

Double Fortification Of Salt With Iron And Iodine

L.L.Diosady¹ and M.G. Venkatesh Mannar²,

¹ Professor of Food Engineering, Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, ON, Canada, M5S 3E5

² Executive Director, The Micronutrient Initiative, International Development Research Centre, 250 Albert St. P.O. Box 8500, Ottawa ON Canada, K1G 3H9

The double fortification of salt with iron and iodine for simultaneous prevention of iron deficiency anemia and iodine deficiency disorders has been a goal of researchers for at least 20 years. The major problem is the interaction between iodine and iron which results in a loss of iodine. We have reviewed the published techniques for double fortification and found that most of the preparations are unstable under normal conditions found in affected areas. Stable double-fortified salt can be achieved with high-purity salt maintained in good packaging using ferrous fumarate and potassium iodide in the presence of a stabilizer. For use with impure salts in high humidity conditions, the iodine must be protected by physical or chemical means. We developed a micro-encapsulation technique that allows production of double-fortified salt stable for at least one year. The production technique and stability are discussed.

1. BACKGROUND

The diet of more than a billion people in the developing countries is deficient in two key micronutrients: iodine and iron. Low iodine levels in the diet lead to iodine deficiency disorders, while low iron intake leads to anemia, which reduces work capacity and resistance to disease (Clydesdale, 1985). Iron deficiency is prevalent in two thirds of the children and women of child bearing age in most developing countries.

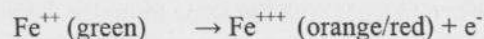
Deficiencies in iodine or iron can be inexpensively eliminated, prevented, or reduced by increasing their dietary intake through fortification of food. However, it is critical that the carrier for the micronutrients be available to the entire population, and it must be consumed at a constant rate independently of social or economic status of each consumer.

Salt is an attractive vehicle in the provision of both iodine and iron, because of its uniform consumption and availability to all segments of the population (Venkatesh Mannar 1989). Cooking salt

has been fortified with iodine in the developed world since the early 1900's, and there is an intensive international effort currently under way to extend the use of iodized salt to all of mankind (Venkatesh Mannar et al. 1987).

Potassium iodate is the iodine compound most often used in salt iodization programs in developing countries. Unfortunately, impure iodated salt can lose most of the added iodine during extended storage at high temperature and humidity (Diosady et al. 1997 and 1998).

Iron is most bioavailable in the ferrous (Fe^{++}) form. Through oxidation, ferrous iron is converted to the ferric form (Fe^{+++}):



This reaction is accelerated by alkaline conditions, oxidizing agents, including air, salt impurities, such as magnesium chloride and magnesium sulphate, and high humidity. Food fortified with ferrous compounds that undergo oxidation often exhibit lowered bioavailability, poor taste and unacceptable discolouration.

Ferrous compounds can be oxidized by iodate resulting in the loss of iodine:



Many researchers have investigated the use of salt as a carrier for iron. Narasinga Rao et al. (1972) fortified salt with several iron compounds. They found that ferrous ascorbate was absorbed most efficiently, while ferric pyrophosphate, sodium iron pyrophosphate and ferric orthophosphate were poorly absorbed. Ferrous sulphate gave a low (~3.5%) but acceptable iron absorption.

The stabilizing effect of various compounds on the iron in fortified salt was investigated by Narasinga Rao et al. (1975). They found that sodium hexametaphosphate (3,125 ppm) with sodium acid sulphate (1,875 ppm), and orthophosphoric acid (3,125 ppm) protected ferrous sulphate from oxidation.

Salt fortified with ferric orthophosphate and sodium acid sulphate was used successfully in a large community trial over a two year period (Nadiger et al., 1980).

Double-fortification of salt has been also extensively investigated. The effects of CaCO_3 , SHMP, STPP, and TSPP on the stability of salt fortified with ferrous sulphate and either of potassium iodide (KI), potassium iodate (KIO_3), or calcium iodate ($\text{Ca}(\text{IO}_3)_2$) were investigated by Narasinga Rao (1994).

He reported that after one month of storage at room temperature batches initially fortified to provide 20 ppm iodine with KI, KIO_3 , and $\text{Ca}(\text{IO}_3)_2$ contained 16.0, 15.8, and 14.6 ppm, iodine respectively. Addition of CaCO_3 to two other control batches containing KI and KIO_3 stabilized the iodine level, maintaining it at 20 ppm after one month. When batches with the same formulae were fortified with ferrous sulphate to provide 1000 ppm iron, the iodine levels dropped drastically within one month.

Polyphosphates were more effective stabilizers. While batches stabilized with STPP turned to a dark brown colour, and lost 40-60% of

their iodine, samples stabilized with 1% SHMP remained unchanged after 3 months.

The use of ferrous fumarate and potassium iodide for the double fortification of purified salt without the use of stabilizers had been investigated and found to be feasible (Venkatesh Mannar et al., 1989). The salt fortified with ferrous fumarate had much more stable, and pleasing flavour than those prepared with ferrous sulphate.

