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Determination of iodine in selected foods and diets by inductively coupled plasma-mass spectrometry*

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Abstract: Iodine is an essential trace element, and its deficiency has caused concern in many countries. Foods are the principal source of iodine, and its levels are generally low. In this study, selected food items were obtained from food market outlets in Brisbane, Australia. Food samples of dietary intakes of selected healthy children in Brisbane, Australia, were also collected for analysis and assessment of iodine nutritional status. In Australia, there has been little study on iodine dietary intakes, particularly in young children. The aims of this study were to provide further information on iodine levels in foods for Australian food composition data, and to estimate the iodine daily intakes of selected healthy children. Food samples were analyzed for iodine concentrations using inductively coupled plasma-mass spectrometry (ICP-MS) after alkaline digestion with tetramethylammonium hydroxide (TMAH), and the method was validated using a certified reference material of nonfat milk (NIST, SRM 1549). The results of this study indicated a wide variation of iodine in foodstuffs, which ranged from <0.02 to 0.101 mg/kg for cereals, 87 to 299 μg/kg for milk, and 86 to 271 μg/kg for cheese products. The study also showed that the daily intakes of iodine in these children (n = 15) varied widely and ranged from 36.9 to 288.1 μg/day (mean ± s.d, 93.1 ± 76.7 μg/day).

Keywords: daily intakes; foods; iodine analysis; inductively coupled plasma-mass spectrometry (ICP-MS); microwave alkaline digestion.

INTRODUCTION

The nutritional importance of iodine is well established, and its deficiency has caused adverse health effects in humans and animals. It is important that iodine is adequately supplied through diet to ensure an effective physiological function of thyroid hormone. Chronic iodine deficiency can lead to disorders which include mental impairment and retardation, and formation of goiter, an enlargement of the thyroid gland [1,2]. Foods are a major source of iodine, and generally, with the exception of seafood and seaweed, the levels in foods are low, which are influenced by its levels in soils. The dietary intakes of iodine in a population vary widely, depending on food production and geographical origin. Concern of

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diseases associated with iodine deficiency in a population has resulted in many countries introducing supplementation programs such as iodine-fortified bread and iodized salts for improved iodine status [3–5]. Despite these supplementation programs, there are still reports of low iodine status in young children in some developed countries such as Australia and New Zealand [6,7]. Like many countries around the world, Australia has reported cases of iodine deficiency and toxicity [8]. Early report of goiter incidence from iodine deficiency in Australia occured in the 1920s in the states of New South Wales and Tasmania, and the program of supplying iodized salt and iodine-fortified bread was introduced to eliminate the problem [9–11]. Reduced incidence of goiter was also a result of increased iodine exposure from miilk and dairy products that were contaminated by iodphore, a cleaning agent used in the dairy industry [12,13].

A concern of re-emerging iodine deficiency in Austalian population has resulted in the government introducing a mandatory fortication of bread with iodized salt for improved iodine dietary intakes and to meet the Australian recommended daily intakes [14]. There is also a need to assess the iodine dietary intakes among the high-risk groups in a population such as pregnant women and young children. In Australia, there has been little study on the assessment of iodine dietary intakes in young children. There are several methods for estimating the daily intakes of iodine from diet, and the most common methods include weighed dietary record, duplicate portion technique, food frequency questionnaire (FFQ), and total dietary survey (TDS). All of these methods have their limitations, and their choice may depend on the importance and urgency of the information that could be used for health risk assessment from the effects of deficiency and toxicity [15–18]. In this study, a duplicate portion technique was adopted because of its relative accuracy to estimate the daily intakes of iodine for a small group of selected healthy children's diet.

Analysis of iodine in food matrices has been a challenge to many investigators because of its low concentration (<1.0 mg/kg) and losses due to volatilization. There are several methods that have been used to determine low-level iodine in foods, and these include gas chromatography, X-ray fluorescence spectrometry, inductively coupled plasma-mass spectrometry (ICP-MS), ICP-isotope dilution MS, and neutron activation analysis (NAA) [19–22]. Because of its volatility, it is important that a suitable digestion procedure that prevents iodine losses is employed. The use of nitric acid alone for normal open digestion has caused iodine losses as volatile hydrogen iodide (HI), even at room temperature [23]. However, iodine losses can be prevented when acidic condition is neutralized by ammonia or the use of ammonium solution alone for sample digestion prior to ICP-MS analysis [20,21,24]. The use of tetramethylammonium hydroxide (TMAH) for sample digestion in sealed digestion vessels at low temperature has increasingly been employed by many investigators to prevent iodine losses [23,25]. In this study, the alkaline TMAH digestion using amicrowave heating system prior to ICP-MS analysis was used for iodine analysis. The aims of this study were to analyze selected foods and estimate the daily intakes of iodine of young children, and to provide further information on iodine food levels that could be included in the Australian food composition data.

