Food Chemistry 127 (2011) 934–942

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Determination of 20 trace elements in fish and other seafood from the French market

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ARTICLE INFO

Article history:
Received 9 September 2010
Received in revised form 24 November 2010
Accepted 19 January 2011
Available online 25 January 2011

Keywords:
Essential trace elements
Toxic trace elements
Fish
Seafood
ICPMS

ABSTRACT

The levels of 20 essential or toxic trace elements in 159 fish, other seafood and seafood products on the French coastal market collected between January and April 2005 were measured by ICP-MS. The concentration ranges (mg/kg of fresh mass) for the elements determined were compared with previous studies. The contents of Co, Cu, Fe, Li, Mn, Se, Zn and Pb found in fish are close to or often lower than previous studies. For other seafood, comparison is difficult due to the lack of data on a more global scale. However, it should be noted that the contents of Ag were found considerably higher in this study.

1. Introduction

In recent decades, much attention has been paid to the study of essential and toxic trace element content in foodstuffs, as a result of a growing concern about the health benefits and risks of food consumption. The evaluation of risks and benefits of the consumption of fish and other seafood has been particularly controversial. Nutritionists consider these products to be an important source of high-quality proteins, minerals and essential fatty acids such as omega 3. Toxicologists tend to regard seafood as a major vector for toxic substances such as metal trace elements and persistent organic pollutants. The scientific reality is more complex and a reconciliation of these two viewpoints requires that we take into consideration both nutritional and toxic substances contained in food products and also consumer behaviour with regard to these products. As a safeguard for human health, guidelines and regulations stipulating maximum permissible levels of cadmium, lead and mercury in fish and seafood have been set by Regulation (EC) No. 629/2008 to limit dietary exposure of consumers to toxic metals.

In France, as regards exposure to trace elements, several recent studies have shown that for the average consumer in the general population the toxicological limits are not exceeded. Nevertheless, the absence of risk for the average consumer does not exclude a risk for heavy consumers, as underlined previously (Leblanc et al., 2005). Moreover, the absence of French data on the levels of "indirect" or "direct" exposure to certain substances (omega 3 and pollutants in particular) of populations consuming large quantities of seafood does not enable a quantified assessment of the benefits or risks associated with these dietary habits, a situation that is obviously prejudicial to the global health risk evaluation and management process. The objectives of the CALIPSO study (*Consommations ALimentaires de produits de la mer et Imprégnation aux éléments traces, PolluantS et Oméga 3*) started in 2004 were to assess food exposure and biomarkers of exposure of the main toxic trace elements present in fish and other seafood and products from a group of frequent consumers (Bemrah, Sirot, Leblanc, & Volatier, 2009; Guérin, Sirot, Volatier, & Leblanc, 2007; Leblanc, 2006; Sirot, Guérin, Volatier, & Leblanc, 2009; Sirot, Oseredczuk, Bemrah-Aouachria, Volatier, & Leblanc, 2008a; Sirot, Samieri, Volatier, & Leblanc, 2008c; Sirot et al., 2008b). The study shows that the contaminant levels measured in fish and other seafood are globally satisfactory when compared with currently applicable regulations, with the exception of a few products. As regards risks, only the highest consumers of our study population present a non-negligible probability of exceeding the reference toxicological values, notably for methylmercury, cadmium, dioxins and PCBs.

However, only cadmium, mercury, arsenic and organotin compounds have been studied and discussed in these products (Guérin et al., 2007; Sirot et al., 2008b, 2008c, 2009), the essential trace elements and several toxic trace elements were not taken

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doi:10.1016/j.foodchem.2011.01.061

into account when assessing CALIPSO and therefore it is believed that these samples could be valuably reused to complement the occurrence data in these fishery products (Ersoy & Celik, 2010; Lavilla, Vilas, & Bendicho, 2008; Sivaperumal, Sankar, & Nair, 2007; Tetsuro et al., 2007; Tuzen, 2009; Türkmen, Türkmen, Tepe, Töre, & Ates, 2009). The main goal of this study was to complete the database of occurrence levels of trace elements in fish and other seafood that can be used at national and international levels for future risk assessment of the general population or high consumers of these food products. Thus, in the present study, the concentrations of 20 elements were measured in edible parts of the 159 fish and other seafood and products sampled in four French coastal areas between January and April 2005 for the CALIPSO study. The results were compared with previous French and worldwide studies.

2. Materials and methods

2.1. Apparatus

Sample digestion was carried out using a microwave digestion system Multiwave 3000 (Anton-Paar, Courtaboeuf, France), equipped with a rotor for eight sample vessels type X (80 ml quartz tubes, operating pressure 80 bars). ICP-MS measurements were performed by a VG Plasma Quad ExCell (Thermo Electron, Courtaboeuf, France), equipped with Collision Cell Technology (CCT) and a CETAC ASX 500 Model 510 auto-sampler (CETAC, Omaha, Nebraska, USA). Further details of the instrumental settings are given in Table 1.

