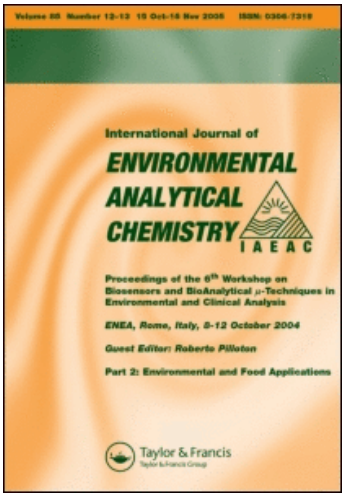

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Determination of Tributyltin in Oysters by Electrothermal Atomic Absorption Spectrometry

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DETERMINATION OF TRIBUTYLTIN IN OYSTERS BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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Graphite-furnace atomic absorption spectrometry for tributyltin in oysters is described. Tributyltin is extracted by *n*-hexane after digestion with hydrochloric acid. The 3σ detection limit for tributyltin is better than 0.01 mg Sn/kg. Typical absorbance values are about 0.10 for tributyltin contents as low as 0.03 mg Sn/kg. Tributyltin contents of 29 oyster samples are given.

KEY WORDS: Tributyltin (TBT), oysters, graphite furnace atomic absorption spectrometry.

INTRODUCTION

Tributyltin oxide (TBT) is used as an antifouling agent in marine paints. There has been considerable concern about its toxicity towards marine fauna. Some of the harmful effects of TBT towards oysters include shell thickening,[1] inhibition of development of oyster larvae,[2] and mortality at low concentration.[3] Oysters are filter feeders and accumulate trace metals from solution and also by ingestion of particulate matter. This creates a potential hazard to human consumers that eat contaminated oysters. A need therefore arises for sensitive methods to quantitate TBT in biological samples such as oysters.

A sensitive atomic absorption spectrometric (AAS) method for TBT in oysters is described. The method involves an *n*-hexane extraction of TBT and other tin compounds from a hydrochloric acid digest of oyster tissue. This is followed by washing with sodium hydroxide to remove inorganic, monobutylated and dibutylated tin compounds. The method is based upon the work of McKie.[4] Procedural differences include the addition of matrix modifier at the TBT concentration step. This enables concentration to dryness without loss of tin. Accurate dissolution in a small volume is then possible, resulting in a much better detection limit. Other differences produce considerable savings in waiting time and reagent quantities.

MATERIALS AND METHODS

Apparatus

Perkin–Elmer model 2380 Atomic Absorption Spectrophotometer, with deuterium-

Table 1 AAS furnace conditions

Step	*Temp (°C)*	*Ramp time (s)*	*Hold time (s)*
1	110	10	5
2	200	10	30
3	1100	60	30
4	1100	1[a]	2
5	2100	0[a,b]	5[c]
6	2700	1	1
7	20	1	5

[a]Argon flow interrupted.
[b]Maximum power heating mode; "read" activated at end of step 4.
[c]Integration time.

arc background correction, HGA-500 graphite furnace and AS-40 auto sampler was used. A tin hollow cathode lamp was operated at 30 mA current. The spectrophotometer was set for a wavelength of 286.3 nm and a slit width of 0.7 nm. Pyrolytically coated graphite tubes with L'vov platforms were used for the furnace. The furnace conditions are given in Table 1. Injection volumes were 10 μl. All laboratory ware was soaked in 2 M hydrochloric acid for at least 24 h and was thoroughly rinsed with demineralised water before use.

Reagents and Standard Solutions

Only analytical-grade reagents and glass-distilled water were used.

Modifier solution consisting of 25% (w/v) ammonium dihydrogen phosphate was filtered through slow filter paper (Whatman 42) to remove insoluble foreign material which could contribute to high reagent blanks.

Calibration standards were prepared in a matrix of 20% nitric acid and 15% (w/v) ammonium dihydrogen phosphate, from tin(IV) chloride solution (titrisol-Merck 9929).

Tributyltin standards used in recovery experiments were prepared in glacial acetic acid from tributyltin oxide (ICN Biomedicals, K & K Labs, Plainview, NY, U.S.A.).

