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SHORT COMMUNICATION

Determination of urinary iodine by inductively coupled plasma mass spectrometry

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Abstract

Background: Mild iodine deficiency is endemic in many countries of Europe including Belgium. Fast, accurate and specific methods for quantification of urinary iodine are needed. We describe in this report a specific ICP-MS method for the quantification of urinary iodine.

Method: Samples and iodate calibrators were diluted 20 times into aqueous solution containing triton X-100, 1.5% HCl and ^{103}Rh as an internal standard. Prior digestion or oxidation was not necessary. Results were compared with those obtained by Sandell–Kolthoff (S–K) spectrophotometric method.

Results: Comparison of both methods showed good agreement. The Passing–Bablok regression between both methods was ICP-MS = 0.986 (S–K)−7.51. The Bland–Altman difference plot showed a small but significant mean difference of −13.3 μg/L for ICP-MS. The between-day coefficient of variation (CV) was 13% at 89 μg/L. Limit of detection was 4 μg/L and limit of quantification was 20 μg/L. No carryover effect has been observed on series containing up to 50 samples.

Conclusion: The ICP-MS method described here is fast, accurate and specific for the quantification of urinary iodine. Compared to the S–K method the urinary iodine concentrations measured by the ICP-MS method were slightly, but significantly lower. Consequently, the results of studies using S–K method should be compared with caution with those using the ICP-MS method.

Keywords: Iodine; Deficiency; Urine; ICP-MS

Introduction

Mild iodine deficiency may affect thyroid function, and related disorders generate increased health care costs [1]. As mild iodine deficiency is endemic in Belgium [2], a reliable method is needed to evaluate dietary iodine intake and to monitor the evolution of iodine status at population level. Urinary iodine concentration reflects dietary iodine intake and has been used as a marker for iodine status in population studies [3].

In this report, we describe a quantitative method for assessment of urinary iodine using an ICP-MS method with rhodium as an internal standard instead of

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tellurium as previously reported [4,5]. This method was compared with the automated Sandell–Kolthoff (S–K) spectrophotometric method [6,7], which has been used in a previous survey of iodine status in Belgium [2,8].

Material and methods

Urine samples were diluted 20 times before the analysis without any digestion step or oxidation. Despite some reports in the literature about memory effects of molecular iodine formed in acidic conditions [9], no background problems or memory effects were observed for series of up to 50 consecutive samples. The combination of a pneumatic nebulizer and the spray chamber in ICP-MS could potentially cause selective evaporation of volatile iodine species resulting in non-quantitative recovery and carryover effect. These difficulties were overcome using a reduced size cyclonic spray chamber that exhibits fewer sample–aerosol interactions as previously described [10] with rinsing time of 4 min.

Samples and iodate calibrator solutions were prepared just before the analysis by dilution 1:20; 500 μL of sample/calibrator plus 9 mL of an aqueous solution of 0.5 mL/L Triton X-100 containing 2.5 μg/L rhodium as an internal standard. Nebulization was improved by adding 500 μL suprapure concentrated HCl (Merck). The water used for dilutions and rinses in the ICP-MS method was de-ionized 18 MΩ water using the Millipore Corporation™ cartridge system. A peristaltic pump introduced the diluted samples into the spray chamber with an argon stream. The I^+ and Rh^+ ions were measured at m/z 127 and 103, respectively. Wash solution consisted of aqueous solution of 0.2 mL/L Triton X-100 and 5 mL/L suprapure nitric acid. This solution was pumped into the sample-introduction system between samples to prevent carryover of the analytes of interest from one sample measurement to the next. Intermediate calibration solutions were prepared by dilution into Milli-Q water from 100 mg/L KIO_3 solution to yield final concentrations of 10, 50, 100, 500, 1000 and 2500 μg/L. Calibrators were prepared as samples by adding 500 μL aliquots of intermediate aqueous KIO_3 solution to diluent and HCl in order to matrix-match the working calibrators with the urine samples being analyzed.

We used a high-resolution double-focusing ICP-MS Element 2 system (Thermo Fisher Scientific™), coupled to a cyclonic spray chamber and a conical nebulizer (Glass Expansion) for sample introduction. A sample time of 10 ms was used for both ^{127}I and ^{103}Rh. The applied RF power was 1.1 kW, and the argon nebulizer gas flow was typically 1.2 L/min. The limit of detection was determined as 3 SD of the concentration in blank samples. The limit of quantification was determined as the concentration for which the coefficient of variation (CV) was about 20%. To compare the ICP-MS method with the S–K, 77 urine samples were selected to cover a large range of concentrations.

Passing–Bablok correlation and Bland–Altman difference plots were used to assess the agreement between results obtained by ICP-MS and those obtained by the S–K method [11].

Results and discussion

The limit of detection by ICP-MS was 4 μg/L and limit of quantification was 20 μg/L. The CV for a low pool (89 μg/L) analyzed for 18 months on 140 results obtained in 70 separate analytical runs was 13%. Recovery varied from 94% to 103% as determined by adding iodide amounts of 100–900 μg/L to urinary samples. Accuracy has been checked on QC control (Seronorm). Linearity was very good from 20 to 2500 μg/L ($r > 0.99$). No matrix effect was observed with dilution of urine samples, and recovery of 90–102% was obtained for serial 1:12 dilutions of urine samples at 239 μg/L.

A strong correlation between the two methods (Pearson, $r = 0.97$) was observed. The urinary iodine values measured by ICP-MS were 18–869 μg/L (median 98 μg/L), and those measured by S–K were 16–790 μg/L (median 113 μg/L).

Passing–Bablok method comparison of the ICP-MS and S–K method (Fig. 1A) showed a very good agreement with y-intercept, −7.51 (95%CI: −15.27 to 0.74); slope, 0.986 (95%CI: 0.897 to 1.067) and $Sx/y = 39$. The individual intervals for intercept and slope at the 95% confidence level include 0 and 1, respectively, and do not indicate significant bias. The differences between the individual results obtained by the two methods were concentration independent, but show a small but significant mean difference of −13.3 μg/L for ICP-MS compared to S–K (95% confidence interval, −4.7 to −22.0 μg/L) over the range of 20–829 μg/L (Fig. 1B). The 95% limits of agreement (i.e. the interval defined by the mean difference ± 2 SD) gave an indication of the variability of the differences between the two methods. Ninety-five percent of all differences between ICP-MS and S–K results can be expected between −88.1 and 61.5 μg/L.

Agreement remained good in the lower range, evaluated on 34 samples with values between 20 and 100 μg/L by ICP-MS. The mean absolute difference between the two methods over this range was −12.1 μg/L (95% confidence interval: −6.3 to −17.8 μg/L) with a Passing–Bablok regression of $y = 0.803x - 0.923$ ($Sx/y = 13$).