Characterization of tin species using HPLC-ICP-MS

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1 Introduction

Organotin compounds are widely used as stabilizers, catalysts and biocides in industry and agriculture resulting in their widespread pollution of various environmental media, including potable water. Once in the environment, these compounds eventually reach marine environments where they may elicit acutely and chronically toxic effects on animals depending upon these systems.

Although historically analyzed using GC-ICP-MS, the Chinese standard HJ 1074-2019 allows for the characterization of organotin species by HPLC-ICP-MS. The advantages of LC over GC for the separation of organo-tin species are simplified sample preparation, minimizing steps which could compromise species integrity and abundance, and faster sample turn-around times.

In this study, HJ 1074 was applied to the separation and analysis of four tin species in tap water using the NexSAR™ HPLC-ICP-MS speciation solution.

Key Features

- Seamlessly integrated HPLC-ICP-MS solution
- Completely metal-free flow path-NexSAR Inert HPLC
- Flexible, tried and tested Clarity™ software
- Robust and versatile NexION ICP-MS system

NexSAR™ Speciation Solution comprised of the NexSAR™ Inert HPLC and the NexION® ICP-MS

Inert, metal-free binary pump

- Post-seal wash reduces seal wear and tear, downtime and service needs.
- Dual-piston binary pump with a high pressure mixer ensuring low pulsation and homogenous mobile phases in gradient elutions.

2 Methodology

Tap water samples were collected in Guangzhou, China and prepared according to the direct injection method described in HJ 1074: acidification with 1% HCl (v/v) and filtering through a 0.22 µm PTFE membrane for analysis.

DBT, TBT, DPT, and TPT (Aladdin Bio-Chem Technology Col, Shanghai, China) were prepared at concentrations of 10, 20, 50, 100, 150, and 200 µg/L in 1% HCl (v/v), in accordance with the recommended concentrations specified in HJ 1074.

In the absence of a certified reference material, a spiked sample (spiked with 2.5 µg/L mixed tin species) was prepared to verify the analytical accuracy of the method.

All analyses were performed using a NexSAR Inert Speciation System (PerkinElmer Inc., Shelton, Connecticut, USA) comprised of the NexSAR 200 Inert HPLC Pump, Cooled-Inert Autosampler, and Solvent Tray with Degasser. The system was coupled to a NexION® ICP-MS (PerkinElmer Inc.). All analyses and the collection of data were performed using Clarity™ chromatography software.

Details pertaining to the HPLC and ICP-MS conditions are shown in Table 1.

Table 1 HPLC and ICP-MS parameters

Parameter	Value
Chromatography	Reversed-phase Chromatography
Mobile Phase	Acetonitrile: water: acetic acid = 65:23:12 (v/v/v), containing triethylamine 0.05%
Separation Scheme	Isocratic
Injection volume	200 µL, Full loop
HPLC Vials	Speciation-tested metal-free
Nebulizer	MEINHARD® plus Glass Type C
Spray Chamber	Glass cyclonic
RF power	1600 W
Injector	2.0 mm I.D Quartz
Mode	Standard
Dwell time	999 ms

3 Results and Discussion

The corresponding calibration curves are shown in Figure 1, each with correlation coefficients greater than the 0.990 specified in HJ 1074, demonstrating excellent linearity across the expected concentration range for Sn in water.

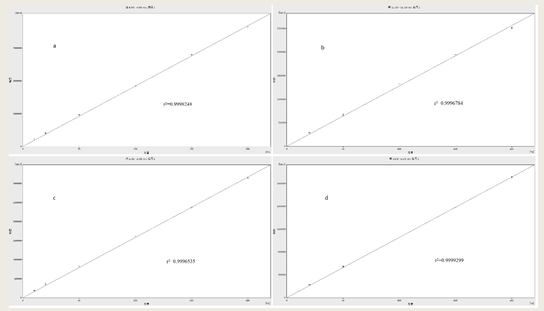

Figure 1 Linear regression of calibration standards ranging in concentration from 10 - 200 µg/L for (a) DBT, (b) TBT, (c) DPT, (d) TPT in 1% HCl, and the respective correlation coefficients.

Figure 2 shows the baseline separation of all species for the calibration standards in under 11 minutes. Peak identification was accomplished by matching retention times with those observed by initially injecting each organotin species individually. The chromatograms in Figure 2 do not show any peak shifting, demonstrating that consistent, reliable, and reproducible flows are delivered by the NexSAR 200 Inert HPLC Pump, allowing for the correct identification of anaytes.

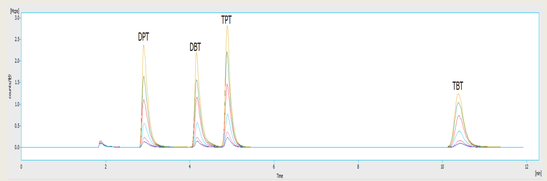

Figure 2 Chromatograms showing overlay of calibration standards (10 – 200 µg/L).

As shown in Figure 3, the detection limits (DLs) are more than an order of magnitude lower than specified in HJ 1074 for all species.

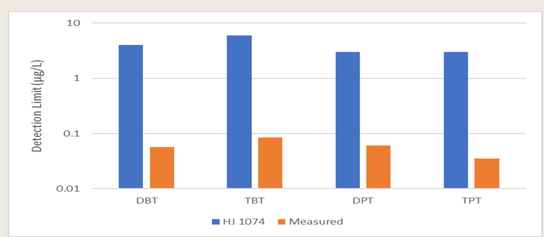

Figure 3 Detection limits specified in HJ 1074 and measured DLs

To check for robustness of the chromatographic method, a tap water sample was spiked with a 2.5 µg/L mixture of the organotin species. The tap water did not contain measurable amounts of any organotin species. However, as seen in Figure 4, the retention times of the spiked species match those of a 2.5 µg/L standard, demonstrating that the water sample does not have any impact on the affect the retention times or peak shapes of the chemical species.

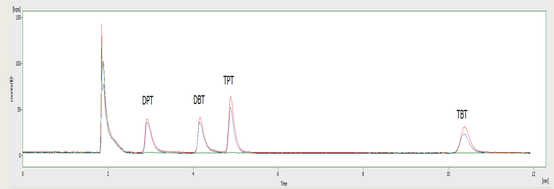

Figure 4 Chromatograms of un-spiked tap water, spiked (2.5 µg/L) tap water, and a 2.5 µg/L standard.

4 Conclusion

This study evaluated the separation, detection, and analysis of dibutyl tin, tributyl tin, diphenyl tin, and triphenyl tin in accordance with Chinese method HJ 1074 using a NexSAR Inert HPLC system coupled to a NexION ICP-MS.

The results show that the complete baseline of organic tin could be achieved in under 11 minutes using the proposed instrumentation and methodology, exceed the requirements stipulated of HJ 1074, and was made possible by two factors:

1. The robust plasma of the NexION
2. The accurate flow of the mobile phase delivered by the NexSAR pump are critical to achieve consistent, repeatable separations and