Method optimization for the determination of total arsenic and selenium content in fish by ICP-MS preceding to speciation studies.

Inês Coelho; Sandra Ribeiro; Isabel Castanheira
ines.coelho@insa.min-saude.pt
Department of Food and Nutrition, National Institute of Health Dr. Ricardo Jorge, Portugal

INTRODUCTION

The present work constitutes the first task of a three year project that aims for the optimization and validation of a methodology to determine the total concentration of Arsenic (As) and Selenium (Se) and its species in fish products by using HPLC-ICP-MS.
Fish and seafood are some of the foodstuffs in which higher concentrations of arsenic may be found. However, not all forms of arsenic share the same level of toxicity and it is known that this element in fish is mainly present in a less toxic form making speciation of arsenic in fish of uttermost importance to correctly evaluate the toxicological risk associated with the consumption of these products.
Prior to initializing speciation studies the method for determination of total arsenic and selenium content was optimized.

MATERIALS AND METHODS

In order to optimize the sample digestion procedure using closed vessel microwave digestion (Ethos 1, Milestone) several HNO_3:H_2O_2 ratios and different time and temperature conditions were studied. Results were evaluated by calculating the extraction yield of trace elements from matrix and trueness of certified reference materials results.
After optimizing the digestion program samples, such as Hake and European plaice, were studied in order to evaluated method repeatability and reproducibility. For assessment of accuracy Reference materials (DORM-3 and BCR-627) and spiked samples were used.
Samples, of the same brand, were acquired at a local market. Prior to the digestion these samples were homogenized and lyophilized. Moisture content was determine so that the presented results refer to fresh weight.
From each fish sample three independent subsamples were analyzed daily throughout three different days. To assure linearity of the calibration curve only curves with r≥0.9998 were accepted.
ICP-MS conditions were optimized on a daily basis and calibration solutions were prepared fresh every day. Yttrium and Indium were used as internal standards.

ICP-MS conditions for ^{75}As and ^{82}Se
THERMO X series II

Forward power: 1400 W
Energy discrimination:
Oct Bias: 0.1 V
QP Bias: - 3 V
Nebulizer flow: 0.82-0.85 ml/min

RESULTS

Tabel 1 – Mean value (fresh weight), Limit of Quantification (LoQ) Repeatability and Reproducibility data

		Mean value (µg/Kg)	Limit of Quantification (µg/Kg)			Repeatability CV_r(%)			Reproducibility CV_r(%)
			day 1	day 2	day 3	day 1	day 2	day 3	
Arsenic	Hake	786	227	471	314	0.60	1.81	1.44	2.15
	European plaice	4141				0.83	0.40,	0.82	3.9
Selenium	Hake	691	489	192	436	2.71	0.32	2.67	14.65
	European plaice	437				---	4.92	---	10.7

Tabel 2 – Microwave program

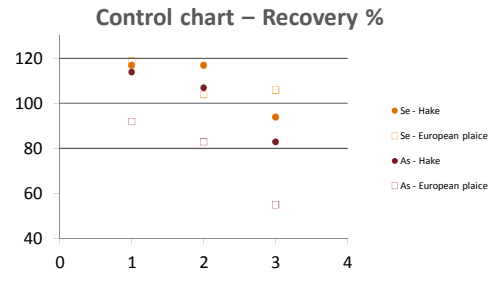
Step	Time (min)	Power (W)	Temperature (°C)
1	10	1000	180
2	5	0	180
3	6	1500	200
4	5	0	200
5	6	1000	90

Formulas

$$CV\% = \frac{SD}{\bar{x}} \times 100$$

$$Z - score = \frac{X_{lab} - X_{ref}}{u} \times 100$$

µ= CRM uncertainty



Tabel 2 – Accuracy data

		Laboratory mean value (µg/Kg)	Reference value (µg/Kg)	Z-score
DORM-3	Arsenic	6680	6880±300	-0.67
	Selenium	3378	3300	---
BCR-627	Arsenic	4731	4800±300	-0.23
PTs 1	Arsenic	1131	1354	-1.1
PTs 2	Arsenic	2593	2550	0.3

CONCLUSIONS

Recovery percentages indicated that digestion conditions are complex and food matrix dependent. In the present work the best results were obtained with the combination of 4ml HNO_3 and 2ml H_2O_2. Also fundamental is matching as much as possible the concentration of nitric acid used in the preparation of calibration solutions to the one from test solutions after microwave digestion.
Recovery using commercial standards and reference materials was the best parameter to assess the adequacy of the analytical procedure. The obtained results were supported by good laboratory performance in proficiency testing schemes (PTs) for arsenic. However more samples should be analyzed to clarify if a negative trend exists as suggested by looking at the control chart for recovery %.
In the case of selenium that suffers interferences which may not be effectively corrected by the interference equations, the use of collision cell technology should be studied. Some European Plaice values for selenium were below the LoQ making it impossible to calculate a daily CV_r%.
In future work methods for identifying and quantifying arsenic and selenium species by using HPLC-ICP-MS will be developed.

References
(1) Martin Nash, Speciation of Arsenic in Fish Tissues using HPLC Coupled with XSeries*II ICP-MS,* Application Note: 40741, Thermo
(2) Food Standards Agency, UK , Arsenic in fish and shellfish, FSIS82/05, 2005

This work was completed on behalf of Project GOODFISH PTDC/SAU-ESA/103825/2008