Food Chemistry 119 (2010) 364–367

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

Determination of total tin and organotin compounds in shellfish by ICP-MS

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ARTICLE INFO

Article history:
Received 17 December 2008
Received in revised form 14 April 2009
Accepted 24 May 2009

Keywords:
HPLC-ICP-MS
Organotin compounds
Speciation
Shellfish

ABSTRACT

A method based on microwave digestion and inductively coupled plasma-mass spectrometric (ICP-MS) analysis was established for the determination of total tin in shellfish samples. Good linearity of the calibration curves was obtained for tin elements ($r = 1.0000$). Detection limit for Sn was 34.6 ng/g. Total tin concentrations in these samples ranged from non-detectable to 0.45 μg/g. High-performance liquid chromatography hyphenated with inductively coupled plasma-mass spectrometry (HPLC-ICP-MS) was applied to the simultaneous determination of five organotin compounds in the shellfish samples. The fresh and freeze-dried shellfish samples were treated by ultrasonic extraction with two different extraction solvents. Four organotin compounds including dibutyltin (DBT), tributyltin (TBT), diphenyltin (DPhT) and triphenyltin (TPhT) in shellfish samples were detected. It was found that the dominate species in the samples were tributyltin (TBT) and triphenyltin (TPhT).

1. Introduction

Organotin compounds (OTs) have been widely used in the production of polyvinylchloride (PVC) materials as heat and light stabilisers and as anti-bacterial and anti-fungal agents in pesticides and anti-fouling applications. Their toxicity, especially tributyltin (TBT) and triphenyltin (TPhT), in coastal environment has resulted in deleterious effects on non-target organisms such as shellfish. OTs can be cumulated in shellfish, which can then impact on human health because of bioaccumulation through the food chains. Generally, the determination of organotin compounds in shellfish has been carried out by gas chromatography (GC) (Munoz, Gallego, & Valcarcel, 2005a, 2005b). However, the derivation step required for GC analysis often results in yield irreproducibility because of matrix interference. High-performance liquid chromatography (HPLC) (Vinas, Lopez-Garcia, Merino-Merono, Campillo, & Hernandez-Cordoba, 2004) does not involve a derivation step, which can eliminate a potential source of uncertainty in the final result. The determination of OTs is usually performed by means of HPLC coupled with various detectors, such as AAS (Minganti, Capelli, & Pellegrini, 1995), AES (Munoz et al., 2005a, 2005b) and MS (Chiron, Roy, Cottier, & Jeannot, 2000). Among the detection techniques used in recent years, ICP-MS offers unique advantages including element specificity, wide dynamic linear range and low detection limits. In this study, a method was developed to determine simultaneously five OTs in fresh and freeze-dried shellfish samples.

2. Experiment

2.1. Reagents

HPLC separations for organotin applications: glacial acetic acid (HAC) was obtained from Fluka; acetonitrile (HPLC grade) and methanol (HPLC grade) were obtained from Merck, Germany; and sodium acetate (NaAC) was obtained from Tianzhi chemical company of Zibo, China. Triethylamine (TEA, HPLC grade) was obtained from ACROS. De-ionised water was obtained from a water purification unit at 18 MΩ (Millipore, USA). Trimetyltinchloride (TMTCl), dibutyltinchloride (DBTCl), tributyltinchloride (TBTCl), diphenyltinchloride (DPhTCl) and triphenyltinchloride (TPhTCl) were all obtained from Aldrich.

2.2. ICP-MS and HPLC-ICP-MS conditions

An Agilent 7500a ICP-MS was used for total Sn and organotin detection. Speed wave MW-3$^+$ microwave digestion system (Berghof, Germany) was employed to digest the samples. An Agilent Technologies 1100 HPLC system was used for HPLC separations. When total Sn was determined, Optimisation of the ICP-MS conditions was achieved by adjusting the torch position and tuning for reduced oxide and doubly charged ion formation with a standard tuning solution containing Li, Y, Ce and Tl in 2% HNO_3. The ICP-MS condition was shown as Table 1. When HPLC was coupled with ICP-MS for organotin separation, there was about 80% organic solvent in HPLC mobile phase, which may cause carbon build-up on the ICP plasma cone. In order to reduce the solvent loading to the plasma, the double-pass spray-chamber was peltier cooled to

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doi:10.1016/j.foodchem.2009.05.079

Table 1
ICP-MS conditions.

Parameter	Value
ICP-MS conditions	
RF power (W)	1350
Sampling depth (mm)	6.5
Carrier gas flow (L/min)	1.1
Make-up gas flow (L/min)	0
O_2/Ar mixed gas	0
Chamber temperature	2 °C
Nebuliser	Babington
Cones	Ni

−5 °C. O_2/Ar mixed gas (30%) was mixed into the make-up gas and added post-nebulisation in order to convert organic carbon to CO_2 in the plasma and avoid carbon build-up on the cones. The HPLC-ICP-MS conditions are given in Table 2.

