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Analysis of iodine in food samples by inductively coupled plasma-mass spectrometry

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Abstract

This work shows a method for the determination of iodine in a variety of food samples and reference materials using inductively coupled plasma-mass spectrometry (ICP-MS) following alkaline extraction. Optimisation of the addition of organic carbon showed that a minimum of 3% 2-propanol was necessary for a constant ratio of iodine to internal standard. The limit of quantification (LOQ), calculated as 30σ for the method, was 36 ng g^{-1} in solid food samples. For method validation, seven standard reference materials (SRM) and 21 fortified food samples were used. The precision (%RSD) of the measurements was in the 2–7% range. Accuracies for the SRMs were 85–105%, while the fortified food samples showed 81–119% recoveries, including a number of samples fortified at 50% of the LOQ.

Keywords

Iodine; ICP-MS; alkaline extraction; carbon addition; validation; reference materials

Introduction

Iodine is an essential micronutrient used by the thyroid gland for the production of hormones. Thyroxine and triiodothyronine, both iodine-containing hormones, have an important role in cell metabolism, reproduction and growth (DeBenoit et al. 2004). Iodine deficiency is associated with thyroid dysfunction leading to goitre. In younger children, as well as pregnant women and fetuses, lower levels of these hormones affect the development and function of several organs, including the brain. Chronic iodine deficiency leads to cretinism, development of abnormalities, increased perinatal mortality and intellectual

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Disclosure statement

No potential conflict of interest was reported by the authors.

disability. Alternatively, excess intake of iodine leads to hyperthyroidism and autoimmune disease of the thyroid gland (DeBenoit et al. 2004; Hetzel 2005). Therefore, a narrow range of 100–1100 $\mu\text{g day}^{-1}$ (based on recommended daily intake and upper level of intake) at which this element is beneficial for proper function of the human body has been established and the content of iodine in food and dietary supplements requires continuous monitoring (Institute of Medicine 2001).

Because the crustal abundance of iodine varies greatly, its concentration is highly variable in foods and water (Houston 2005). The quantities of iodine in foods are usually in the ng g^{-1} range, with the exception of seafood which varies from ng g^{-1} to $\mu\text{g g}^{-1}$. High consumption of seaweed and marine fish provides adequate quantities of iodine, but with the exception of coastal communities, seafood is not a major part of the diet. Besides seafood, the main sources of iodine in the daily diet are from eggs and milk products. However, these products do not provide sufficient daily supply of iodine. Major efforts have been taken to increase the intake of iodine through the fortification of food and dietary supplements. Examples include but are not limited to iodine-fortified infant formula, iodised salt and iodised vegetable oil. The adult recommended dietary allowances for iodine in the United States ranges from 150 to 290 $\mu\text{g day}^{-1}$. Similar ranges are established for the European Union and many other countries (Institute of Medicine 2001; Houston 2005).

Iodine is a volatile element and can be oxidised and reduced easily. Because of the low concentrations in most food products, the determination of iodine provides a challenge in micronutrient analysis. Many analytical methods have been developed for the analysis of iodine in food products (Mello et al. 2013). Neutron activation analysis provides high accuracy and minimal sample preparation, but has poor sensitivity and is not readily available (Norman & Iyengar 1998); ion selective electrodes offer low cost, but poor sensitivity (AOAC Official Methods of Analysis 2000); spectrophotometric methods based on colorimetric reactions provide moderate sensitivities at low costs, but require tedious and long sample preparation (Knapp & Spitzzy 1969; Aumont & Tressol 1986; Knapp et al. 1998; Judprasong et al. 2015). Flame atomic absorption is low cost but has poor sensitivity (Bermejo-Barrera et al. 1999); X-ray fluorescence requires minimal sample preparation, but has poor sensitivity (Varga 2007); cathodic stripping voltammetry (Yang et al. 1991) and ion chromatography with conductivity, UV or ICP-MS detection are used when species specific analysis is required, but with poor sensitivities for UV and conductivity detection (Mello et al. 2013); inductively coupled plasma optical emission spectroscopy is highly selective, but with poor sensitivity (Oliveira et al. 2010; Picoloto et al. 2015).