MATERIALS AND METHODS

Reagents and standards

TMAH (25 % w/w, Aldrich) was used for the digestion. High-purity potassium iodate (99.998 %, Sigma-Aldrich) was used for preparation of the iodine stock standard. The iodine working standards were prepared from the stock standard after appropriate dilution with deionized water (18 mΩ, Millipore Element System).

The certified reference material of nonfat milk (NIST, SRM1549) and in-house reference material of freeze-dried bread (QAC 291) were used for validating the accuracy of the method.

Food samples and children's diets

The normal healthy children (15 subjects, 4 boys, 11 girls, 4–12 y) were recuited from the Royal Children's Hospital (RCH), Brisbane, Australia. These children were involved in a larger and comprehensive study of micronutrient status assessment for selected age groups. Informed consent was obtained from the parents or legal guardians of these children. The ethical approval was obtained from the RCH and The University of Queensland.

The dietary food intakes and drinks of three consecutive days were collected for one time only for each subject for the study. The diets of these children were divided into two duplicate portions, and one portion was taken for analysis. These portions of food samples were weighed, homogenized, and analyzed as composite samples. Drink samples were analyzed individually. Other core food samples (milk, cheese, cereal products) were obtained from Queensland market outlets.

Sample preparation and analysis

The food samples were macerated and homogenized, and a subsample was accurately weighed into microwave digestion vessels (0.25–0.5 g of dried solid sample and 1.0–2.0 g of liquid sample). An aliquot of 10 mL high-purity water and 2 mL TMAH (25 % w/w) was added to each vessel. The digestion was heated using microwave digestion system (CEM MD2100, Mathews, NC), with programmable time and pressure settings, equipped with CEM advance composite vessels. The heating program used for TMAH digestion is shown in Table 1. The digested solutions were filtered (Environmental Express, FilterMate), and the iodine analysis was performed by ICP-MS (Agilent 7500a, Japan), equipped with a Babington nebulizer, quartz spray chamber, and CETAC 500 autosampler. Tellurium and antimony were used as internal standard for iodine calibration range of 0.05 to 100 μg/L in 2 % TMAH solution. The ICP-MS instrumental settings and parameters for iodine analysis are shown in Table 2.

Table 1 TMAH microwave digestion program for iodine analysis in cereals.

Stage	1	2	3	4
Power (%)[a]	20	25	30	35
Temperature (°C)	40	50	65	80
Pressure (psi)	20	40	60	70
Time (min)	5	5	10	10

[a]1 percentage (%) is equivalent to 9.5 watts (W).

Table 2 Instrumental settings and parameters for iodine analysis by ICP-MS.

Radio frequency power (W)	1420
Radio frequency matching (V)	1.68
Carrier gas flow rate (L/min)	1.1
Make-up gas flow rate (L/min)	0.1
Peristaltic pump flow (rps)	0.07
Sampler and skimmer cone composition	Ni
MS resolution	0.7–0.75 amu at 10 % peak height
Oxide ratio ^{156}CeO, ^{140}Ce	0.5 %
Doubly charged ratio $^{70}Ce^{2+}$, $^{140}Ce^{+}$	2.0 %
Mode of data acquisition	Quantitative
Integration time (s)	0.10
Sampling period (s)	0.31

Quality control and assurance

The certified reference material of nonfat milk (NIST, SRM 1549) and in-house reference material (QAC 291, freeze-dried bread) were used for quality control and assurance.

RESULTS AND DISCUSSION

Detection limit, precision, and accuracy

The selection of a reliable and sensitive method for analysis of low-level iodine in foods is important for accuracy of results. The use of ICP-MS was found to be sensitive and accurate for analysis of a range of food samples after microwave alkaline digestion. The detection limit of the method was estimated at 0.02 mg/kg. It was calculated as three standard deviation of the blanks, from a series of blank measurements ($n = 20$), and based on 0.30 g sample in 50 mL final solution. The accuracy of the method was validated by analyzing standard reference material, and recovery for iodine was satisfactory and within the certified value (Table 3). The method gave good precision with the coefficient of variations (CV) of 7.7 % for within-batch analysis and 7.1 % for between-batch analysis for over a two-month period (Table 3).

Table 3 Precision and accuracy of iodine analysis by ICP-MS.

