

Max Haldimann · Rita Wegmüller ·
Michael Zimmermann

Determination of iodine concentration in salt dual fortified with iron and iodine

Received: 2 June 2003 / Revised: 4 August 2003 / Published online: 19 September 2003
© Springer-Verlag 2003

Abstract The applicability of the iodide catalyzed reaction (Sandell-Kolthoff) between Ce^{4+} and As^{3+} for the determination of iodine in salt samples fortified with iron and iodine has been studied. A method verification program is presented; the catalytic method was compared with isotope dilution inductively coupled plasma-mass spectrometry (ICP-MS), for which the long-lived iodine nuclide ^{129}I was used. Two-way analysis of variance (ANOVA) revealed that both methods yielded consistent iodine results across salt samples from Morocco and the Ivory Coast that were either free of iron or fortified with different iron species. Although some bias was present, no influence of iron on the catalytic reaction was detected.

Keywords Dual fortification · ICP-MS · Iodine · Iron · Isotope dilution · Salt Sandell-Kolthoff

Introduction

Deficiencies of iron and iodine are major problems worldwide. Dual fortification of salt with iodine and iron can be an effective approach to combating iron and iodine deficiency [1]. The stability of iodine in salt and the levels of iodization are essential questions in salt iodization programs. Ensuring the stability of iron and iodine in dual-fortified salt has remained problematic as both elemental species can interact [2]. Thus, it is important to monitor the concentrations of the potentially volatile iodine. However, analytical complications may arise from the presence of iron, especially if kinetic procedures are

used for the determination of iodine in dual-fortified salt. Kinetic procedures are accepted as being sensitive and have been applied for the determination of a variety of ions. The most practical application is based on the catalytic effect of iodide on the redox reaction between the yellow Ce^{4+} and As^{3+} , which yields the colorless Ce^{3+} and As^{5+} . The decrease in absorption is related to the iodine concentration. For comparable concentrations of reactants, I^- can also be oxidized by Ce^{4+} to an inactive form, i.e., IO_3^- . Therefore the reducing reactant As^{3+} must be present in excess of Ce^{4+} to prevent loss in catalytic activity. The reaction was studied and first reported by Sandell and Kolthoff [3]. Despite the large volume of literature which exists for this reaction the synergistic catalytic effect of iron on iodide kinetic reactions has not been studied in detail [4, 5]. This study describes the dependence of the Sandell-Kolthoff reaction upon the iodine catalyst, which was contained as iodide or iodate in dual-fortified salt samples from Morocco and the Ivory Coast, respectively. For this purpose, a comparison of methods was made to determine the accuracy of the catalytic reaction method against a reference method. Isotope dilution inductively coupled plasma-mass spectrometry (ICP-MS) was chosen as a reference method because of the soundness of its analytical principles and its accuracy in predicting the true value [6]. By inducing a deliberate change in an isotope ratio of an element, it is possible to determine its concentration in a sample. In the case of iodine, only the isotope ^{127}I occurs in terrestrial material, therefore the long-lived radioisotope ^{129}I was added to the sample. The application of iodine isotope dilution ICP-MS in food analysis has been validated by measuring certified standard reference materials and by comparison with neutron activation analysis [7].

Materials and methods

Chemicals

Water was purified and deionized (18 MOhm) using the cartridge system Easy Pure LF (Barnstead, Dubuque, IA, USA). Suprapur

M. Haldimann (✉)
Division of Food Science, Swiss Federal Office of Public Health,
3003 Bern, Switzerland
e-mail: max.haldimann@bag.admin.ch
Tel.: +41-31-322 95 58
Fax: +41-31-322 95 74

R. Wegmüller · M. Zimmermann
Human Nutrition Laboratory,
Institute for Food Science and Nutrition,
Swiss Federal Institute of Technology, Zürich, Switzerland

Table 1 Comparison of two methods for the determination of iodine salt samples from Morocco and Côte d'Ivoire the Ivory Coast fortified with different iron species: randomized complete-block plan; ICP-MS, inductively coupled plasma-mass spectrometry

Fortified iron Chemical form	Concentration (mg/g)	Method	
		ICP-MS	Catalytic reaction
Fumarate (II)	1	X ₁₁ ... X ₁₅	Y ₁₁ ... Y ₁₅
Fumarate (II), encapsulated ^a	1	X ₂₁ ... X ₂₅	Y ₂₁ ... Y ₂₅
Pyrophosphate (III)	2	X ₃₁ ... X ₃₅	Y ₃₁ ... Y ₃₅
Sulfate (II)	1	X ₄₁ ... X ₄₅	Y ₄₁ ... Y ₄₅
Sulfate (II), encapsulated ^a	1	X ₅₁ ... X ₅₅	Y ₅₁ ... Y ₅₅
No iron added	0	X ₆₁ ... X ₆₅	Y ₆₁ ... Y ₆₅