ICP-MS provides excellent selectivity and sensitivity for the measurement of iodine (Oliveira et al. 2010; Pacquette et al. 2012; Sullivan & Zywicki 2012; Picoloto et al. 2015). In recent years there have been numerous methods developed for the determination of iodine using ICP-MS detection in biological samples and food products (Andrey et al. 2001; Fernandez-Sanches et al. 2007; Benhedda et al. 2009; Oliveira et al. 2010; Mello et al. 2013; Judprasong et al. 2015). However, because of its chemical properties, iodine provides unique challenges. Sample decomposition is a critical step, and because iodine is volatile, it can form I_2 and HI during sample preparation, resulting in low recoveries. The high ionisation

potential of iodine results in relatively few iodine ions entering the mass spectrometer. Conversion of iodide to iodine in acidic media can cause significant memory effects by adsorption to glass. High backgrounds from reagents and memory effects can lead to increased LODs.

In order to reduce iodine loss, several decomposition media have been investigated for sample preparation. Techniques range from acid microwave or hotplate digestions in oxidising media to alkaline extractions and microwave combustion (Oliveira et al. 2010). Acid digestions include nitric acid or a combination of nitric acid with either perchloric acid or hydrogen peroxide to decompose the matrix and oxidise volatile iodine species to non-volatile iodate. Analysis is then performed in acidic media (Larsen & Ludwigsen 1997; Haldimann et al. 2005; Benhedda et al. 2009) or the samples are neutralised and then analysed by ICP-MS (Pacquette et al. 2012). Another alternative is to use a microwave combustion technique or calorimetric bombs in alkaline media, with these techniques offering low LODs because of the use of reduced quantities of reagents (Knapp & Spitzky 1969; Mesko et al. 2010; Picoloto et al. 2015). However, the procedure requires the use of microwave systems designed for combustion decomposition and suffers from low sample throughput. Others have reported alkaline extractions using either NaOH, KOH or tetramethyl ammonium hydroxide (TMAH) using a hot plate, oven or microwave assisted decomposition (Knapp & Spitzky 1969; Fecher et al. 1998; Andrey et al. 2001; Fernandez-Sanches et al. 2007; Mesko et al. 2010; Sullivan & Zywicki 2012; Leufroy et al. 2015). Sample preparation and analysis in basic solutions eliminates the formation of volatile iodine species and reduces the adsorption of iodine to glassware. However, as the extraction does not completely decompose the matrix, certain sample types may suffer from low iodine recoveries. Thus, a thorough investigation of the extraction efficiency for a particular sample matrix is necessary. Additional difficulties in iodine ICP-MS analysis are associated with the adsorption to glass and plastic ware leading to high backgrounds and increased rinse times. Haldimann et al. showed that a low flow self-aspirating nebuliser and a low volume spray chamber can minimise iodine background signal and improve LODs (Haldimann et al. 2005). In food and biological samples, in cases when partial digestion techniques are used, residual carbon in the matrix might affect the ionisation of iodine. In general, residual carbon in the matrix increases the iodine ionisation. The increased iodine signal in a carbon containing analytical solution, relative to the external calibration standards, results in a high bias for concentration measurements. Grindlay et al. estimated iodine to be only 29% ionised in an ICP-MS and concluded that iodine charge transfer with carbon in an ICP was highly probable (Grindlay et al. 2013). Larsen used a methanol–water mixture for iodate analysis in acidic solution and showed an enhancement of iodine signal by 54% as a function of RF power (Larsen & Ludwigsen 1997). While a more thorough investigation of the carbon effect on iodine is necessary, of central importance is also the effect of organic modifiers on internal standards used for iodine quantification.

In the present work, a routine method for the determination of iodine was developed for a variety of food samples, infant formula and dietary supplements using a hotplate TMAH extraction followed by ICP-MS analysis. A surfactant was used to minimise adsorption of iodine to the surface of peristaltic pump tubing, nebuliser and spray chamber. Addition of 2-

propanol to the samples ensured the uniform ionisation of iodine between blanks, standards and unknown samples, eliminating the need to use matrix-matched standards. Rhodium, tellurium and antimony were used as internal standards. The method presented here was validated using a certified reference materials and samples fortified with iodine spanning all groups of the Association of Analytical Communities (AOAC) food triangle (Wolf & Andrews 1995; Sharpless et al. 2004).

