the two phases were allowed to separate. The clear upper layer (nonpolar hexane layer) was transferred to an autosampler vial for analysis.

Sample preparation



Chromatographic parameters

GC system	Agilent 7890A GC
Column	Agilent HP-5 MS UI capillary column, 30 m × 0.25 mm, 0.25 µm (p/n 19091S-433UI)
Oven temperature program	50 °C hold 1.5 minutes, at 10 °C/min to 300 °C, hold 1 minute
Carrier gas	Helium
Flow rate	1.1 mL/min
Injection port temperature	280 °C
Injection volume	2 µL
Injection mode	Splitless, purge on after 1 minute

Mass spectrum parameters

Mass system	Agilent 7000B MS/MS
Ion source	EI
Ionization voltage	70 eV
Ion source temperature	230 °C
Interface temperature	280 °C
Collision gas	Nitrogen 1.50 mL/min
Quenching gas	Helium 2.25 mL/min
Solvent delay	2.0 minutes

MRM parameters are shown in Table 1.

Table 1. Retention Time and MRM Parameters of 17 Derivatives of Organotin Compounds

No.	Compound name	RT (t/min)	Precursor ion (*m/z*)	Product ion (*m/z*)	Collision energy (eV)
1	Trimethyltin*	2.72	165	135	15
			163	133	15
2	Dimethyltin*	3.86	179	151	5
			151	135	10
3	Monomethyltin*	5.35	193	165	5
			165	137	5
4	Monobutyltin*	9.45	179	151	5
			179	123	10
5	Tripropyltin*	10.38	193	151	5
			193	123	10
6	Tetrapropyltin*	11.35	207**	165	5
			207**	123	10
7	Dibutyltin*	11.66	179	151	5
			263	207	5
8	Monophenyltin*	12.92	255	199	15
			255	277	5
9	Monoheptyltin*	13.29	179	151	5
			179	123	10
10	Tributyltin*	13.54	291	179	10
			207**	123	15
11	Monooctyltin*	14.49	179	151	5
			179	123	10
12	Tetrabutyltin*	15.16	235	179	5
			291	179	10
13	Diphenyltin*	17.78	303	275	5
			303	197	15
14	Diheptyltin*	18.00	249	151	5
			249	123	15
15	Dioctyltin*	19.83	263	151	5
			263	123	15
16	Tricyclhexyltin*	21.80	351	197	20
			349	195	20
17	Triphenyltin*	21.80	233	151	5
			233	123	15

* Organotin compound after derivatization with $NaBEt_4$

** While 207 *m/z* shares signal from column bleed for a 5 phase GC column, it produces high signal and low noise when run through the transitions shown.

Results and Discussion

Chromatographic separation results

GC analysis was finished in 22 minutes with baseline separation for 15 of 17 compounds. Although the last two OTCs could not be separated by this method, the MRM function of the 7000B GC/MS/MS allowed the two coeluting compounds to be separated based on the transition ions. The results are shown in Figure 1. The order and retention time is shown in Table 1.

Calibration curve, linear fit, and recovery results

Most of the OTCs calibration curves were prepared at 1.0–200.0 µg/L (1.0, 5.0, 10.0, 20.0, 50.0, 100.0, 200.0 µg/L, seven points), and the results are shown in Table 2. The MRM chromatograms for the analysis of the 17 organotin standard mixture after derivatization with $NaBEt_4$ (5.0 µg/L) are shown in Figure 2.

