

Arsenic Speciation in Marine products by HPLC-ICP-MS

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Introduction

The accumulation of arsenic in marine biota is relevant since fish and fishery products are important ingredients for human consumption. The chemical form of arsenic controls the toxicity of the element; inorganic arsenic (i-As) arsenite (As^{3+}) and arsenate (As^{5+}) are more toxic compared to the organic arsenic (o-As) like monomethyl arsonic acid (MMA), dimethyl arsinic acid (DMA) and arsenobetaine (AsB).

In marine biota arsenic is mainly organic, metabolized from i-As species present in seawater and soil, or accumulated from algae. Not all biota is able to transform the i-As into o-As species, accumulation of i-As also occurs.

To analyze the quality/toxicity of human food based on fishery products a method for arsenic speciation was developed based on HPLC-ICP-MS. i-As is quantified as sum of As^{3+} and As^{5+} . Therefore arsenite is oxidized to arsenate by H_2O_2 . Organic species like AsB, DMA, MMA are also analyzed in marine products.



HPLC-ICPMS setup used for speciation.

Sample pre-treatment

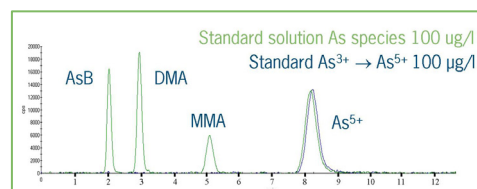
- Homogenisation of sample by milling particles down to 0.5 mm
- 0.2 g + 10 ml extraction solvent (9 ml 0.07 M HCl + 1 ml 30% H_2O_2)
- Microwave extraction (90°C for 25 min)
- Dilution of sample extract to 50 ml with HPLC eluent 30 mM $(NH_4)_2CO_3$; pH 8.9
- Centrifugation (10 min at 3500 rpm)

Instrumentation

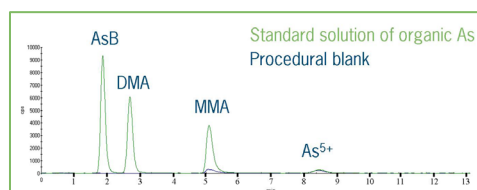
HPLC: Thermo Fisher; Column: Hamilton PRP-X100; Injection volume: 100 μ l; Eluent: 30 mM $(NH_4)_2CO_3$; pH 8.9; Flow: 1.2 ml/min.

ICP-MS (Thermo Xseries II); RF 1400 W; Cones: Platinum; Nebulizer: Concentric.

Redox reaction of arsenite by H_2O_2

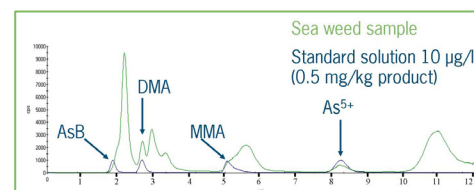


Standard mixture of AsB, DMA, MMA, arsenate (As^{5+}) and oxidized arsenite (=arsenate).

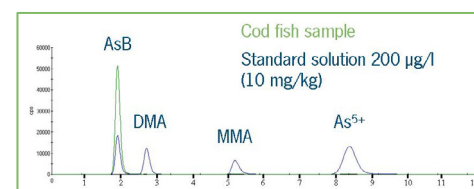


Standard solution of AsB, DMA and MMA, treated with H_2O_2 for 25 min at 90°C; DMA, MMA and AsB are not oxidized to arsenate by H_2O_2 and therefore do not interfere with the i-As measurements. Trace of arsenate were present in the procedural blank.
LOQ for i-As is 0.2 mg/kg product.

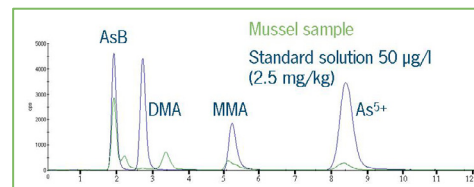
HPLC-ICP-MS Results



Sea weed sample and a standard solution 10 μ g/l (corresponds to 0.5 mg/kg). Besides the indicated species arsenosugars species are also present.



Cod fish sample and a standard solution of 200 μ g/l (corresponds to 10 mg/kg). Arsenic is mainly present as AsB.



Mussel sample and a standard solution of 50 μ g/l (corresponds to 2.5 mg/kg). AsB, MMA and arsenosugars are present.

QC- results

Matrix	As species	PT mg/kg	RIKILT mg/kg
Sea Weed - FAPAS	i-As	90.8	93.5
Tuna - BCR 627	AsB	9.2	8.8
Tuna - BCR 627	DMA	0.27	0.35

Conclusion

HPLC-ICPMS is a fast technique for the detection of arsenic species in marine products. Redox oxidation of As^{3+} to As^{5+} is quantitative. For i-As the limit of quantification is 0.2 mg/kg product.

Acknowledgement

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