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Analytical Methods

Determination of total iodine in French Polynesian foods: Method validation and occurrence data

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ABSTRACT

Pacific Island populations show some of the highest incidences of thyroid cancer in the world, and iodine deficiency is suspected to play a role. Iodine content was determined in 124 different French Polynesian food samples using inductively coupled plasma-mass spectrometry after alkaline digestion. For samples containing starch, the method was optimised by including an additional enzymatic treatment step. This analytical method was validated with an accuracy profile approach, using certified reference materials with iodine contents ranging from 0.027 to 4.95 mg iodine kg^{-1} dry weight. The trueness bias ranged from −5.8% to 22.4% and the highest observed intermediate precision coefficient of variation CV_R was 11% in starchy materials. Tested Polynesian foods showed large variation in iodine content, with values of 0.014–0.032 mg kg^{-1} for fruits, 0.014–0.081 mg kg^{-1} for starchy samples, 0.027–1.85 mg kg^{-1} for green vegetables, 0.222–5.19 mg kg^{-1} for fish, 6.51–85.6 mg kg^{-1} for shellfish, and 0.004–1.39 mg kg^{-1} for beverages.

1. Introduction

Iodine is a vital component of thyroid hormones and therefore plays an important role in human health (WHO, 1996). Iodine deficiency is a major public health problem worldwide because it can lead to a number of functional and developmental abnormalities known as iodine deficiency disorders (IDDs), the most well-known of which is goitre, i.e., the enlargement of the thyroid gland (WHO, 2004). Iodine levels in food, except in seafood and seaweed, geographical depends on food processing methods and origin (Anke, Groppel, Müller, Scholz, & Krämer, 1995). Many countries have introduced supplementation programmes, promoting the use of iodised table salt or iodised vegetable oil to prevent iodine deficiency.

Pacific Island populations have one of the world's highest thyroid cancer incidence rates (Curado et al., 2007). As of the Epi-Thyr research programme on the role of genetic and environmental factors in the risk of differentiated thyroid cancer, a set of population-based case-control studies has been conducted in France, Cuba, New Caledonia and French Polynesia. An initial analysis of the role of dietary iodine intake in the risk of differentiated thyroid carcinoma in French Polynesia has been published (Cléro et al., 2012), but information on iodine content was based on diet questionnaires and on French CIQUAL-REGAL tables (Favier, Ireland-Ripert, Toque, & Feinberg, 1995), because iodine is not included in the FAO's Pacific Islands food composition tables (Dignan, Burlingame, Kumar, & Aalbersberg, 2004). This initial analysis, based on 229 cases of differentiated thyroid carcinoma and 371 controls, indicated that French Polynesia is a mild iodine deficiency area in which higher consumption of food from the sea and higher dietary iodine intake are significantly associated with a decreased risk of thyroid cancer (Cléro et al., 2012). Nevertheless, due to the importance of this issue in French Polynesia and the potential exposure of its population to radioactive iodine from nuclear test fallout (de Vathaire et al., 2010), more information was collected on iodine concentration in foods from French Polynesia to study more in depth the role of dietary iodine intake on thyroid cancer risk.

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Because of its low concentration in food matrices, and losses due to its high volatility, iodine is challenging to analyse in food. A variety of analytical methods have been used to determine iodine content in food (Shelor & Dasgupta, 2011). For a long time, the catalytic method developed by Sandell and Kolthoff (1937) was the most widely used technique to determine trace iodine levels. Other techniques are now employed, such as neutron activation analysis (El-Ghawi & Al-Sadeq, 2006; Fecher, Goldmann, & Nagengast, 1998; Hou et al., 1997), X-ray fluorescence (Varga, 2007), atomic absorption spectrometry (AAS) (Bermejo-Barrera, Aboal-Somoza, & Bermejo-Barrera, 1999), inductively coupled plasma optical emission spectrometry (ICP-OES) (Naozuka, Da Veiga, Oliveira, & de Oliveira, 2003; Oliveira, Trevizan, & Nobrega, 2010; Varga, 2007) and, the commonly used technique, inductively coupled plasma mass spectrometry (ICP-MS), which has excellent sensitivity and high selectivity (Benkhedda, Robichaud, Turcotte, & Béraldin, 2009; Fecher et al., 1998; Julshamn, Dahl, & Eckhoff, 2001; Mesko et al., 2010; Oliveira, Trevizan, & Nobrega, 2010; Pacquette, Levenson, & Thompson, 2012).

Sample preparation is a critical step for iodine determination, and extraction using concentrated acids should not be used due to the formation of volatile species as HI or I_2 which may result in low recoveries (Fecher et al., 1998; Julshamn et al., 2001; Knapp, Maichin, Fecher, Hasse, & Schramel, 1998). To overcome these difficulties, an alkaline solution is often used as an extraction medium or neutralisation medium after acid extraction (Benkhedda et al., 2009; Pacquette et al., 2012; Tinggi, Schoendorfer, Davies, Scheelings, & Olszowy, 2012).

