Review

Arsenic Speciation in Manufactured Seafood Products

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ABSTRACT

The literature on the speciation of arsenic (As) in seafoods was critically reviewed. Most research has been directed toward fresh seafood products with few papers dealing with As speciation in manufactured seafoods. Predictions concerning As species made on the basis of fresh seafood products cannot be extrapolated to manufactured seafoods. Therefore, due to the numerous species of As, the scarcity of data concerning their presence in foods, the transformations each species may undergo during industrial processing and cooking, and the lack of legislation on permitted As levels in seafood products, As species in manufactured seafood products need to be determined and quantified.

Speciation of an analyte is the process of obtaining evidence concerning the atomic or molecular form of the analyte (8). This new and rapidly developing line of research belongs to analytical chemistry but is also part of a multidisciplinary field which includes biology, toxicology, nutrition, geology, food science and technology, environmental science, and medicine. In all these areas, speciation is key to the resolution of many outstanding problems.

In food technology one of the high-priority research areas is chemical and microbiological food safety. The total amount of trace elements in food, while permitting an estimate of dietary intake, does not give any information on human toxicity. An estimation of toxicity of trace elements depends on the physical and biochemical properties of the chemical species (57). Trace element speciation has provided useful insights in toxicological, metabolic, and kinetic understanding (10). Thus, a growing number of official organizations are recommending the determination of trace element species in foods (24, 34). It is expected that future legislation regarding some trace elements will refer to the maximum content allowed for each species rather than the total (57).

At present, a significant portion of the global diet consists of foods of aquatic origin, either fresh or processed and from fresh or salt water. This consumption has had a positive economic impact on commercial fishing and the associated food processing industries, and each year a wide variety of manufactured seafood products are launched on the market. The need to include more seafood, particularly fish, in the human diet has been emphasized with regard to its lower levels of saturated fat, cholesterol, and caloric intake compared with meat, poultry, and dairy products (6).

In the 1970s, concentrations of the element arsenic (As) found in marine organisms were much higher than those found in land organisms (32), and this has been corroborated in subsequent studies (34). Therefore, with the exception of populations exposed to the consumption of water and foods which are highly contaminated with As of industrial or geological origin, for most consumers seafood is the most significant source of As in the diet. This is a consequence of the increase in the consumption of these products and of their high As content.

ARSENIC IN MARINE ORGANISMS: CHEMICAL SPECIES

The presence of As in marine organisms was detected by Bertrand in the early 1900s (9). It was not until 1969 that As was shown to occur in the form of a number of different organic and inorganic chemical species (31). The development by Braman and Foreback in 1973 of a hydride generation procedure capable of the individual determination of several inorganic and methylarsenic compounds at low concentrations marked the beginning of comprehensive environmental As speciation (11). The chemical structures of the main species of As detected in marine organisms are shown in Figure 1.

TOXICITY OF ARSENIC COMPOUNDS

Arsenic has long affected human life in different ways. Whether it is an essential trace element in the human body is still debated, but the toxicity of higher doses of As is beyond dispute (60). Inorganic As compounds are known carcinogens, but no reports exist concerning the effect which organoarsenic compounds have on humans. The body's toxic response depends on the As species, the route and dose of exposure, and individual and local tissue susceptibilities. Inhalation of inorganic As increases the risk of lung cancer, and ingestion of inorganic As causes skin cancer (50) and

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skin alterations, increasing the risk of developing lung, bladder, kidney, and liver cancers (21).