Procedure

Weigh 5.0 g of homogenised oyster into a 100 ml stoppered volumetric flask and add 25 ml of concentrated hydrochloric acid. Rotate the flask for 90 min using a laboratory suspension mixer. Add accurately 50 ml of hexane to the flask and mix for a further 50 min to extract the TBT. Transfer the contents of the flask to a 100 ml separating funnel and remove as much of the lower aqueous layer as possible without losing any of the emulsion. Break the emulsion by adding 5–10 g anhydrous sodium sulfate. Pour off as much emulsion-free hexane as possible (usually about 40 ml) through the top of the separating funnel into a second separating funnel. Add 50 mL of 3% sodium hydroxide solution and shake vigorously for about 1 min. Carefully discard as much of the aqueous layer as

possible without losing any emulsion (if present). Add a further 25 ml of the sodium hydroxide solution and shake vigorously again for 1 min. Discard the aqueous layer, and decant the clean emulsion-free hexane layer through the mouth of the separating funnel into a 100 ml beaker.

Measure the volume of hexane recovered. Add 5 ml of concentrated nitric acid and 1.5 ml of 25% (w/v) ammonium dihydrogen phosphate to the beaker. Place a bent glass tubing spacer and watchglass on the beaker and evaporate the hexane on a boiling water bath. Transfer the beaker with its cover glass to a hot plate set for about 160 °C and evaporate the contents until just a few drops of liquid remain. Remove the beaker and allow to cool. Add 2.5 ml of 20% nitric acid and warm briefly to aid dissolution of the residue. A small amount of non-oxidised organic residue will be present, but this does not affect the quantitation. Transfer the contents of the beaker to an autosampling vial for quantitation, using furnace conditions described in Table 1. Prepare a calibration curve from inorganic tin standards with concentrations between 0.02–0.20 mg/l.

RESULTS AND DISCUSSION

Twenty-nine oyster sample homogenates from several locations in New South Wales were analysed for TBT by the described method. Ten samples had levels of 0.003–0.01 mg Sn/kg, eleven samples were between 0.011 and 0.020 mg Sn/kg, two samples were between 0.021 and 0.030 mg Sn/kg, three samples were between 0.04 and 0.05 mg Sn/kg, while the remaining samples had 0.07, 0.09 and 0.17 mg Sn/kg. The highest two levels were from samples known to have been growing in contaminated water and are consistent with levels found in the United Kingdom by Thain and Waldock[5] in samples from areas with heavy pleasure craft activity.

Recoveries of TBT were estimated by spiking 5 g samples at four levels in the range of 0.018–0.18 mg Sn/kg. The recoveries were between 80 and 101%. Six 0.18 mg Sn/kg spikes had recoveries of 87–101% with a mean of 95%. The recoveries obtained should be a reasonable approximation of TBT bound in oyster tissue, because acid digestion completely dissolves oyster tissue before hexane extraction.

The reproducibility of the method was tested on a sample which had a TBT level of 0.09 mg Sn/kg. The sample was analysed eight times and gave a range of 0.087–0.094 mg Sn/kg, with a mean of 0.091 and a coefficient of variation of 3.8%.

The possibility of inorganic, monobutyl or dibutyl tin species interfering with the tributyltin determination was investigated. Solutions containing 250 μg of inorganic and monobutyltin, and a solution containing 25 μg of dibutyltin were subjected to the same extraction procedure as a sample. No measurable tin could be detected in the inorganic or monobutyltin extractions, and only 0.05 μg of tin (0.01 mg/kg for a 5 g sample) was detected in the case of the dibutyltin extraction. It is possible that the dibutyltin compound used (98% pure) contained traces of tributyltin as an impurity, and that no dibutyltin remained after sodium hydroxide washing. This is supported by the fact that additional sodium hydroxide washes did not significantly reduce the level of tin from the dibutyltin extract. McKie[4] also found that dibutyltin did not interfere.

Typical blank absorbances were around 0.01–0.02. The mean of 10 blank determinations was 0.011 with a standard deviation of 0.0023. This represents a 3σ detection limit of 0.002 mg Sn/kg for a 5 g sample.

The calibration curve was linear up to concentrations of 0.20 mg Sn/L for an injection volume of 10 μl. A typical blank corrected absorbance for a 0.10 mg/l standard was 0.179.

The described method offers a simple and sensitive procedure for the determination of TBT in oysters.

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