Sensitive Determination of 17 Organotin Compounds in Beverages Using Agilent 7890A / 7000 Series GC-MS/MS System

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Introduction

Organotin compounds (OTCs) have been widely used as polymerized preservatives, insecticides and pesticides. The highest amount of OTCs found among coating materials in boats to prevent biological attachment in the ocean can reach to over 20% of the total which addressed great concerns. OTCs are identified as endocrine disruptive chemicals (EDCs) which may cause negative impact on human health via food chain.

OTCs were found in ocean water, sediments, textiles and human urines however studies on OTCs in food were relatively less. There were studies on analysis of OTCs by GCMS (single Quadrupole) and ICPMS or LC-ICPMS, yet conventional GCMS method is with limited separation and sensitivity capacity, which can normally detect less than 10 OTCs in one run. So far, speciation studies of OTCs by GC triple Quadrupole mass spectrometer (GC-MS/MS) technique are seldom seen.

Agilent 7000 Series GC-MS/MS was applied in this research work to establish a precise, rapid and reliable method to study 17 OTCs in beverages. 11 kinds of beverages samples were tested to check preliminary contamination status of OTCs in the market which could be polluted by Tin containers.

Experimental

Samples, Reagents

The beverages were obtained from local grocery stores.
Acetate buffer: 82g/L sodium acetate in water, adjusted to pH 4.5 with acetic acid.
Derivatization reagent :Dissolve 2g $NaBEt_4$ in 10mL ethanol. This solution should be freshly prepared.
Ethanol, Hexane, Methanol : chromatography grade purity

Experimental

Standards , Derivatization method

Standards: The standards were dissolved in methanol at 1000 ppm (1mg/mL) concentration and were further diluted, depending on the derivatization method used.
Derivatization method: To 1 mL standard solution , 1 mL acetate buffer and 50 µL derivatization reagent are added. The solution is shaken and allowed to react for 30min. After addition of 5mL water, the derivatized compounds are extracted in 1 mL hexane. The mixture is vortexed for 10 s and the two phases are allowed to separate. The clear upper layer (apolar hexane phase) is transferred to an auto sampler vial for analysis.

Sample preparation

Weight 10 mL beverage sample into 22mL bottle, add 5.0 mL Methanol, ultrasonic extraction 10 min.

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To this solution, 2 mL acetate buffer and 200 µL derivatization reagent are added. The sample is shaken and allowed to react for 30 min.

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The derivated compounds are extracted in 1 mL hexane. The mixture is vortexed for 30 s and the two phases are allowed to separate.

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The clear upper layer (apolar hexane phase) is transferred and filtered to an autosampler vial for analysis.

Experimental

Chromatographic Parameters

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

Mass Spec Parameters

Mass system : 7000 Series MS/MS;
Ion source: EI;
Ion source polarity: Positive ion;
Ionization voltage: 70 eV;
Ion source temperature: 230°C;
Interface temperature: 280°C;
•Collision Gas : Nitrogen 1.5 mL/min;
•Quenching Gas : Helium 2.25 mL/min;
•Solvent delay: 2.0 min;

Results and Discussion

Chromatographic separation results

GC separation was finished in 22 min with 15 of 17 compounds ideally separated. Although the last two OTCs could not be separated as expected, extraction of transition ions and precise quantitation were accomplished by unique feature of GC-MS/MS given that appropriate ions were selected, extracted and monitored, at meantime, optimized GC and MS parameters were applied.

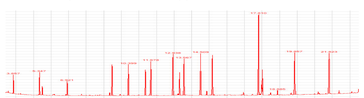


Figure 1. GC-MS/MS chromatogram for analysis of 17 Organotin standard mixture.

Results and Discussion

Calibration Curve, Linear Fit

Calibration curves were prepared at 1.0-200 µg/L(1.0、5.0、10.0、20.0、50.0、100.0、200.0 µg/L 7 points), the results were shown in the following Figure .

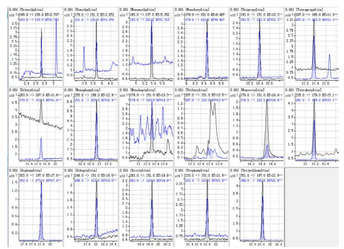


Figure 2. MRM Chromatogram for Analysis of 17 Organotin Standard Mixture (1.0 µg/L).

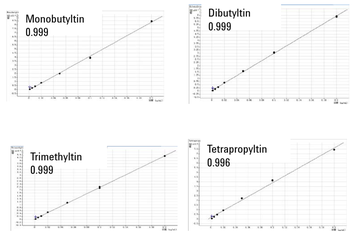


Figure 3. Standard Calibration Curve Results of Organotin Compounds

Results and Discussion

No.	Compound	RT(min)	Linear range (µg/L)	R^2
1	Trimethyltin	2.72	1-200	0.999
2	Dimethyltin	3.86	1-200	0.995
3	Monomethyltin	5.34	1-100	0.999
4	Monobutyltin	9.45	1-200	0.999
5	Tripropyltin	10.38	1-200	0.996
6	Tetrapropyltin	11.35	1-200	0.996
7	Dibutyltin	11.66	1-200	0.999
8	Monophenyltin	12.92	1-200	0.998
9	Monoheptyltin	13.29	1-200	0.999
10	Tributyltin	13.54	1-200	0.999
11	Monooctyltin	14.49	1-200	0.997
12	Tetrabutyltin	15.16	1-200	0.998
13	Diphenyltin	17.78	1-200	0.998
14	Diheptyltin	18.00	1-200	0.999
15	Dioctyltin	19.83	1-200	0.999
16	Tricyclhexyltin	21.80	1-200	0.998
17	Triphenyltin	21.80	1-200	0.999

Figure 4. The Linear Range and R^2 of 17 Organotin Compounds.

Recovery Results

Beverage samples were spiked with 10 µg/L and 50 µg/L mixed standard thus precision and recovery study of the method were conducted, majority of RSDs were within 10% and recoveries within 70-120%,the result shown in figure 5 .

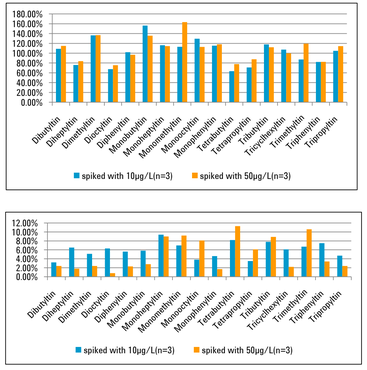
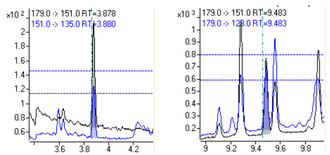


Figure 5. The Recovery and RSD Result

Analysis results of 11 Kinds of Beverages

11 kinds of Beverages were tested with above established method for the 17 OTCs among which Dimethyltin and Monobutyltin were detected in one sample, the result shown in figure 6 .

Analysis results of One Beverage Sample



OT	RT（min）	Concentration（µg/L）
Dimethyltin	3.86	0.27
Monobutyltin	9.46	0.39

Figure 6. The Result of One Beverage Sample

Conclusions

Agilent 7000 Series GC-MS/MS technique with MRM mode has the advantage of eliminating background interferences, highly sensitive and selective, so that it turned out to be suitable and effective in analyzing 17 OTCs in beverages.