The acute toxicity of As species on the basis of their 50% lethal dose (LD50) in mice and rats decreases progressively from AsIII to arsenobetaine (AB) species, suggesting that as the degree of methylation of arsenic compounds increases the acute toxicity is reduced (Table 1). This does not hold true for tetramethylarsonium ion (TMAs+), the most highly methylated species of arsenic. Its acute toxicity against mice is even higher than that of monomethylarsonic acid (MMA) and dimethylarsinic acid (DMAs), and it is the organoarsenic compound present in marine organisms which...
TABLE 1. LD₅₀ values of arsenic species

<table>
<thead>
<tr>
<th>Arsenic species</th>
<th>LD₅₀ (g/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As³⁺</td>
<td>0.0345</td>
</tr>
<tr>
<td>MMA</td>
<td>1.8</td>
</tr>
<tr>
<td>DMA</td>
<td>1.2</td>
</tr>
<tr>
<td>TMAs⁺</td>
<td>0.89</td>
</tr>
<tr>
<td>TMAsO</td>
<td>10.6</td>
</tr>
<tr>
<td>AC</td>
<td>&gt;6.5</td>
</tr>
<tr>
<td>AB</td>
<td>&gt;10.0</td>
</tr>
</tbody>
</table>

Data from reference 43.

For names of arsenic species cited as acronyms, see Figure 1.

TABLE 2. Percentage of total As represented by AB in fresh seafood

<table>
<thead>
<tr>
<th>Product</th>
<th>Number of samples</th>
<th>Range (%)</th>
<th>Mean ± SD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fish</td>
<td>68</td>
<td>24-118</td>
<td>91 ± 22</td>
</tr>
<tr>
<td>Bivalves</td>
<td>25</td>
<td>24-90</td>
<td>52 ± 23</td>
</tr>
<tr>
<td>Cephalopods</td>
<td>6</td>
<td>82-119</td>
<td>100 ± 14</td>
</tr>
<tr>
<td>Crustaceans</td>
<td>10</td>
<td>8-109</td>
<td>78 ± 27</td>
</tr>
<tr>
<td>Gastropods</td>
<td>8</td>
<td>35-123</td>
<td>68 ± 27</td>
</tr>
</tbody>
</table>

References 1, 2, 3, 4, 7, 14, 16, 17, 26, 27, 28, 45, 46, 51.
TABLE 3. Data reported for As species other than AB in real seafood samples

<table>
<thead>
<tr>
<th>MMA (22, 25, 27, 53)</th>
<th>Contents: &lt;0.2 to 85 ng As per g (wet weight). Percent As contributed by MMA with respect to total As varies between &lt;0.006 and 3%.</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMAs (1, 4, 22, 25, 53)</td>
<td>Percent As contributed by DMAs with respect to total As: 0.003 to 12%.</td>
</tr>
<tr>
<td>AC (27, 45)</td>
<td>Common, although minor, compound in marine ecosystems. Percent As contributed by AC with respect to total As: 0.07 to 4%.</td>
</tr>
<tr>
<td>TMAs + (14, 15, 27, 38, 41, 44)</td>
<td>Percent As contributed by TMAs + with respect to total As: 0.03 to 48%.</td>
</tr>
<tr>
<td>TMAsO (12, 27, 37)</td>
<td>High levels are found in red prawns (0.98 ng of As per g) and mussels (33 to 53 ng of As per g). Arsenosugars (41) Arsenosugars are found to be major arsenic compounds in marine algae. High levels are found in bivalves, and in some cases these are the major species. Arsenolipids (15, 38) Few studies have been conducted on the presence of arsenolipids in seafood products. Glycerylphosphorylarsenochoelmine has been detected in mussels and phosphaidyalsenochoelmine in red mullet (2% of the total As). As III and As V (4, 5, 27, 30, 42, 49, 56, 59) In marine animals the quantity of inorganic As is low. The percentages of inorganic As with respect to total As vary from 0 to 22%. Levels of each of the inorganic species are as follows: As III, 15 samples, 1 to 40 ppb; As V, 19 samples, 9 to 280 ppb.</td>
</tr>
</tbody>
</table>

which As speciation studies were almost nil until the publication of our data (51, 54, 55). For these foods, the toxicological significance of the levels of As contributed by the As species to the diet have not been taken into account.

For the other As compounds, studies have been directed more toward identification of species than quantification, and data concerning their contents in seafood are scarce (Table 3).