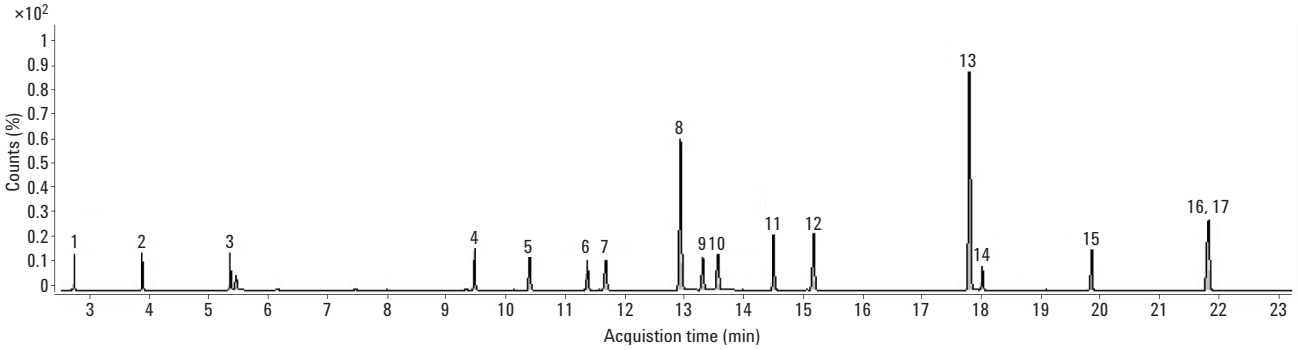


Figure 1. GC-MS/MS chromatogram for the analysis of 17 organotin standard mixture after derivatization with $NaBEt_4$.