This paper describes a method for iodine determination in food based on a European standard (CEN, 2007) that involves alkaline extraction using tetramethylammonium hydroxide (TMAH), optimised with an additional enzymatic treatment for samples containing starch, followed by ICP-MS analysis. A complete single-laboratory validation was performed according the accuracy profile approach (AFNOR, 2010; Mermet & Granier, 2012), and this method was used to determine the iodine content in the main foods consumed by French Polynesians.

2. Materials and methods

2.1. Instrumentation

Sample extraction in alkaline media was performed in a 48-well heating block (*Digi*PREP, SCP Science, Courtaboeuf, France) equipped with 50 mL polypropylene flasks. Iodine determination was conducted using an inductively coupled plasma mass spectrometer (Agilent Technologies 7700x, Courtaboeuf, France) equipped with a concentric nebuliser and an impact bead spray chamber at 3 °C. Sample solutions were delivered by a peristaltic pump from tubes arranged on an ASX 500 autosampler model 510 (CETAC, Omaha, Nebraska, USA). An integrated sample introduction system (ISIS system) was also fitted to obtain the required productivity gains, and further improve long-term matrix tolerance. Torch position, gas flow rates and the ion lens settings of the ICP-MS system were optimised daily to maximise sensitivity and minimise interference effects from oxide levels (CeO/Ce < 2%) and doubly charged ions (Ce2+/Ce < 2%). The linearity of the response in pulsing and in analogical mode (P/A factor determination) was verified daily using PA tuning 1 and 2 solutions. Memory effects observed after analysis of solutions containing a large amount of iodine were reduced by using an ISIS system and rinsing with appropriate solutions. Further details of the instrument settings and data acquisition parameters are given in Table 1.

Table 1
Instrumental conditions for ICP-MS.

ICP-MS parameters	
Operating conditions	
Rf power	1520 W
Reflected power	<5 W
Argon flow rates	
Cooling	14.9 L min^{-1}
Auxiliary	0.8 L min^{-1}
Nebuliser	0.9–1.0 L min^{-1}
Sample cone	Nickel, 1.0 mm orifice
Skimmer cone	Nickel, 0.75 mm orifice
Sample load time	20 s
Wash out	2% NH_4OH for 12 s
	0.5% TMAH for 10 s
Acquisition parameters	
Monitored signals	*m/z* 127 (^{127}I), *m/z* 115 (^{115}In)
Integration time	3 s (^{127}I), 0.1 s (^{115}In)
Number of repetitions	3

TMAH, tetramethylammonium hydroxide.

2.2. Chemicals

All solutions were prepared with analytical reagent-grade chemicals and ultrapure water (18 MΩ cm) produced by purifying distilled water with a Milli-QTM PLUS system combined with an Elix 5 pre-system (Millipore S.A., Saint-Quentin-en-Yvelines, France). Calibration and internal standard solutions were prepared using commercially available stock solutions. Standard iodine solution (1000 mg L^{-1} potassium iodide) and standard indium solution (1000 mg L^{-1}), used as internal standards, were purchased from Analytika (Prague, Czech Republic). Tetramethylammonium hydroxide (TMAH) (25% v/v) of high purity was obtained from Waco chemicals (Neuss, Germany). α-Amylase was obtained from Sigma Aldrich (Saint-Quentin-Fallavier, France). Multi-element standard solutions (tuning solution, PA tuning solutions 1 and 2) (Agilent, Courtaboeuf, France) were used to prepare tuning solutions in 6% (v/v) nitric acid (Suprapur, 67%, VWR, Fontenay-sous-Bois, France). Ultrapure grade carrier gas (argon (Ar)) was supplied by Linde (Montereau, France).

2.3. Reference materials

Certified reference materials (CRMs) SRM 1568a (rice flour) from the National Institute of Standards and Technology (NIST), NIM-GBW 10014 (cabbage) and NIM-GBW 10015 (spinach) from the National Institute of Metrology of China, ERM-BC402a (potato powder) from European Reference Materials, BCR-422 (cod muscle) from the Institute for Reference Materials and Measurements (IRMM) were purchased from LGC Standards (Molsheim, France), and SRM 1548a (typical diet) from the NIST was purchased from CAS (Mont-Saint-Aignan, France). They were all used as provided, without further grinding.

2.4. Samples

The Laboratory for the Study and Monitoring of the Environment at the French Institute for Radiological Protection and Nuclear Safety (IRSN/LESE) sampled 124 composite food samples, including fruit, vegetables, seafood, and beverages in French Polynesia during the Epi-Thyr-2 project between 2011 and 2013 in seven areas: Tahiti and Maupiti (Society Islands), Hao and Rangiroa (Tuamotu Archipelago), Mangareva (Gambier Islands or Mangareva Islands), Tubuai (Austral Islands) and Hiva Oa (Marquesas Islands). Foods were selected so as to cover the typical diet of the French Polynesian population. Each of the composite samples from the seven areas of sampling was composed of up to five sub-samples from five different locations.