2.2. Reagents

All solutions were prepared with analytical reagent-grade chemicals and ultrapure water (18 MΩ-cm) generated by purifying distilled water with the Milli-QTM PLUS system connected to an Elix 5 pre-system (Millipore S.A., St Quentin en Yvelines, France). Suprapur nitric acid (HNO_3 67% (v/v)) was purchased from VWR (Fontenay-sous-Bois, France). Standard stock solutions containing 1000 mg l^{-1} of each element (Li, Al, V, Cr, Fe, Mn, Co, Ni, Cu, Zn, Ga, Ge, Se, Sr, Mo, Ag, Sb, Te, Ba and Pb) and internal standard solutions containing 1000 mg l^{-1} of Scandium (Sc), Yttrium (Y), Indium (In), Rhenium (Re) and Bismuth (Bi) were purchased from Analytika (Prague, Czech Republic) and were used to prepare calibration and internal standards. Working standards were prepared daily in 6% (v/v) HNO_3 67% and were used without further purification. A solution of 10 mg l^{-1} multi-element solution (Merck, Darmstadt, Germany) was used to prepare a tuning solution with 29 elements such as Indium (In), Uranium (U), Barium (Ba) and Lithium (Li), capable of covering a wide range of masses. Ultra-pure grade carrier and collision gases (Argon (Ar), Helium (He) and Hydrogen (H_2), 99.9995% pure) were supplied from Air Liquide (Nanterre, France). Certified Reference Material (CRM): ERM® CE-278 (mussel tissue) from the Institute for Reference Materials and Measurements, and IAEA 407 (fish tissue) from the International Atomic Energy Agency, were all purchased from LGC Standards (Molsheim, France) and used without further grinding.

Table 1
ICP-MS instrumental parameters.

Operating conditions	
Nebulizer: concentric type pumped at 0.9 ml min^{-1}	
Spray chamber: Scott-type double-pass water cooled	
Expansion stage:	2.7 mbar
Intermediate stage:	2.0 10^{-4} mbar
Analyser stage:	4.6 10^{-6} mbar
Sampling cone: nickel,	1.0 mm orifice
Skimmer cone: nickel,	0.75 mm orifice
Standard mode (adjusted daily)	
RF power:	1350 W
Reflected power:	<5 W
Plasma gas flow:	15 l min^{-1}
Nebulizer gas flow:	0.75–0.9 l min^{-1}
Auxiliary gas flow:	0.90 l min^{-1}
Collision gas	
H_2:	1.50 l min^{-1}
He:	0.50 l min^{-1}
Acquisition parameters	
Mass range:	7–208 uma
Number of channels:	500
Dwell time:	160 µs
Number of sweeps:	500
Total acquisition time:	60 s
Peak jumping mode	

2.3. Sample selection and preparation

Based on a validated food frequency questionnaire (FFQ), 63 seafood products including fish, molluscs, crustaceans and seafood-based dishes were selected in four French coastal areas, covering 88–100% of total seafood consumption (Bemrah et al., 2009). Local sampling took into account the frequencies and quantities consumed, and the purchase place of consumers for each species according to the methodology developed previously (Leblanc et al., 2005). Thus, 159 products were sampled between January and April 2005, including 138 fresh and frozen fish, molluscs and crustaceans, along with 21 canned products, smoked fish and seafood-based dishes. All the sample preparation methodology has already been described (Sirot et al., 2008a).

2.4. Analytical methods

The digestion programme was optimised previously (Noël, Dufailly, Lemahieu, Vastel, & Guérin, 2005). 0.2–0.6 g of diet samples were weighed precisely in quartz vessels and wet-oxidised with 3 ml ultrapure water and 3 ml ultra-pure grade HNO_3 (67% v/v) in the microwave digestion system. After cooling, sample solutions were quantitatively transferred into 50 ml polyethylene flasks with 100 µl of internal standard solution (1 mg/l) and the digested samples were then completed with ultrapure water to the final volume before analysis by ICP-MS. The ICP-MS methods have already been fully validated (including participation in proficiency tests) for the simultaneous analysis of cadmium, lead, mercury, arsenic (in standard mode), chromium, iron and selenium (in CCT mode) content in foodstuffs of animal origin (Dufailly, Noël, & Guérin, 2006; Noël et al., 2005, 2009). The performance criteria of the method for all other elements have also been estimated and all proficiency tests were satisfactory for fish and seafood samples (Millour et al., 2011; Noël et al., 2009).

Five standards with standard linear regression and internal standardisation were prepared at levels ranging from 0 to 20 µg/l for Li, V, Co, Ni, Ga, Ge, Mo, Ag, Sb, Sr, Te, Ba and Pb, from 0 to 50 µg/l for Mn and Cu and from 0 to 100 µg/l for Cr, Fe, Se, Al and Zn. The calibration curve was plotted from six points, including the calibration blank. The isotopes ^{7}Li, ^{27}Al, ^{51}V, ^{52}Cr,^{55}Mn, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{65}Cu, ^{64}Zn, ^{66}Zn, ^{71}Ga, ^{74}Ge, ^{82}Se ^{88}Sr, ^{92}Mo, ^{98}Mo, ^{107}Ag, ^{121}Sb, ^{125}Te, ^{137}Ba, ^{138}Ba, ^{206}Pb, ^{207}Pb and ^{208}Pb were selected in ICP-MS standard mode and ^{56}Fe, in ICP-CCT-MS.

2.5. Quality assurance

All test batches were evaluated using an internal quality approach and validated if they satisfied the defined Internal Quality Controls (IQC) discussed earlier (Millour et al., 2010). For each experiment, a run included three blanks, two CRMs, two different