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Comparison of methods for iodine analysis in foods ☆

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ABSTRACT

Spectrophotometric and ICP-MS methodology for iodine determination was compared. Samples were alkali dry-ashed, dissolved in water, and iodine assayed by spectrophotometry and by ICP-MS. Iodine content in the studied foods ranged from 3 to 1304 μg/100 g. There was no significant difference ($p > 0.05$) between iodine values determined spectrophotometrically using an external calibration curve and values determined using a standard addition. Foods containing low iodine concentrations (4–25 μg/100 g) also showed no significant difference ($p > 0.05$) between iodine concentrations determined spectrophotometrically and concentrations determined by ICP-MS. For food items with more than 25 μg/100 g, the spectrophotometric methods yielded markedly higher ($p < 0.05$) concentrations than the standard ICP-MS method (relative positive bias 25–122%), especially in foods with high sodium and/or iron contents. A catalytic effect of sodium and iron on the Sandell and Kolthoff reaction, leading to false high values in the spectrophotometric determination of iodine was demonstrated. ICP-MS is recommended for iodine determination in foods.

1. Introduction

Iodine is one of the most important trace elements in human nutrition. It forms a vital component of the hormones produced by the thyroid gland. Thyroid hormones, including thyroxin (T4) and triiodothyronine (T3), are crucial regulators of the metabolic rate, and physical and mental development in humans (Zimmermann, Jooste, & Pandav, 2008). In 2013, the International Council for the Control of Iodine Deficiency Disorders (ICCIDD, 2013) reported on national iodine status, using urinary iodine as an indicator for iodine deficiency. It was found that several countries still have an Iodine Deficiency Disorders (IDD) problem. Thailand was classified as a country of optimum iodine nutrition. However, this is not so for every region in Thailand (Rajatanavin, 2007). North and north-east regions of Thailand still have mild iodine deficiency. One strategy to combat IDD is endorsed in the Thai Notification on fortification of iodine in table-salt (20–40 mg kg^{-1}), fish sauce and soy sauce (2–3 mg L^{-1}) (The Department of Health, Thailand, 2008).

Several methods, including spectrophotometry, have been used for iodine determination in biological matrices. The Sandell and Kolthoff (1934) spectrophotometric method is the most commonly used method for iodine analysis in biological and food samples. Iodide acts as a catalyst for reducing Ce(IV) to Ce(III) by As(III), in acid medium. The spectrophotometry measures the reduction of the yellow colour of ceric to the colourless of cerous. There are five AOAC methods available for iodine analysis in foods, which include titration (AOAC, 2005, 935.14), reversed-phase ion-pair liquid chromatography (AOAC, 2007, 992.22), ion-selective electrode (AOAC, 2005, 992.24) and Inductively Coupled Plasma Mass Spectrometry, ICP-MS (AOAC, 2012, 2012.14 & 2012.15), which give reliable and accurate results. A spectrophotometric method is not included in AOAC standard methods. However, the method has been applied in many laboratories (Chavasit, Malaivongse, & Judprasong, 2002; Cressey, 2003; Longvah, Toteja, & Upadhyay, 2013; Longvah et al., 2012; MOPH, 2001; Moxon & Dixon, 1980; Travnicek, Herzig, Kursa, Kroupova, & Navratilova, 2006; Waszkowiak & Szymandera-Buszka, 2008; Yaping, Dongxing, Jixiang, Tianshiu, & Huiqin, 1996) because it is not complicated, does not require sophisticated instrumentation and is comparatively low in cost. This study compares a spectrophotometric method using two techniques for iodine measurement, -external calibration curve and standard addition-, with the reliable ICP-MS standard method.

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2. Materials and methods

2.1. Food sampling and sample preparation

The top ten commonly consumed food items were identified from the Thai national food consumption survey (Kosulwat et al., 2006). They were jasmine rice (*Oryza sativa* Linn), kale (*Brassica alboglabra*), boiled banana prawn (*Penaeus merguiensis*), steamed short-bodied mackerel (*Rastrelliger brachysoma*), iodine-enriched hen egg, yard-long bean (*Vigna unguiculata* subsp. Sesquipedalis), chicken thigh (*Gallus gallus*), milk powder, fermented fish and shrimp paste. Each food was randomly purchased from three markets/supermarkets. Fresh food samples were kept in an ice box and transported to the laboratory without delay.

The edible part of studied samples was individually prepared and homogenised using an appropriate food mixer or homogeniser; for example, vegetables were cleaned, the edible part was prepared, and then blended by food mixer. All samples, except jasmine rice and milk powder, were lyophilised. The prepared samples were kept in acid-washed screw-capped plastic bottles, and stored at −20 °C, until analysis.