ARSENIC SPECIES IN PROCESSED SEAFOOD PRODUCTS

In our laboratory studies of a wide range of processed products showed the following.

1. AB expressed as As ranged from 0.03 to 23 µg/g (wet weight).

2. The mean % AB in manufactured products (51, 55), frozen (47% ± 24%, n = 8) or canned (30% ± 21%, n = 28), are less than those in fresh products (80% ± 27%, n = 117) (Table 4). In some samples, such as canned “chipirones” (a kind of squid), the AB content represents a very low percentage (<5%) of the total As, whereas the quantities of total As detected are relatively high (2.9 µg of As per g, wet weight) (55). This shows that in many manufactured products of marine origin AB may not be the dominant As species and contradicts the extrapolations based on fresh seafood products (51). This needs to be corroborated in speciation studies of a greater number of fresh and processed seafood products.

3. In canned products there is a transfer of AB and DMAs to the accompanying liquid with AB being the major species in the brine (55). The transfer may be due to a diffusion mechanism, which could cause the AB solubilized in the intercellular liquids in fish to be released into the brine. The transfer may be enhanced by the weakness of the electrostatic interaction between AB and fish muscle tissue. The loss of As caused by this transfer could explain the lower As levels for canned products (55).

4. DMAs is present in all products analyzed with the mean content being higher in manufactured products than in fresh products. The % As contributed by DMAs (53), expressed as mean ± standard deviation, is 1% ± 0.4% (n = 10) for fresh products and 4% ± 2.9% (n = 14) for preserved products.

Given the lower % AB and the higher % DMAs in manufactured products compared with fresh products, it is conceivable that degradation of AB may occur during the processing of fresh seafood for subsequent sale or consumption (refrigeration, freezing, canning, fermentation, cooking). There are few studies of AB degradation in processed or cooked seafood products intended for human consumption, and there is no consensus about the degradation of AB (12, 19, 33, 35, 36). Laboratory experiments have shown the degradation of AB to less methylated As compounds by marine microorganisms from sediments, suspended substances, macroalgae, and marine mollusc intestine (20), and the degradation sequence proposed is AB → trimethylarsine oxide (TMAsO) → DMAs → MMA → As V. In postmortem studies under natural conditions complete degradation of the AB accumulated in shark muscle and liver to inorganic As was also observed (18). Chemical and toxicological studies on As compounds in processed food are needed (43). Such studies would be important for evaluating the toxicity of As in products consumed by humans.

We determined the As contributed by species other than AB, MMA, and DMAs (53). The highest mean percentage is found in processed seafood products (>69%, n = 13), whereas in fresh products the percentage is lower (<24%, n = 9). In some cases, as for frozen sole, the As levels of these species expressed on a wet weight basis reached values.
of 4.8 μg/g (53). The evaluation of toxicity for these processed products will necessitate identification and quantification of the As species present.

**FUTURE OUTLOOK**

Although advances have been made in the quantitative and qualitative analysis of the As species in fresh seafood, As speciation in manufactured seafood products is needed. The following studies are proposed.

1. Develop precise, accurate, sensitive, fast, and cost-effective methodologies for the detection and quantification of As species in manufactured seafood products.

2. Prepare As reference materials for validating new methodologies.

3. Determine the effect of industrial processing and cooking treatments on modifications of As species in fresh seafood products. This study may recommend regulations for conservation and cooking treatments to avoid or reduce the presence of toxic As species.

4. Substantiate the transfer of As species to accompanying liquid (sauces or oils) during the shelf life of the product.

5. Establish preregulatory studies aimed at controlling levels of toxic As species in seafood products for consumption, import, and/or export purposes.

6. Conduct bioavailability studies to provide reliable information about the toxicity of As species.

7. Develop biochemical treatments for detoxifying seafood products containing high levels of toxic As species.

These research areas connect with food safety within the programs of the more developed countries. In the 21st century, technological progress should not be at the expense of food safety. This will lead to establishing quality assurance for seafood based on the individual contents of As species rather than the total As value.

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**REFERENCES**