Materials and methods

Reagents and instrumentation

Tetramethyl ammonium hydroxide (electronic grade, purity > 99.9999%) was purchased from Alfa Aesar (Ward Hill, MA, USA). High purity 2-propanol (Optima LC-MS grade) was obtained from ThermoFisher (Waltham, MA, USA). Triton X-100 was from Lab Chem Inc. (Pittsburgh, PA, USA). Iodine, tellurium, antimony and rhodium standards were prepared gravimetrically from 10 mg g⁻¹ stock solutions (Inorganic Ventures, Christiansburg, VA, USA). All solutions were prepared using distilled deionised water (MilliQ Element, Millipore, Billerica, MA, USA).

Iodine extractions were performed using a DigiPrep hotblock (SCP Science, Champlain, NY, USA). The extracts were analysed on a magnetic sector ICP-MS (ThermoElectron, West Palm Beach, FL, USA) in low resolution ($m/m = 300$) equipped with 20 ml miniature cyclonic spray chamber (Meinhard Inc., Golden, CO, USA), PFA-ST nebuliser and a SC-E4 DXS autosampler (Elemental Scientific Inc., Omaha, NE, USA). Solution was transferred to the ICP-MS using a 0.381 mm i.d. peristaltic pump tubing (Meinhard Inc., Golden, CO, USA).

Sample preparation procedure

Food samples were homogenised using a Retch Grindomix GM200 knife mill (Verder Scientific, Inc., Newtown, PA, USA). Samples that were difficult to grind or homogenise (e.g., seaweed snack, chocolate bars) were mixed with dry ice and then ground at cryogenic temperature using the same knife mill. Multivitamin tablets were homogenised using a tube mill (IKA Works, Inc., Wilmington, NC, USA). Samples of 0.3–1 g for solid foods were weighed and placed into 50 ml BD Falcon centrifuge tubes (BD Biosciences, Bedford, MA, USA). For most beverage and liquid samples, an analytical mass portion of 2 g was used. Blank determinations were performed using 1 g of deionised water. After addition of 10 ml of 5% TMAH, the samples were vortexed for 1 min followed by a heating step at 85° C for 3 h. TMAH decomposes at approximately 90°C, thus 85°C was chosen as the highest possible extraction temperature. After cooling, the tubes were vortexed and gravimetrically diluted to approximately 50 g with water. The samples were mixed again by vortexing and centrifuged at 3000 rpm for 10 min. The supernatant was aliquoted into autosampler tubes and analysed by ICP-MS. In cases when dietary supplements were analysed, an additional 100-fold dilution was performed with 1% TMAH in order to have the iodine concentrations in the calibration range.

Samples and reference materials

Certified reference materials (certified for iodine content) NIST (National Institute of Science and Technology) 1573a (tomato leaves), NIST 1549 (non-fat milk), NIST 1566a (oyster tissue), NIST 8435 (whole milk powder), NIST 1572 (citrus leaves), NIST 1548a (typical diet) and NIST 3280 (multivitamin tablets) were purchased from NIST (Gaithersburg, MD, USA). The reference materials were used as provided without further homogenisation except for NIST 3280 (multivitamin tablets) which were homogenised using a tube mill. For method development 10 foods samples were analysed to investigate the effect of carbon content on iodine quantification. Additionally, 21 food products from multiple groups of the AOAC food triangle obtained from local grocery stores were analysed for method validation (Figure 1). All foods were analysed in triplicate on different days and were also fortified at approximately 50%, 100% and 150–400% of the iodine content found in the particular food item. Samples with iodine levels below the LOQ were fortified with 50%, 100% and 200% of the LOQ.