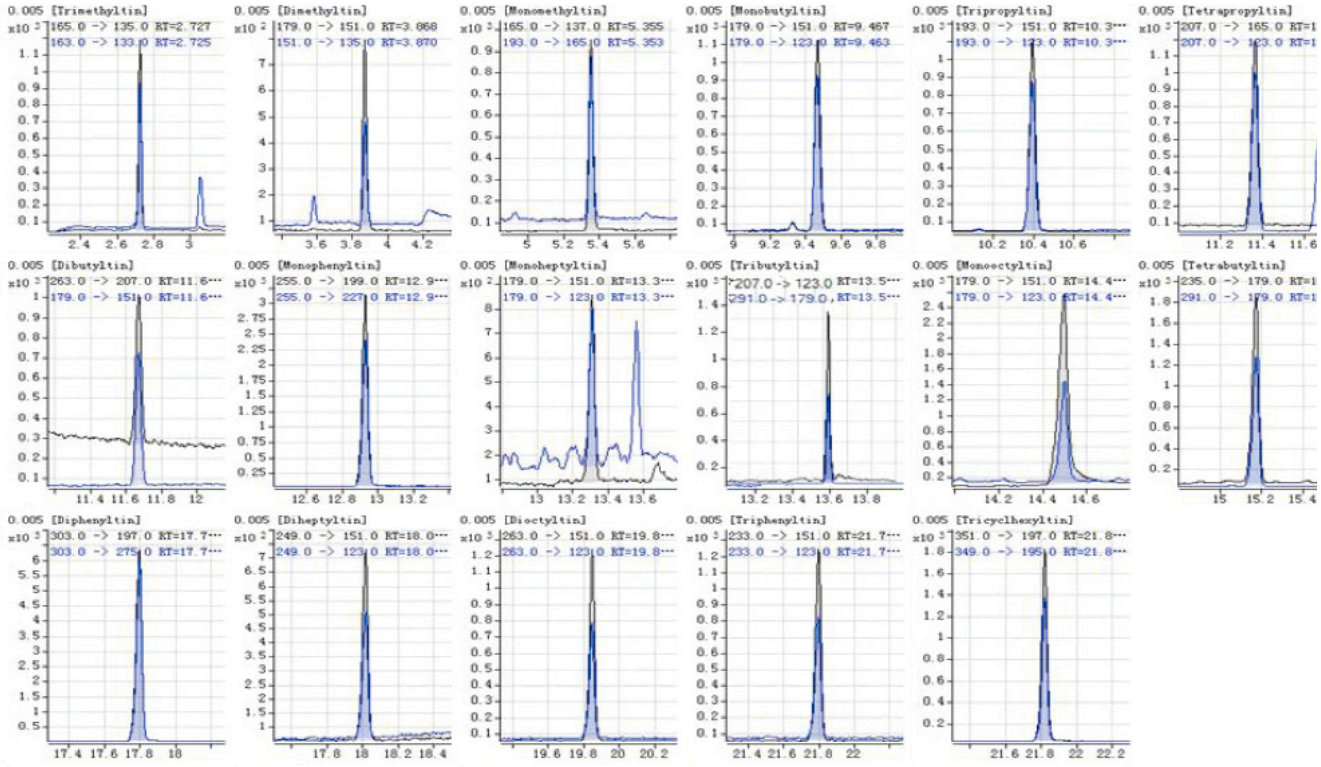


Figure 2. MRM chromatogram for analysis of 17 organotin standard mixture after derivatization with $NaBEt_4$ (5.0 µg/L).

Precision and recovery studies were performed in triplicate on beverage samples that were spiked at concentrations of 0.01 mg/L and 0.05 mg/L in hexane, which correspond to 0.001 mg/L and 0.005 mg/L in sample. The majority of RSDs were within 10%, and recoveries within 70–120%. The results are shown in Table 2.

Analysis results of 11 types of beverage

Eleven beverages were tested with above established method for the 17 kinds of OTCs. Dimethyltin and monobutyltin were detected in one sample with concentrations of 0.27 µg/L and 0.39 µg/L respectively.

Conclusion

The Agilent 7000 Series GC-MS/MS system in the MRM mode has the advantage of eliminating most background interferences resulting in high selectivity. This experiment demonstrates this analytical system's effectiveness in analyzing 17 organotins a variety of beverages.

Table 2. Linear Range, R^2, Recovery and RSD of 17 Organotin Compounds

				0.001 mg/L (n = 3)		0.005 mg/L (n = 3)	
No.	**Compound name**	**Linear range (mg/L)**	**R^2**	**% Recovery**	**% RSD**	**% Recovery**	**% RSD**
1	Trimethyltin (TMT)*	0.001–0.200	0.999	87.3	6.7	119.5	10.6
2	Dimethyltin (DMT)*	0.001–0.100	0.997	136.3	5.1	136.8	2.4
3	Monomethyltin (MMT)*	0.001–0.100	0.999	113.0	7.0	116.8	5.5
4	Monobutyltin (MBT)*	0.001–0.200	0.999	133.6	6.5	135.7	2.8
5	Tripropyltin (TPhT)*	0.001–0.200	0.996	104.9	4.7	114.3	2.4
6	Tetrapropyltin (TrPhT)*	0.001–0.200	0.996	71.0	3.5	87.7	6.1
7	Dibutyltin (DBT)*	0.001–0.200	0.999	108.9	3.2	114.9	2.4
8	Monophenyltin (MPhT)*	0.001–0.200	0.998	115.4	4.6	118.0	1.7
9	Monoheptyltin (MHT)*	0.001–0.200	0.999	116.2	9.4	114.4	9.0
10	Tributyltin (TBT)*	0.001–0.200	0.999	117.9	7.8	112.1	8.9
11	Monooctyltin (MOcT)*	0.001–0.200	0.997	129.4	3.8	112.8	8.1
12	Tetrabutyltin (TeBT)*	0.001–0.200	0.998	63.4	8.2	77.9	11.3
13	Diphenyltin (DPhT)*	0.001–0.200	0.998	76.0	6.5	83.7	1.8
14	Diheptyltin (DHT)*	0.001–0.200	0.999	102.1	5.6	96.7	2.3
15	Dioctyltin (DOcT)*	0.001–0.200	0.999	67.5	6.3	75.5	0.8
16	Tricyclhexyltin (TCyT)*	0.001–0.200	0.998	107.4	6.1	99.8	2.2
17	Triphenyltin (TPhT)*	0.001–0.200	0.999	82.2	7.5	82.4	3.4

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