*Applied Organometallic Chemistry* (1989) 3 351–353
Longman Group UK Ltd 1989

0268–2605/89/03408351 $03.50

**COMMUNICATION**

# Compounds of arsenic, antimony, and tin in mollusc shells

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*Received 6 February 1989* *Accepted 11 April 1989*

**Inorganic arsenic(III) and arsenic(V), methylarsenicals, antimony(III), and antimony(V), and butyltin derivatives are present in the shells of molluscs found in the coastal waters of British Columbia.**

**Keywords: molluscs, shells, arsenicals, antimony, organotin, speciation, methylarsenicals, butyltin, mass spectrum**

Apart from a rather vague reference to the presence of methylarsenicals in shells[1] and the observation that radioactive arsenate added to seawater is found in (or on) the shells of gastropods,[2] the literature is essentially silent regarding the presence of arsenic compounds in the shells of molluses. There are no reports of tin derivatives in mollusc shells even though organotin compounds have been implicated in the shell growth anomalies of oysters.[3] Biogeochemical knowledge of antimony is only recently being developed[4–7] and again apart from some information regarding the uptake of radioactive antimony-124 by tissue,[7] no measurements on shells have been reported.

The results of some studies on mollusc shells collected from coastal British Columbia are given in Table 1. The following comments can be made about the data: (1) the neutron activation results are in reasonable agreement with those determined by atomic absorption spectroscopy (exact agreement is not expected because of the 'organic content' of shells[8]); (2) arsenic concentrations are greater than antimony for a given species; (3) arsenic concentrations vary considerably with geographical location – for example, Hastings Arm is a pristine wilderness area in Northern British Columbia, whereas Patricia Bay and Cole's Bay are near the metropolitan area of Victoria; (4) arsenic concentrations in gastropods seem to be higher than in bivalves, although Alice Arm (which is near Hastings Arm) is a site contaminated by mine tailings, and these could be the source of the arsenic. The effect of this source is more evident in the manganese content of the shells, where the neutron activation values for Jordan's colus and the Phoenician whelk are 3970 ± 14 and 1310 ± 14 $\mu g\ g^{-1}$ respectively. For comparison the manganese content of the shell of a Soft-shell clam from Hastings Arm is 60 ± 2 $\mu g\ g^{-1}$. High manganese concentrations (2085 ± 114 $\mu g\ g^{-1}$) have been reported for an intertidal periwinkle found in Nigeria.[9]

Data on the species of arsenic and antimony compounds found in some bivalve shells are listed in Table 2. No methylantimony species appear to be present and antimony is found mainly as antimony(V). Inorganic arsenic is present in both oxidation states with arsenate predominating and all the samples contain low levels of methyl- and dimethyl-arsenic compounds. These methylarsenicals are probably salts of $MeAsO(OH)_2$ and $Me_2AsO(OH)$, although methylarsenic(III) species cannot be completely ruled out because of the method of detection. For some as-yet unknown reason the ratio [total As]/[total Sb] is lower for these samples than those reported in Table 1.

Organotin compounds are also present in bivalve shells.[10] For these determinations the crushed shell (12–36 g) was dissolved in concentrated hydrochloric acid (50 $cm^3$) and the resulting solution diluted to 100 $cm^3$. Aliquots (50 $\mu L$) of this solution were injected onto a Waters $C_{18}$ $\mu$-Bondapak steel column, [3.9 mm (i.d.) × 30 cm]; the mobile phase was 98% (2% acetic acid in acetone) and 2% tetrahydrofuran.

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**Table 1** Arsenic and antimony concentrations in mollusc shells

| Species | Origin | Arsenic concn ($\mu g\ g^{-1}$)[a,b] | Antimony concn ($\mu g\ g^{-1}$)[b,c] |
|---|---|---|---|
| Bivalves | | | |
| Soft-shell clam (*Mya arenaria*) | Hastings Arm | 26.3 ± 0.8 (25.9 ± 0.2) | (0.51 ± 0.04) |
| | Anyox (slag heap) | 4.4 ± 0.2 (4.0 ± 0.2) | (0.14 ± 0.06) |
| | Patricia Bay | 0.4 ± 0.04 | |
| | Coles Bay | 0.4 ± 0.05 | |
| *Native littleneck* clam (*Protothaca staminea*) | Patricia Bay | 0.3 ± 0.05 | |
| | Coles Bay | 0.3 ± 0.05 | |
| Butter clam (*Saxidomus giganteus*) | Thetis Island | 0.6 ± 0.02 | (<0.2) |
| Blue mussel (*Mytilus edulis*) | Hastings Arm | 0.15 ± 0.01 (<0.2) | (<0.2) |
| | Rupert Inlet | 0.10 ± 0.01 | |
| Gastropods | | | |
| Jordan's colus (*Colus jordani*) | Alice Arm | 16.3 ± 6.5 (25.1 ± 0.3) | (1.3 ± 0.1) |
| Lyre whelk (*Bucinuum plectrum*) | Alice Arm | 5.1 ± 0.09 (2.3 ± 0.2) | (<0.2) |
| Phoenician whelk (*Neptunea phoenicius*) | Alice Arm | 5.8 ± 0.8 (7.8 ± 0.2) | (0.2 ± 0.1) |
| Northwest neptune (*Neptunea lyrata*) | Alice Arm | 1.9 ± 0.2 (2.3 ± 0.2) | (<0.2) |

[a]Shells were crushed and dissolved in hydrochloric acid (1 g in 1 $cm^3$ of 2 mol $dm^{-3}$ HCl). The solutions were filtered and arsenic concentrations were determined by the UV/HG AA technique described in Ref. 11.
[b]Values in parentheses were determined on crushed shells by using neutron activation analyses (Analytical Services of Queens University, Ontario, Canada). The precision of these measurements is at the 95% confidence level according to counting statistics.
[c]Antimony concentrations were not determined by hydride generation procedures in this series of experiments.