Iodine determination

The quantitative analysis of iodine was performed by ICP-MS. Operational conditions of the instrument were set to optimise the detection of iodine and internal standards Rh, Sb and Te, as summarised in Table 1. During method optimisation, signal stability and sensitivity were the primary and secondary priorities, respectively. Signal stability was critical because iodine blank intensity, albeit very stable, was never zero and required blank subtraction. An eight-point calibration curve (0, 0.01, 0.05, 0.2, 1, 5, 20 and 50 ng g⁻¹) was prepared using serial dilution in 1% TMAH of a 1000 µg g⁻¹ iodine working stock solution. Iodine concentrations were determined using external standardisation and linear regression through zero. Internal standards of 2 ng g⁻¹ Rh, Sb and 10 ng g⁻¹ Te were mixed with the blanks, standards and samples via a mixing tee. The same size peristaltic pump tubing (0.381 mm, green/green) was used for both the sample and internal standard lines and thus both sample and internal standards were diluted two-fold as they entered the nebuliser. The matrix for the internal standard was made of 1% TMAH, 0.01% triton X-100 and 6% 2-propanol. The optimal concentration of 2-propanol was determined by measuring the iodine and internal standard intensities at 0–8% 2-propanol levels. A 3-min rinse between samples ensured that iodine signal was down to background levels following a sample concentration of 50 ng g⁻¹. The instrument detection limit (IDL) for iodine, determined using blank measurements ($n = 10$) consisting of 1% TMAH, was calculated as follows:

$$IDL \text{ (or) } ASDL = 2t_{95}\sigma\sqrt{(1+1/n)} \quad (1)$$

where σ is the standard deviation of the blank measurements; t_{95} is the one-sided Student's t at a 95% confidence level; and n is the number of blank measurements (Currie 1999). The analytical solution detection limit (ASDL) was calculated using equation (1) and blank samples that underwent the sample preparation procedure. These method blank measurements ($n = 24$) were pooled from nine extractions performed on different days and analysed over a period of 2 months. The LOQ was calculated using 30 times the standard

deviation of the method blanks and was adjusted by the dilution factor. This approach for the determination of the LOQ extends not only to ICP-MS measurement variability but also encompasses other sources of uncertainty including sample preparation (USFDA 2014).

Results and discussion

Effect of 2-propanol on iodine and internal standard elements

Residual carbon introduced to the ICP may affect the accuracy in elemental quantification by producing both spectral and matrix interferences. Spectral interferences can be overcome by the use of collision/reaction cell technology or high-resolution instruments. High temperature acid microwave assisted digestions with added hydrogen peroxide can oxidise carbon and release it as CO₂, so the digest has less residual carbon. However, in TMAH extractions, the temperature is too low to achieve carbon oxidation and thus it is essential to minimise the effect of carbon on iodine ICP analysis. Carbon-induced matrix effects can cause signal enhancement or deterioration caused by charge transfer reactions, change in the nebulisation or shift of the zone of maximum ion density in the plasma (Pettine et al. 2007). Figure 2 shows the effect of the addition of 2-propanol in the sample introduction solution. Iodine and the internal standard elements show an increase with a maximum around 1% 2-propanol and then a subsequent decrease in sensitivity. All analyses were performed in 1% TMAH. In Figure 2(A), the nebuliser gas flow was optimised with no additional 2-propanol and was kept the same during the addition of 0–4% alcohol. Sampling depth and RF power were also kept constant. Iodine and tellurium show an enhancement as the carbon content is increased (maximum at 1% 2-propanol) and then as the ion density in the plasma is shifted, all elements show a decrease in ion intensity. Iodine shows an 8% enhancement in signal, while Te intensity is increased by 25%. At 1% 2-propanol, Sb shows no enhancement, while the Rh intensity is decreased by 12%. As the carbon in the mixture is increased to 4%, the four elements investigated here show a 65–80% drop in sensitivity. However, when 2% or more carbon is added, the ratios of iodine to any of the three internal standard elements stay relatively constant: I/Te at 0.9, I/Sb at 0.65 and I/Rh at 0.3, indicating that iodine can be quantified accurately without being impacted by carbon originating from the extraction step in the proposed method. Table 2 shows the recoveries of 1 ng g⁻¹ I using a calibration constructed in 1% TMAH and no 2-propanol in the standards. Recoveries of 98–100% were obtained from 1 ng g⁻¹ check I solution using any of the three internal standards. When 1% 2-propanol was added to the check solution, the recovery for I using the Te was 92%, while Rh and Sb resulted in 106% and 108% recoveries. Further addition of 2-propanol to the sample resulted in even higher deviation from the reference value with 119% recovery for I with Rh as internal standard.