^a In hydrogenated vegetable oil

ammonia solution (14 mol/L) was obtained from Merck (Darmstadt, Germany). The iodine concentration of these reagents was below 0.1 ng/mL. The NIST SRM 4949C radioactivity ¹²⁹I standard is suitable for isotope dilution analysis. The activity of the solution was certified at 3451±22 Bq/g, which is equal to a ¹²⁹I concentration of 528 mg/L. The standard contains 84 mg/L ¹²⁷I. Analytical grade ammonium persulfate, arsenic trioxide, sodium chloride, sulfuric acid (9.8 mol/L), ceric ammonium sulfate, potassium iodide and potassium iodate were obtained from Fluka (Buchs, Switzerland).

Salt samples

Potassium iodide and iodate were used to obtain iodine concentrations of 5 and 30 µg/g in salt samples from Morocco and the Ivory Coast, respectively. Because the native iodine content of the Ivory Coast salt was at least 10 µg/g salt, the expected concentration levels in the fortified Ivory Coast salt were accordingly higher. At each of these iodine concentrations, the salt samples were fortified with iron compounds (Table 1).

Catalytic method with spectrophotometric detection

Water was added to 10 g of salt to obtain a solution of 100 g using an ultrasound bath. 8 g of this solution was further diluted to 100 g. 250 µL of the sample solution was pipetted into a test tube, followed by 1 ml 1.0 mol/L ammonium persulfate solution. The test tubes with blank, standard and sample solutions were kept in a heating block at 95 °C for 60 min. After the solutions cooled down to ambient temperature 3.5 ml–0.1 mol/L arsenious acid solution (in 0.5 mol/L sulfuric acid and 0.4 mol/L sodium chloride) was added to each solution. The solutions were thoroughly mixed and allowed to stand for 15 min. A volume of 350 µL 0.08 mol/L ceric ammonium solution (in 1.75 mol/L sulfuric acid) was added and the contents were again mixed quickly. Constant intervals of 30 s were kept between additions to successive tubes. Exactly 33 min after the addition to the first tube, the absorbance was read at 405 nm in an Uvikon spectrophotometer 940 (Kontron Instruments, Watford, Herts, UK), and then each tube was read consecutively at 30 s intervals, so that the time between addition and reading was exactly 33 min.

Isotope dilution ICP-MS

1.0 g sample solution aliquots were spiked with 1.0 g of a solution (NIST SRM 4949C ¹²⁹I radioactivity standard) containing a mass of 40 ng ¹²⁹I in 0.14% ammonia and then diluted to 10 mL. The measurements were performed with an Element2 (Finnigan-MAT, Bremen, Germany), which is a sector field instrument. ¹²⁷I/¹²⁹I ratios were measured by rapidly scanning the acceleration voltage while the magnetic field was kept constant, thereby achieving quasi-simultaneous acquisitions on neighboring masses. A MicroMist low flow nebulizer, operated at a gas flow of 1.0 L/min, (AR30-1-FM02, Glass Expansion, Vevey, Switzerland) and a Twinnabar spray chamber (809-0416) were selected in an effort to achieve consistent precision, and low memory effects. A micro auto sampler (CETAC ASX-100, Omaha, NE, USA) was used with a low pulsation tubing

pump at an uptake of 0.2 mL/min (IPC, Ismatec, Zurich, Switzerland). The isotopes ¹²⁷I and ¹²⁹I were acquired at a resolution setting of 300 with 20 points per mass peak. An integration window of 50% was selected. 25 scans were accumulated per analysis. Blanks were repeated after five consecutive samples in order to monitor potential memory effects. In addition, the spike solution was repeatedly measured after five samples, and thus the ¹²⁷I/¹²⁹I ratio was continually updated as monitoring of instrument condition. Each measurement was initiated after a take-up time of 2 min and was followed by a wash time of 4 min.

Statistical analysis

A two-way analysis of variance (ANOVA) was computed to uncover the main effects *method* and *iron* and the effect of the *interaction* between the two variables (Table 1) using statistical software (SAS 8, Cary, NC, USA). Residual analysis was performed by generating normal probability plots to verify that the overall errors were normally distributed; outliers were removed. In addition, squared multiple correlations were computed.