Accuracy			
Standard reference material	Concentration (mg/kg)		Recovery (%)[a]
	This study	Certified value	
NIST SRM 1549 Nonfat milk	3.48 ± 0.16 ($n = 12$)	3.38 ± 0.02	103
Precision			
In-house reference material	Within-batch analysis	Between-batch analysis[b]	
QAC 291, freeze-dried bread	0.39 ± 0.03 ($n = 18$)	0.41 ± 0.03 ($n = 12$)	
C.V. (%)[c]	7.7	7.1	

[a]Recovery (%) = (determined mean/certified mean) × 100.
[b]Analysis was carried out over a two-month period.
[c]C.V. (%) - coefficient of variation = (mean/s.d.) × 100.

Our laboratory is also participating in a proficiency trial for analysis of trace heavy metals including iodine in food for quality control and assurance, which is organized by the Food Analysis Performance Assessment Scheme (FAPAS), UK. Our results for iodine analysis in milk products have been satisfactory and consistently within the consensus values assigned by FAPAS.

Iodine levels in foods

The levels of iodine in foods can be influenced by the levels in soils, which generally reflect the iodine status in livestock and subsequently in human population. The levels in foods can vary widely, and high levels are found in marine fish and seaweed. The typical levels of iodine in foods are shown in Table 4. The levels of whole cow's milk and skim milk in this present study were relatively high, but comparable with most values reported from other countries. However, the levels of iodine in cheese were comparatively lower than other countries (Table 5).

Table 4 Typical levels of iodine in foods.

Food group	Iodine concentration (mg/kg, fresh weight)
Marine fish	0.32–1.44
Freshwater fish	0.003–0.41
Vegetables	<0.020–0.28
Seaweed (dried)	35–7000[a]
Fruits	<0.020–0.08
Meat	0.020–0.09
Poultry	0.25–0.43
Milk and dairy products	0.050–0.550
Bread	0.020–0.815
Cereal products	0.02–0.43

[a]Concentration is expressed in dry weight.

Table 5 Iodine levels (μg/kg) in dairy products by country.

Dairy products	Country									This study
	USA	Finland	UK	New Zealand	Norway	Italy	Spain	Switzerland	Australia	
Milk, whole	20 ± 8	78–260	50–500	40–250	17–365	333 ± 76	251 ± 61	52.8–177.1	90–210	237–299 (n = 9)
Milk, low fat	23 ± 9	77–230		36–312	63–272				120–190	
Milk, skim	21 ± 10	72–240		40–150		283 ± 69	273 ± 52			87–131 (n = 6)
Cheese	270–460	310–2100		50–580	103–1360			83.2–754.1	130–290	
Cheddar cheese			200–580							109–271 (n = 4)
Flavored cheese										86–206 (n = 9)
Ref.	[36]	[37]	[38]	[39,40]	[41,42]	[43]	[44]	[45]	[46]	

In many western countries, cereal products such as ready-to-eat breakfast cereals are widely consumed by young children, and considered as a good source of minerals including iodine. In this study, a wide range of cereal products, produced from corn, oat, rice, and wheat, was analyzed. Relatively low levels of iodine were found in these breakfast cereals, with wheat-based cereal products contained higher iodine levels (Table 6). The low levels of iodine found in these breakfast cereals would be considered to have little contribution to iodine dietary intakes, particularly in children.

Table 6 Iodine levels in Australian ready-to-eat breakfast cereals made from various cereal types.

Cereal type	Iodine (mg/kg)
Corn-based cereals	<0.02–0.083 (n = 9)
Oat-based cereals	<0.02–0.030 (n = 6)
Rice-based cereals	<0.02–0.061 (n = 14)
Wheat-based cereals	<0.02–0.101 (n = 29)

Iodine daily intakes

As an essential trace element, iodine status in a population is regularly monitored in many countries to ensure that young children and pregnant women who are high-risk groups receive adequate intake of iodine. In Australia, there has also been little study on the dietary intakes of iodine in the population, particularly in young children. However, owing to concern that low iodine status may have an effect on the mental development of children, there have been recent studies on the assessment of iodine status in Australian children [6,26,27]. These investigators used levels of iodine in 24-h urine samples and thyroid volume for assessing iodine status, and found mild iodine deficiency in these children. Low urinary iodine levels have also been reported for Australian pregnant women, indicating a low iodine status [28–30]. Because of wide individual variation in urinary iodine levels, it has been recommended that the assessment of iodine status is to be carried out in a larger population group for statistical evaluation to obtain better estimation of iodine status [31,32].

In our study, a duplicate portion technique for estimating dietary intakes was found to be sufficient for assessing iodine status in a small group of young children. The use of 24-h urine samples was not carried out in this study because it is less reliable and less practical for a small study subject. Our study showed a wide variation of iodine dietary intakes among these young children, which ranged from 36.9 to 288.1 μg/day (mean ± s.d, 93.1 ± 76.7 μg/day). The levels of iodine dietary intakes in this present study were comparable with other Australian studies and other countries which use a TDS to estimate a stimulated dietary intake for children of similar age (Table 7).