Figure 2(B) shows the same addition of 2-propanol (0–4%), with the nebuliser gas flow optimised at each step, and thus minimising the effect carbon has on the maximum ion density position. Iodine (IP 10.45 eV) has slightly lower ionisation potential when compared with carbon (11.36 eV) and thus its sensitivity is improved in the carbon-containing matrix (Figure 2(A)). Similarly, the tellurium (first ionisation potential of 9.01 eV) signal is also increased. The other internal standards, Rh (IP 7.46 eV) and Sb (IP 8.61 eV) have lower

ionisation potentials and thus their sensitivity is not improved, unless the nebuliser gas flow is optimised. As shown in Figure 2(B), all monitored elements exhibited an enhancement when 1–2% 2-propanol was added with a difference in the maxima and shapes of the curves. Iodine and Sb show a 43% and 65% enhancement in 1.5–2% 2-propanol, respectively; Te – a 72% increase at 1–1.5% 2-propanol; and Rh – a 6% increase at 1% 2-propanol.

Figure 2(C) describes the ratio of iodine to the three possible internal standard elements as a function of the 2-propanol concentration. The nebuliser gas flow was optimised at each step to ensure maximum signal stability and intensity. In the range of 0–2.5% 2-propanol, there is a change in all ratios with I/Sb becoming constant at above 1% 2-propanol, I/Te – above 2% and I/Rh – above 3%. At higher levels of 2-propanol, the ratios are constant, indicating that either Rh, Te or Sb may be used as internal standards for iodine determination without a concern for the additional amount of carbon that originates from the samples. The second set of analysis in Table 2 shows the recoveries of 1 ng g⁻¹ I using a calibration constructed in 1% TMAH and 6% 2-propanol in the internal standard solution. A check sample containing 1 ng g⁻¹ iodine and varied amounts of 2-propanol showed good recoveries, 96%–103% upto 2% 2-propanol added to the iodine check solution. At 3% 2-propanol in the sample, a deviation of approximately 5% was observed. For all subsequent analyses, 6% of 2-propanol was added to the internal standard solution which was then mixed with the blanks, standards and samples; resulting in a final concentration of 3% to the nebuliser. In most sample preparation techniques, there is residual carbon in the extraction or digestion mixtures. Thus, depending on sample size and type, and the total dilution, as high as 1–2% carbon might be introduced in the plasma. Thus, careful matrix matching or high dilution (sacrificing low level detection by increasing the quantification limit) is necessary in order to achieve accurate iodine quantification. By adding 2-propanol to the internal standard and mixing this with the samples prior to nebulisation, matrix matched standards are unnecessary while using the method described in this paper.

The analyses of food samples fortified with 500 ng g⁻¹ I (sample basis) using calibrations with and without the presence of 2-propanol is presented in Table 3. When 2-propanol was absent in the internal standard mix, recoveries for I were 96–112%, 102–118%, and 90–104% with Te, Rh and Sb as internal standards, respectively. Positive bias was most pronounced for Rh and least pronounced for Sb and depended on sample composition. Highest deviation was observed for high fat samples, such as mayonnaise and ice cream. With the addition of 2-propanol to the internal standard mixture, recoveries for I were 93–103%, 94–107%, and 89–100% with Te, Rh and Sb as internal standards, respectively. While Sb provided best match for iodine analysis, significant Sb levels were observed in food SRMs (NIST 1573a) and samples (processed cheese) and this resulted in negative bias during the iodine quantification. In the presence of 2-propanol Rh and Te showed similar performance. Thus, for all further analyses and method validation Rh was chosen as internal standard element.