**Table 2** Arsenic and antimony species in mollusc shells[a,b]

| Bivalve | Origin | Sb(III) | Sb(V) | As(III) | As(V) | MeAs(V) | $Me_2As(V)$ |
|---|---|---|---|---|---|---|---|
| Butter clam (*Saxidomus giganteus*) | Patricia Bay | 4.5 | 114 | 5.1 | 41.6 | 1.2 | 3.8 |
| Bent-nose clam (*Macoma natsuta*) | Patricia Bay | [c] | 34.9 | 18.8 | 46.1 | 3.7 | 1.2 |
| Soft-shell clam (*Mya arenaria*) | Patricia Bay | [c] | 28.3 | 15.4 | 198.2 | 1.9 | 1.1 |
| Blue mussel (*Mytilus edulis*) | Mayne Island | [d] | [d] | 17.6 | 86.5 | 5.9 | 2.0 |

[a]Concentrations are given in ng of the element per g of shell and are reliable to ±5%.
[b]Shells were crushed and dissolved in hydrochloric acid. The solution was filtered, neutralized (pH 7), and the concentration of the species determined by hydride generation procedures by using gas chromatography for separation and atomic absorption for detection as described in Ref. 12.
[c]Not detected.
[d]Not determined.

Graphite furnace atomic absorption spectroscopy was used for detection. This system can be used to separate and quantitate solutions containing $Bu_3SnX$ and $Bu_2SnX_2$ although $BuSnX_3$ cannot be separated from $Bu_2SnX_2$.[10] As an example, oyster shells (*Crassostrea gigas*) from Denman Island contain 2.8 ± 0.6 $\mu g\ g^{-1}$ of $Bu_3SnCl$ and 20 ± 1 $\mu g\ g^{-1}$ of $Bu_2SnCl_2$, both given as tin.

Because the identity of the butyltin compounds in the shells is based only on retention times and tin content, it was deemed desirable to establish the nature of the species with more certainty. Thermospray mass spectrometry seemed ideal for this purpose; however, in our hands the application of this technique to dichloromethane extracts of the acid solutions proved to be not sensitive enough to detect the tin compounds.

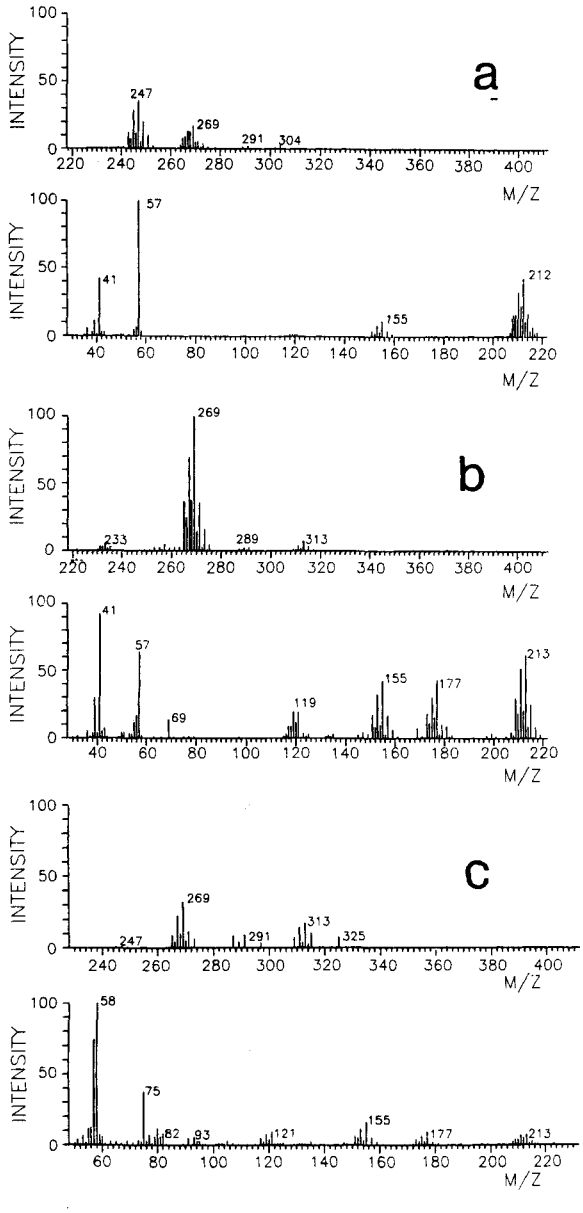


**Figure 1** Electron impact mass spectrum of (a) $(n\text{-}C_4H_9)_2SnCl_2$; (b) $(n\text{-}C_4H_9)_3SnCl$; (c) extracts of a hydrochloric acid solution of the shell of the Bent-nose clam (*Macoma nasuta*).

Some success was achieved by using electron impact mass spectroscopy of the residue obtained after evaporation of the dichloromethane extracts. Such a spectrum is shown in Fig. 1. Here the original shell is that of the Bent-nose clam which has a high concentration of butyltin compounds as determined by HPLC/GF AA. The spectrum of the extract (Fig. 1c) is seen to be predominantly that of tributyltin chloride when it is compared with the spectra of the two standard compounds. Some dibutyltin dichloride may be present in the shell, judging from the peaks at *m/z* 247.

*Acknowledgements* Financial assistance from the Natural Sciences and Engineering Research Council of Canada, the Federal Department of Fisheries and Oceans and the Department of National Defence (Academic Research Program) is gratefully acknowledged.

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