Results and discussion

The repeated control measurements of the ¹²⁹I spike solution (NIST SRM 4949C) yielded constant ratios

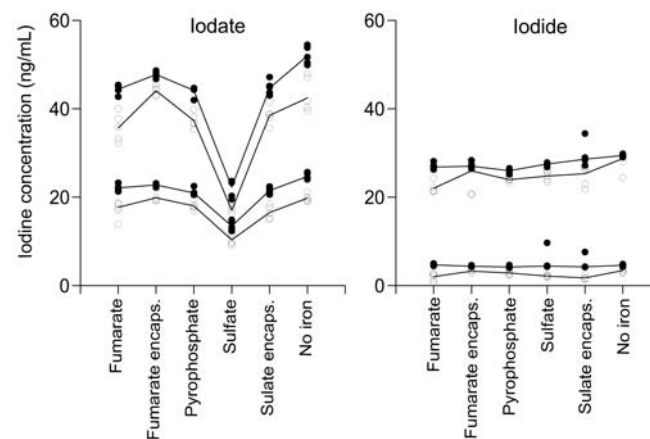


Fig. 1 Effect of different iron fortifications on the determination of iodine as iodide and iodate in dual fortified salt by isotope dilution inductively coupled plasma-mass spectrometry (ICP-MS) and the catalytic reaction between Ce⁴⁺ and As³⁺ (Sandell Kolthoff reaction). The black and colorless dots represent ICP-MS and catalytic reaction results, respectively. Least square fitting lines were drawn through the point sets of the two methods to illustrate the parallel responses. Each iodine species was measured on two different concentration levels

Table 2 Two-way analysis of variance

Iodine, level	Method (<i>P</i> -values)	Factors Iron (<i>P</i> -values)	Interaction (<i>P</i> -values)	Mean difference between methods ±standard error (μg/kg)	Relative mean difference (%)	Squared multiple correlation (<i>r</i> ²)
Iodide, low ^a	<0.001	<0.001	<0.001	1.14±0.26	23	0.90
Iodide, high	<0.001	<0.001	0.158	1.29±1.09	4	0.66
Iodate, low ^a	<0.001	<0.001	0.060	4.93±0.58	33	0.96
Iodate, high	<0.001	<0.001	0.059	8.72±1.29	19	0.97

^a Outlier removed

throughout the ICP-MS measurements. The relative standard deviation was 0.4% (n=10). The concentration levels of the iodide and iodate measured by ICP-MS and catalytic reaction in salt fortified with iron are illustrated in Fig. 1. The plot displays that the catalytic reaction caused a response relative to ICP-MS which was smaller and resulted in an overall bias. The magnitude of the relative error was higher for samples with low levels of iodine. The deviations were of acceptable magnitude for iodide; however, a bias towards the ICP-MS measurements was obtained for iodate. The low concentrations of the iodine catalyst used made it difficult to identify the source of error. In any case, the oxidized iodine species were permitted to react for some time with As³⁺, in that way iodate was reduced to a state which has catalytic activity equal to iodide. However, on the basis of these experiments it was impossible to determine whether the lower iodate values resulted from specific losses in the course of the analytical process or trace amounts of some interfering ions present in the Ivory Coast salt that partially inhibit the catalytic activity of iodine.

As expected after examination of Fig. 1, the ANOVA (Table 2) showed conclusively that the main factors *method* and *type of iron* had a significant effect on the iodine levels. The interaction between the two variables measures the extent to which the methods obtain consistent results among the double fortified salt samples. Non-significant interaction terms were seen in all cases, except for low level iodide. Leaving aside the low level iodide measurements for which kinetic data appear to be erratic, the ANOVA showed that the two methods measure the

different samples in a parallel way, regardless of the presence of iron or its form. In essence, no synergistic catalytic effect between iron and iodine on the kinetic Ce⁴⁺/As³⁺ redox system was observed under the conditions specified in this study, because isotope dilution ICP-MS is a method that is not susceptible to matrix-induced changes in sensitivity. As graphically illustrated in Fig. 1, the variable iodine concentrations on the two levels reflect losses that must occur before the initiation of the analytical procedure, i.e., splitting of the samples. Although more detailed analysis of interfering species may be necessary, the performance of the catalytic reaction according to Sandell and Kolthoff is useful for the purpose of iodine monitoring in salt dual fortified with iron and iodine.

References

- Zimmermann MB, Zeder C, Chaouki N, Saad A, Torresani T, Hurrell RF (2003) *Am J Clin Nutr* 77:425–32
- Wegmüller R, Zimmermann MB, Hurrell RF (2003) *J Food Sci* 68:2129–2135
- Sandell EB, Kolthoff (1934) *J Am Chem Soc* 56:1426
- Rodriguez PA, Pardue HL (1969) *Anal Chem* 41:1376–1380
- Wang J, He R (1996) *Microchem J* 53:376–384
- Heumann KG (1988) *Isotope dilution mass spectrometry*. In Adams F, Grijbels R, van Grieken R (eds) *Inorganic mass spectrometry*. Wiley, New York, pp 301–76
- Haldimann M, Eastgate A, Zimmerli B (2000) *Analyst* 125:1977–1982