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Optimization of an IC-ICP-MS analytical method for determination of inorganic arsenic in algae and algae based-products

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Overview

Purpose : Optimize a robust LC-ICP-MS analytical method for inorganic arsenic (Asi) determination in algae

Methods : Comparison of two extraction methods in acidic oxidizing medium + Two different anion exchange columns / gradient elution conditions

Results : Both extraction and LC-ICP-MS methods result in similar Asi concentrations with sufficient peak resolution

- **Algae are known for their nutritional benefits and they are increasingly used as feed and food in EU countries [1]**
- **They are also known to accumulate arsenic (As) in different chemical forms**
- **Health effects of inorganic forms (Asi) are considered more toxic [2]**
- **Precise determination of Asi is needed to assess the potential harmful effects**
- **Algae matrices contain complex As species, as arsenosugar (AsSug) compounds, which can co-elute with Asi during chromatographic separation**
- **Current CEN standards (EN16802:2016 & EN17374:2020) may require optimization to improve the resolution and quantification of Asi**

Methods

- **Samples & reference material**

- Algae meal feed (*Ascophyllum*) from Ireland, France and Norway + food supplements containing *Fucus vesiculosum* or *Ascophyllum nodosum* species
- Certified reference materials Hijiki seaweed (NMIJ7405-b), brown rice flour (NMIJ7532-a) and kelp powder (NIST 3232) were used for method validation and identification of common AsSugars

- **Extraction (0.1 M HNO_3 in 3% H_2O_2; 0.15-0.25 g of sample)**

- Microwave-assisted extraction (MAE) at 90°C during 20 min
- Water bath extraction at 90°C during 1h

- **Analytical methods (Anion-exchange chromatography coupled with ICP-MS)**

- HPLC (Varian ProStar) - ICP-MS (Varian MS820; m/z 75; KED)
- IC (Dionex ICS-6000 SP) - ICP-MS (iCap RQ 2ch; m/z 75; KED).

Details about the chromatographic separation -> see chromatograms.

Results

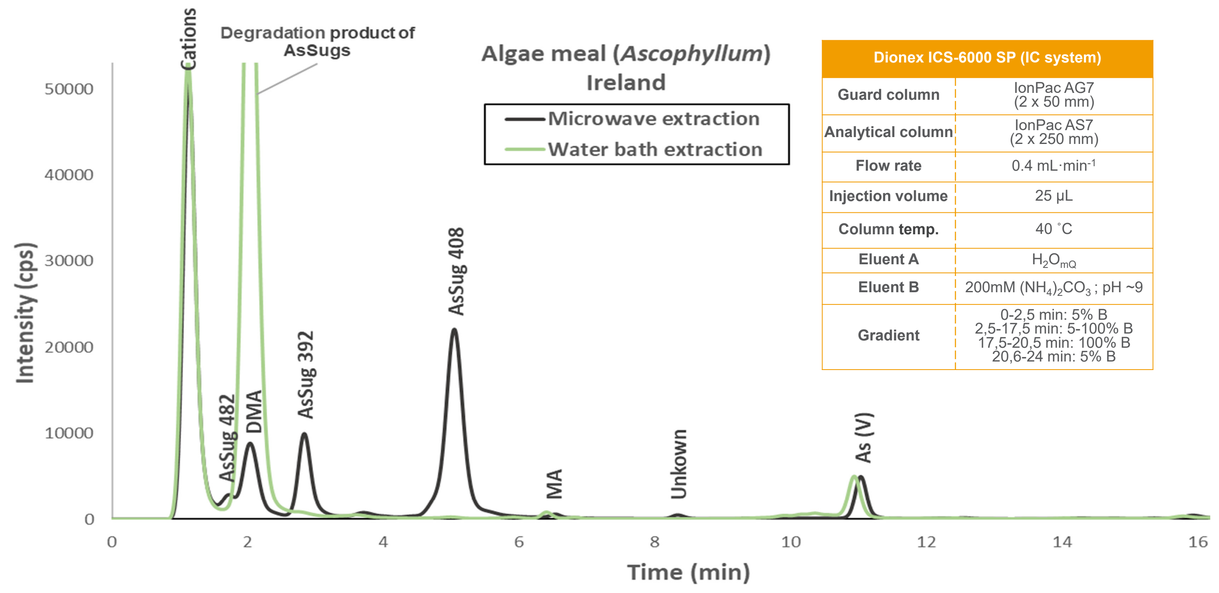
- Optimized IC-ICP-MS systems provide sufficient peak resolution of the Asi (AsV) with other adjacent arsenic species (Res > 2) and different methods result in similar Asi concentrations
- MAE has the least impact on the integrity of AsSugs and may within certain limits provide semi-quantitative information

NOTE : the moment of analysis after extraction might influence the amount of AsSugs degradation -> see MAE chromatograms (Dionex ICS-6000 SP : 1 day after extraction vs Varian ProStar system : 1 month after extraction)