Table 7 Iodine dietary intake (μg/day) of children by country.

Age group	Country	Methodology	Iodine intake (mg/day)	Reference
4–13 y	Norway	Simulated diet, TDS	98–121	[42]
4–13 y	Australia	Simulated diet, TDS	51.2–221.5	[46]
4–10 y	The Netherlands	Simulated diet	151–223	[47]
5–14 y	New Zealand	Simulated diet, TDS	62–88	[48]
9–15 y	Iceland	Simulated diet, TDS	145–151	[49]
6–11 y	USA	Simulated diet, TDS	117–265	[50]
4–12 y	Australia (Brisbane)	Duplicate diet study	36.9–288.1 (n = 15)	This study

It was also found in this present study that 11 out of 15 children had iodine daily intakes below the Australian RDI (Fig. 1). Even though our present study used only a small group of subjects, it supports the earlier studies that Australian children are mildly deficient in iodine as indicated by low 24-h urine iodine levels [6]. A number of factors may contribute to mild iodine deficiency in Australia, and these include decreased intakes of iodized salts and reduced levels of iodine in cow's milk and dairy products [27,33]. Even though some children in this study consumed a considerable amount of milk, it had little contribution to iodine intake. In the past, milk contributed to a significant intake of iodine as a result of contamination from iodophor used in a cleaning agent in the dairy industry. After iodophor use was stopped and replaced with other cleaning reagents, there was a trend of low iodine status in the population, and in particular in young children [33]. Low iodine status has also been reported in young children in New Zealand, and this could also be the result of reduced levels of iodine in cow's milk after the replacement of iodophors with other cleaning compounds such as quaternary ammonium compounds, and a decrease in iodized salt consumption [7,34,35].

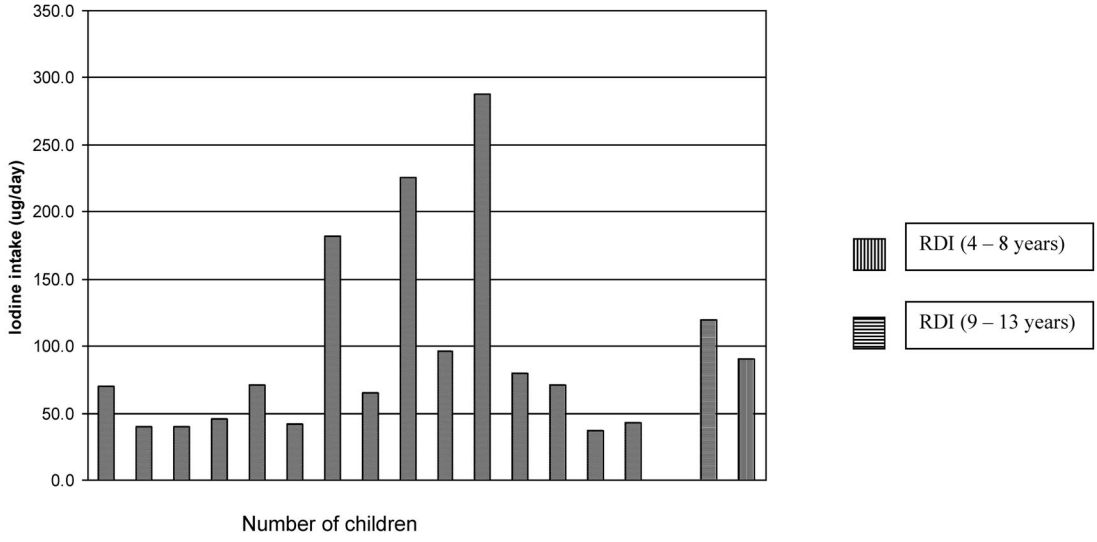

Fig. 1 Comparison of iodine intakes (μg/day) with the Australian dietary intake (RDI).

CONCLUSIONS

As an essential trace element, it is important that the iodine content in foods and its status in a population is regularly monitored, and in particular among young children, who are at greater risk from deficiency that may affect their mental and physical development. The iodine food analysis by ICP-MS after alkaline digestion was found to be sensitive with good accuracy and precision. However, some cereal samples contained very low iodine and were below the detection limit of the method. Young children tend to consume more milk and cereal products, and reduced and low iodine levels in these foods may contribute to their low iodine status, and this is a cause of concern. The recent mandatory introduction of iodine fortification in bread in Australia may address this concern. It is likely that this iodine-fortified bread program may have a significant impact in improving iodine status in the general population. However, its benefit for improved iodine status in the Australian population needs to be verified through future study.

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