2.2. Iodine determination

2.2.1. Sample treatment by alkali ashing (Moxon & Dixon, 1980)

A sample was first alkali treated with 30% w/v potassium carbonate and 10% w/v zinc sulphate, evaporated on a steam bath until dry and then dry-ashed in a muffle furnace at 550 °C for 2 h to remove all organic materials. If ashing is not complete, add 1 mL 10% zinc sulphate solution and break the charred residue with a glass rod to disperse it in the solution. Heat samples on the steam bath until dry. Repeat ashing until white ash is obtained. The residue was dissolved in deionised water (resistivity 18.2 MΩ cm^{-1} equivalent to a conductivity of 0.055 μS cm^{-1}), prepared by a Millipore water purification system (Millipore RiOs-DITM134, Bedford, MA, USA) and coupled with ultra-pure water systems (SG®, Integra and Ultra Clear, Berlin, Germany).

2.2.2. Iodine determination

The test solution was then divided into three portions for three different measurement procedures. All food samples were analysed, in triplicate, by spectrophotometric and ICP-MS methods. The first two portions were analysed for iodine by spectrophotometric procedures which based on the kinetic catalytic colorimetric method of Sandell and Kolthoff (1934). The kinetic reaction involves iodide acting as a catalyst for reducing Ce(IV) to Ce(III) by As(III) in acid medium, resulting in the kinetic changing of the yellow colour of ceric to the colourless of cerous. The amount of iodine in the sample is directly proportional to the decreasing rate of absorbance. The kinetic reaction at a specific period was measured by two specific spectrophotometric procedures at 410 nm. In the first spectrophotometric procedure, the amount of iodine is measured using an external calibration curve whereas the second spectrophotometric procedure uses a standard addition technique.

The third portion of the test solution was diluted with 5% (v/v) ammonia solution. Indium (In) was added as internal standard at the concentration of 5 mg/L. Then, iodine was measured by an Inductively Coupled Plasma Mass Spectrometer (ICP-MS, Elan 6000, Perkin-Elmer, Norwalk, CT, USA). Parameters for ICP-MS measurement of AOAC method 2012.14 (AOAC, 2012) were followed, except using indium as internal standard instead of tellurium.

2.3. Analytical quality control

Non-fat milk powder (SRM 1549, NIST, USA) and whole milk powder (RM 8435, NIST, USA) were used as quality control standard reference materials and reference material, respectively for accuracy checking. For internal quality control system, milk powder was used as quality control sample for iodine analysis by spectrophotometry and by ICP-MS. Recovery was checked by adding a separate set of standard iodine into quality control (QC) samples. Method precision was checked by analysis of 10 QC samples in triplicate. The relative standard deviation (%RSD_r) was compared to the Horwitz predicted relative standard deviation between laboratories (pRSD_R) (AOAC, 2012) at the mean iodine levels (pRSD_R was calculated from the Horwitz equation = $2C^{-0.1505}$). Horwitz Ratio (HORRAT) was calculated by RSD_r/pRSD_R. Limit of detection (LOD) and limit of quantitation (LOQ) were calculated from standard deviation of ten time analysis of sample containing lowest iodine content. All food samples were analysed by three studied procedures in triplicate.

2.4. Statistical analysis

The results of all measurements were presented on a fresh weight basis as mean ± standard deviation. Iodine measurements by the spectrophotometric methodology and the ICP-MS

Table 1A
Method validation of iodine analysis: accuracy testing.

Parameters	Iodine content (μg/100 g)	
	SRM 1549 Non-fat milk powder (n = 7)	RM 8435 Whole milk powder (n = 7)
Certified values	338 ± 2	230 ± 40
Determined by spectrophotometry	325 ± 23	217 ± 18
Absolute difference between mean of measured value and certified value (Δm)	13	13
Combined uncertainty (u_Δ) of measured value (u_m) and certified value (u_{CRM}) $u_\Delta = \sqrt{u_m^2 + u_{CRM}^2}$	7	21
Expanded uncertainty (k = 2)	15	42
Summary of the comparison of measurement result with the certified value (Linsinger, 2005)	Not significant	Not significant
Determined by ICP-MS	330 ± 16	225 ± 11
Absolute difference between mean of measured value and certified value (Δm)	8	5
Combined uncertainty (u_Δ) of measured value (u_m) and certified value (u_{CRM}) $u_\Delta = \sqrt{u_m^2 + u_{CRM}^2}$	5	20
Expanded uncertainty (k = 2)	10	41
Summary of the comparison of measurement result with the certified value (Linsinger, 2005)	Not significant	Not significant