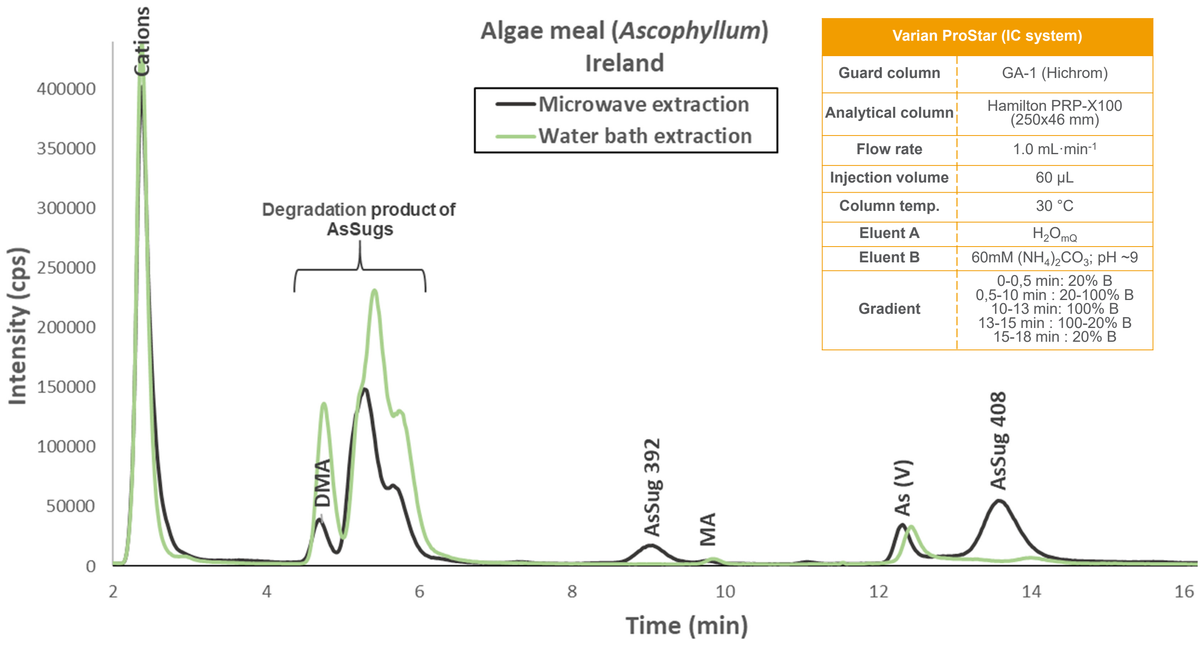
Concentrations of Asi (ppb) in algae based-products

	MAE		Water bath	
	IonPac As7	Hamilton PRP-X100	IonPac As7	Hamilton PRP-X100
Algae meal-Ireland_*Ascophyllum*	1000	975	972	1081
Algae meal-France_*Ascophyllum*	290	218	363	406
Algae meal-Norway_*Ascophyllum*	167	130	135	134
Food supplement_*Ascophyllum*	25	24	35	37
Food supplement_*Fucus*	94	113	110	147

Note : LOQ (DF10) IonPac As7 = 2ppb ; LOQ (DF10) Hamilton PRP-X100 = 10ppb



Dionex ICS-6000 SP (IC system)	
Guard column	IonPac AG7 (2 x 50 mm)
Analytical column	IonPac AS7 (2 x 250 mm)
Flow rate	0.4 mL·min^{-1}
Injection volume	25 µL
Column temp.	40 °C
Eluent A	H_2O_{mQ}
Eluent B	200mM $(NH_4)_2CO_3$; pH ~9
Gradient	0-2,5 min: 5% B 2,5-17,5 min: 5-100% B 17,5-20,5 min: 100% B 20,6-24 min: 5% B



Varian ProStar (IC system)	
Guard column	GA-1 (Hichrom)
Analytical column	Hamilton PRP-X100 (250x46 mm)
Flow rate	1.0 mL·min^{-1}
Injection volume	60 µL
Column temp.	30 °C
Eluent A	H_2O_{mQ}
Eluent B	60mM $(NH_4)_2CO_3$; pH ~9
Gradient	0-0,5 min: 20% B 0,5-10 min : 20-100% B 10-13 min: 100% B 13-15 min : 100-20% B 15-18 min : 20% B

Conclusions

- Both extraction and IC-ICP-MS methods provide similar results for Asi by limiting interference with AsSugs
- An interlaboratory comparison should elucidate if the proposed methods can serve as a base for an international standard for Asi determination in algae and algae products

REFERENCES

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2. EFSA. Panel on contaminants in the food chain (CONTAM). Scientific Opinion on Arsenic in Food. EFSA Journal. 2009;7:1351–5.

ACKNOWLEDGEMENTS

This work was partly funded by the European Commission (EC) to perform work in accordance with their Specific Agreement regarding standardization of algae and algae products (EN/2019/ENER/C2/452-2019/SI2.832375)

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