Figures of merit/analytical performance

Table 4 shows the analytical performance of this method. The IDL was 0.003 ng g⁻¹ in 1% TMAH solutions ($n = 10$). The estimated ASDL (equation 1) was 0.043 ng g⁻¹, whereas the

LOQ (30σ of method blanks) in solid food samples was 36 ng g^{-1} based on 100-fold dilution from the solid to the analytical solution ($n = 24$). The LOQ was calculated from the standard deviation of the method blanks measured from multiple sample preparations over a period of 2 months. Iodine is adsorbed to glass and plastics and is also present, albeit in trace quantities in most chemical reagents. The background for iodine was $2600 \pm 13 \text{ cps}$, originating from both the instrumentation and reagents and it was stable over both short (over a 24 h analysis sequence) and long (period of 2 months) time periods. To ensure accurate quantification at low concentrations, a blank subtraction was necessary. The precision (%RSD) associated with the quantitative measurements of iodine was 2–7% and were calculated using food samples (unfortified and fortified) and SRMs. These reproducibility measurements were performed over a 2-month period, rather than a single day analysis, and represent variations from both the extractions and instrumental determinations.

Method validation

The method validation was achieved through experiments from a single laboratory using one ICP-MS instrument. The method's accuracy, precision, linearity, ruggedness and robustness were examined. The method was found to be linear over three orders of magnitude, from the ASDL of $0.043\text{--}50 \text{ ng g}^{-1}$ (highest standard in the calibration curve). To verify the accuracy of the method, seven SRMs were analysed in duplicate, at a minimum, on two or more different days (Table 5). The matrices of the reference materials ranged from milk powder and typical diet to tomato leaves and multivitamin tablets. The range of iodine concentrations in the SRMs was from 759 ng g^{-1} in the typical diet NIST 1548a SRM to $132\,000 \text{ ng g}^{-1}$ in the NIST 3280 multivitamin tablets. An additional 100-fold dilution was performed on the multivitamin tablets in order to obtain concentrations within the analytical calibration curve. Conversely, analysing samples at concentrations higher than 50 ng g^{-1} I in the analytical solution requires longer washout times because even with the precautions taken, iodine still adsorbs to tubing and instrument components. The recoveries for SRMs used in the validation experiments ranged from 85% for typical diet to 102% for oyster tissues (Table 3). While all the recoveries were between 80% and 120%, tomato leaves analyses were consistently 10–15% below the reference values. The recoveries for NIST 1548a, typical diet were also at 85%. Possible reasons for the low recoveries of these SRMs include incomplete extraction, matrix effects, or residual moisture in the SRM.

There is a lack of reference materials certified for iodine that encompass all groups of the AOAC food triangle. The method described here targets a wide variety of food samples and thus a second verification of the method was performed using 21 food samples from multiple AOAC food triangle groups (Figure 1). Table 6 is a summary of the iodine quantification for 21 food and nutrient samples. To determine the precision of the method on a wide range of matrices, the 21 samples were prepared in triplicate on three different days, resulting in a total of nine replicates. Fourteen of the samples were above the LOQ and the remaining seven were between the LOD and LOQ. Reproducibility (%RSD) for the samples above the LOQ was 1–7%, while samples below the LOQ showed significant variation (8–64%) that can be attributed both to the sample preparation and method variance at levels

below the LOQ. Egg and milk containing products showed variable iodine concentrations, 94–942 ng g⁻¹. Sea sourced items also contained a significant amount of iodine, with seaweed being the highest at 24 000 ng g⁻¹.

The 21 food and nutrient samples were fortified with iodine at 3 different concentrations and the samples were analysed on different days over a period of 2 months. The fortification levels ranged from 13% to 377% of the iodine concentrations in the samples. Table 7 shows the fortification levels in ng g⁻¹ for each nutrient sample and the recoveries achieved by the method. All fortifications were prepared in triplicate and analysed on separate days. All 21 samples and all fortification levels, including the ones where the initial iodine was between the LOD and the LOQ, exhibited recoveries in the 81–119% range.