2.3. Sampling and pretreatment

The marine biological samples were collected from located market. The biological samples included jewfish, shrimp, scallop, oyster and others. The samples were first unshelled and the soft tissues were pooled and thoroughly rinsed with de-ionised water to remove extraneous impurities, then they were freeze-dried and powdered before digestion and extraction.

2.4. Total tin determination

Before ICP-MS determination, the samples were digested in microwave digester. A measure of 0.2 g milled powder, 5 mL of HNO_3 and 1 mL H_2O_2 were placed in a Teflon digestion vessel, predigested over night at room temperature and then digested according to the US EPA method 3052. The temperature was raised to 120 °C in 5 min, then raised to 180 °C from 5 to 10 min and held for10 min at 180 °C. The digested solution was diluted with pure water to 25 g. The standard solution and reagent blanks were digested in the same way. The total tin concentration was directly determined by ICP-MS.

2.5. Extraction procedures

2.5.1. Mobile phase extraction of freeze-dried samples

About 0.2 g of dried and powdered seafood was weighted precisely in the plastic tubes and the extraction was carried out with 3 ml of CH_3CN:H_2O:CH3COOH:TEA (65:23:12:0.05%, v/v/v/v pH 3.0), The samples were extracted by ultrasonic extraction for 30 min and then centrifuged (20 min, 8000 rpm). The supernatants were filtered by 0.45 μm membrane and analysed by HPLC-ICP-MS.

Table 2
HPLC-ICP-MS conditions.

Parameter	Value
ICP-MS conditions	
RF power (W)	1550
Sampling depth (mm)	6.5
Carrier gas flow (L/min)	0.6
Make-up gas flow (L/min)	0.2
O_2/Ar mixed gas	30%
Chamber temperature	−5 °C
Nebuliser	PFA
Cones	Pt
HPLC conditions	
Column	Agilent TC-C18 (4.6 × 250 mm, 5 μm)
Mobile phase	CH_3CN:H_2O:CH_3COOH:TEA = 65:23:12:0.05% (v/v/v/v) pH 3.0
Injection	20 μL
Flow rate	0.4 mL/min

2.5.2. Mobile phase extraction of fresh samples

About 3 g of fresh shellfish sample was weighted precisely in the plastic tubes and the extraction was carried out with 5 ml of CH_3CN:H_2O:CH_3COOH:TEA (65:23:12:0.05%, v/v/v/v pH 3.0), The samples were ultrasonically extracted for 30 min and then centrifuged (20 min, 8000 rpm). The supernatants were filtered by 0.45 μm membrane and analysed by HPLC-ICP-MS.

2.5.3. HAC-NaAC extraction of freeze-dried samples

About 0.2 g of dried and powdered shellfish was weighted precisely in the plastic tubes and the extraction was carried out with 1.5 ml of HAC-NaAC (pH 4.5) and 1.5 ml methanol. The samples were extracted for 30 min and then centrifuged (20 min, 8000 rpm). The supernatants were filtered by 0.45 μm membrane and analysed by HPLC-ICP-MS.

3. Results and discussion

3.1. Total tin determination

3.1.1. Selection of isotopes of tin

The total tin in shellfish samples was determined by Agilent 7500a ICP-MS. The detector of Agilent 7500a ICP-MS was a quadrupole MS. The major disruptions in analysis were isobars interference, oxide ion interference, doublely charged ions interference and polyatomic ions interference from aqueous solution and carrier gas. There are ten tin isotopes, and studies were carried out to select the isotope with the smallest analytical interference and maximum sensitivity. Among these isotopes, the natural abundances of ^{112}Sn, ^{114}Sn and ^{15}Sn are lower than 1%. At the same time, ^{115}Sn was disturbed by In while ^{124}Sn was disturbed by YCl. The abundances of ^{118}Sn and ^{120}Sn are the highest. The two isotopes were less disturbed by oxides, polyatomic ions and hydride. ^{118}Sn was selected for analysis. Because ^{118}Sn was less disturbed than ^{120}Sn by chloride and argon.

3.1.2. The calibration study, detection limits and method precision

A series of Sn standard solutions of 0 μg/L, 0.5 μg/L, 1 μg/L, 10 μg/L, 100 μg/L were used to construct the calibration curve, for which a good linear relationship was observed. The linear equation was $Y = 0.1936X + 0.0087$ with a correlation coefficient of 1.0000.

Under the optimal conditions of the apparatus, replica blank samples were measured for seven times. Detection limit was set at three times of the relative standard deviation, i.e., 34.6 μg/kg.

The Oyster sample was measured for five times and the RSD was 1.78%, which showed that the method was very precise.

3.1.3. The accuracy of method

To establish the accuracy of this method, the TORT-2 standard reference material was analysed. The measured result of Sn at 0.042 mg/kg was in good agreement with the reference value of 0.040 mg/kg, which shows the high accuracy of the method.

3.1.4. Sample analysis

The results of total tin concentrations in shellfish samples are given in Table 3. All concentration values presented in this paper are calculated based on dry weight of the sample. It was shown that total tin concentrations in these samples ranged from undetectable to 0.45 mg/kg.