Conclusions

We have validated a method for the determination of iodine in food samples by ICP-MS after alkaline extraction. Addition of organic carbon in the form of 2-propanol indicated that there is a significant enhancement of iodine signal and, more importantly, a difference between the enhancement of iodine and the possible internal standard elements. Above 3% 2-propanol, the iodine to internal standard element ratios were constant, indicating that the addition of organic carbon is essential for accurate quantification of iodine in biological samples in which there is incomplete digestion of the matrix. The limit of quantification of 36 ng g⁻¹ is sufficient for the analysis of iodine in food samples. Accuracies measured using NIST SRMs ranged from 85% to 102%. A fortification study with variety of samples from the AOAC food triangle showed excellent precision and accuracy, with day-to-day reproducibility of 1–7% and spike recoveries ranging from 81% to 119%, including a number of samples fortified at the LOQ.

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Figure 1.
Distribution of food samples in the AOAC food triangle.

Figure 2.

(A) I, Rh, Te and Sb normalised intensity as a function of 2-propanol concentration. Nebuliser gas flow was optimised with no 2-propanol in the plasma. (B) I, Rh, Te and Sb normalised intensity as a function of 2-propanol concentration. Nebuliser gas flow was optimised at every 2-propanol concentration. (C) I/Rh, I/Te and I/Sb normalised ratios as a function of 2-propanol concentration. Nebuliser gas flow was optimised at every 2-propanol concentration.

Table 1

Instrumental conditions.

RF power	1250 W
Sampling depth	−2.5 mm
Cool gas flow rate	16 l min ^{−1}
Auxiliary gas flow rate	0.95 l min ^{−1}
Sample gas flow rate	0.9 l min ^{−1}
Sample uptake rate (nebuliser)	0.6 ml min ^{−1} (glass concentric nebuliser)
Sample cone	Nickel
Skimmer cone	Nickel
Spray Chamber	20 ml baffled cyclonic
Scan mode	Fixed magnet, electric scan
Dwell time	10 ms
Samples per peak	10
Runs, passes per isotope	5, 10

Table 2

Recoveries of 1 ng g⁻¹ in the presence and absence of 2-propanol.

	No 2-propanol			6% 2-propanol in ISTD mix		
	Te	Rh	Sb	Te	Rh	Sb
1 ng g ⁻¹ I	98%	100%	99%	99%	103%	99%
1 ng g ⁻¹ I, 1% 2-propanol	92%	106%	108%	98%	100%	98%
1 ng g ⁻¹ I, 2% 2-propanol	88%	115%	114%	97%	98%	96%
1 ng g ⁻¹ I, 3% 2-propanol	86%	119%	116%	95%	94%	94%

Table 3

Analysis of I in food samples with and without the addition of 2-propanol.

	Te as internal standard			
	0% 2-propanol		6% 2-propanol	
	I (ng g ⁻¹)	Fortified I recovery (%) ^a	I (ng g ⁻¹)	Fortified I recovery (%) ^a
Soy infant formula	116	103%	117	101%
Baby bisquits	201	103%	194	100%
Ice cream	388	112%	371	103%
Processed cheese	454	104%	401	93%
Enriched white bread	2686	96%	2538	96%
Mayonnaise	60	110%	55	102%
Bagels	900	105%	871	103%
Pepperoni pizza	89	102%	82	96%
Salmon	49	103%	47	100%
Pudding	71	100%	70	100%
<i>Rh as internal standard</i>				
Soy infant formula	124	107%	117	99%
Baby bisquits	230	113%	202	104%
Ice cream	424	116%	376	107%
Processed cheese	475	102%	396	94%
Enriched white bread	2802	118%	2592	94%
Mayonnaise	67	117%	55	102%
Bagels	994	109%	899	100%
Pepperoni pizza	97	110%	80	95%
Salmon	51	109%	46	97%
Pudding	78	109%	72	105%
<i>Sb as internal standard</i>				
Soy infant formula	116	101%	114	99%
Baby bisquits	189	98%	188	97%
Ice cream	370	102%	363	100%
Processed cheese	395	90%	389	89%
Enriched white bread	2573	90%	2483	95%
Mayonnaise	56	103%	54	100%
Bagels	847	104%	857	98%
Pepperoni pizza	84	94%	80	94%
Salmon	47	99%	46	97%
Pudding	71	101%	69	98%

Note:

^a All samples were fortified with 500 ng g⁻¹ iodine (sample basis).

Table 4

Figures of merit.

Sample weight (g)	0.3–2
Background iodine (cps)	2690
Sensitivity (cps per ppb)	138 000
Instrument detection limit in aqueous solutions (ng g ⁻¹)	0.003
Method detection limit in aqueous solutions (ng g ⁻¹)	0.043
Limit of quantification (30σ in solid food samples, ng g ⁻¹)	36
12-h recovery of QC solution (%)	95–98
Uncertainty (%)	2–7

Table 5

Iodine analysis of SRMs.

Description	Reference level (ng g ⁻¹)	Measured level (ng g ⁻¹)	<i>n</i>	Recovery (%)
NIST 1573a, tomato leaves	850	740 ± 48	18	87
NIST 1549, non-fat milk	3380	3420 ± 130	14	101
NIST 1566a, oyster tissue	4460	4530 ± 160	15	102
NIST 8435, whole milk powder	2300	2510 ± 30	2	93
NIST 1572, citrus leaves	1840	1700 ± 2	2	101
NIST 1548a, typical diet	759	642 ± 9	2	85
NIST 3280, multivitamin tablets	132 700	131 000 ± 2000	2	99

Table 6

Iodine levels of food samples.

Food	<u>Level found</u> (ng g⁻¹)	<u>Reproducibility</u> (%RSD, <i>n</i> = 9)
Roasted seaweed snack	24 000	6%
Mini Wheats cereal	< LOQ	47%
Hershey chocolate bar	157	3%
Crunchy peanut butter	< LOQ	64%
Stewed tomatoes	< LOQ	11%
Ranch dressing	94	6%
Canned potatoes	< LOQ	56%
Baby clams	1590	4%
Fruit cocktail in heavy syrup	84	2%
Iodised salt	44 700	7%
Canned pink salmon	214	6%
Apple juice	< LOQ	8%
Whole milk	505	1%
Low-fat yoghurt	399	3%
Hardboiled eggs	242	3%
Grated cheese	342	3%
Breaded fish tenders	298	3%
Honey battered chicken tenders	< LOQ	37%
Mashed potatoes	127	2%
Infant formula	942	2%
Banana puffs	< LOQ	45%

Table 7

Iodine fortification of food samples and recoveries.

Food	50% Fortification level (ng g ⁻¹)	Recovery (n = 3)	100% Fortification level (ng g ⁻¹)	Recovery (n = 3)	200% Fortification level (ng g ⁻¹)	Recovery (n = 3)
Roasted seaweed snack	5730	96–109%	20 700	94–97%	20 300	95–98%
Mini Wheat cereal	15.5	92–100%	33.5	90–92%	67.5	90–92%
Hershey chocolate bar	91.3	92–96%	261	91–96%	593	93–96%
Crunchy peanut butter	13.6	91–119%	41.7	97–103%	61.9	94–101%
Stewed tomatoes	13.1	90–97%	28.9	90–99%	67.1	95–100%
Ranch dressing	60.6	90–97%	104	93–103%	212	94–98%
Canned potatoes	14.1	93–102%	48.7	89–97%	50.4	89–97%
Baby clams	450	105–109%	996	93–112%	1790	87–103%
Fruit cocktail in heavy syrup	24.3	81–103%	45.7	96–101%	108	97–100%
Iodised salt	16 900	95–101%	41 200	84–101%	88 900	96–101%
Canned pink salmon	117	95–100%	237	96–98%	465	95–104%
Apple juice	6.7	96–103%	13.4	95–100%	26.5	99–103%
Whole milk	65	112–120%	131	109–113%	258	81–117%
Low-fat yoghurt	182	99–112%	354	100–102%	669	99–104%
Hardboiled eggs	90.4	92–98%	181	93–99%	399	96–100%
Grated cheese	238	100–107%	514	95–104%	862	101–107%
Breaded fish tenders	179	99–102%	302	99–102%	462	100–104%
Honey battered chicken tenders	23.6	101–104%	61.6	97–105%	85.2	98–104%
Mashed potatoes	41.9	94–108%	80.6	97–106%	202	98–101%
Infant formula	340	104–118%	610	101–118%	1440	109–119%
Banana puffs	22.2	98–103%	48.7	99–104%	93	98–104%