The role of stabilizers in double fortification is to bind iron or iodine in a form that prevents their reactions, yet dissolve in the digestive system, to be nutritionally useful. Stabilization may be also achieved by encapsulation of the iodine compound in a digestible matrix

2. OBJECTIVES

The objective of the program was to evaluate the double fortification systems reported earlier and to identify other potentially useful systems, that could economically provide a double fortified salt with acceptable stability and organoleptic properties.

3. EXPERIMENTAL METHODS

3.1 Materials

Food grade, un-iodized salt was obtained from Toronto Salt Chemical Co., Toronto. All other reagents were analytical grade, obtained from BDH Chemicals, Toronto.

3.2 Equipment

Solid ingredients were mixed using a 5L ribbon blender from LeRoy Somer - LSTronics, Montreal, Canada. Some compounds were ground before addition to the salt using a Moulinex coffee and spice mill, model 980.

Samples were stored under controlled temperature and humidity using a laboratory oven and an environmental chamber manufactured by Associated Environmental Systems Division of Craig Systems Corp.

3.3. Encapsulation by spray drying

The encapsulating agent (30 g) was dissolved in 200mL hot water (15% w/v) in a 500 mL Erlenmeyer flask. The iodine compound was

added to the solution at the level of 0.5, 1.0 or 2.0 %, based on the weight of encapsulating agent. The solution was maintained at $\sim 90^{\circ}\text{C}$ under agitation on a hot-plate magnetic stirrer. The solution was shielded from light by covering the Erlenmeyer flask with aluminum foil. The solution was fed to a Büchi model 190 laboratory spray drier, and dried at a rate of approximately 100 mL/h.

3.4. Salt Fortification

Appropriate amount of ferrous sulphate heptahydrate or ferrous fumarate was added to 3 kg salt in a ribbon blender. Some 50 g of the salt from the weighed 3 kg batch was pre-mixed with potassium iodide or iodate containing 150 mg iodine, (50ppm) to obtain a concentration of 50 mg iodine/kg of salt (50 ppm) in the 3 kg batch. The premix was added to the ribbon blender and mixed at 24 rpm for 10-15 min., until visual homogeneity was achieved. At this point an iron compound (1000ppm Fe in the salt) was added, with or without a stabilizer

In some cases the batch was prepared by adding KI as a solution with dextrose, as a stabilizer, after which calcium silicate was added to the salt, as a free-flowing agent.

3.5. Packaging and Storage

Each 3 kg batch was divided into three 1 kg samples and stored in high density polyethylene bags. The bags were stored over a period of 6 months, under three conditions:

Ambient temperature and humidity

(22 $^{\circ}\text{C}$, 50-70 % RH);

High temperature and humidity

(40 $^{\circ}\text{C}$, 100 % RH); and

High temperature and low humidity

(40 $^{\circ}\text{C}$, 60 % RH).

Samples were analyzed for iodine, iron, and moisture content, to determine their stability under both blending and storage conditions, immediately after blending, and three times during storage, including the final analyses after 6 or 12 months. If the iodine content in the salt dropped below 20 ppm, no further analyses were performed on the sample.

3.6. Analytical Methods

To ensure a representative sample all of the 1 kg batch was passed through a 2 necked powder funnel, which divided the sample into two nearly equal heaps. One of these was then passed through the funnel again, and the procedure was repeated until a sample of ~ 20 g was obtained. Samples for analysis were taken from this 20 g batch.

3.6.2. Iron Determination

The total concentration of iron in the batches was measured by atomic absorption spectrometry (AAS) according to AOAC Official Method 3.6.1.2 (Williams 1984). To estimate the changes in bioavailability of iron, the amount of iron soluble in 1 N hydrochloric acid was determined, by first dissolving 150 mg salt in 40 mL 1N HCl. The solutions were analyzed directly by measuring their absorbances at 248.3 nm using a Perkin Elmer Model 703 atomic absorption spectrometer.

The ratio of ferrous to ferric iron was determined in some of the samples by titrating for ferrous iron with 1,10-Phenanthroline, and determining the ferric iron by difference (Harvey et al., 1955).

3.6.2. Iodine Analysis

The iodine content of the samples was measured using epithermal neutron activation analysis (NAA) with the University of Toronto's Slowpoke nuclear reactor. The technique is described in general by Hancock (1978).

3.6.3. Moisture Determination

The moisture content of the salt samples was determined gravimetrically, by drying 5 g samples to constant weight at 110 $^{\circ}\text{C}$.

4. RESULTS AND DISCUSSION

The stability of the iron and iodine additives on their own were first established. A batch of salt containing 1080 ± 40 ppm ferrous sulphate heptahydrate had oxidized after one month of storage to a canary yellow colour and developed the unpleasant odour associated with water from rusty pipes, while salt fortified with ferrous fumarate was stable, in terms of appearance and taste.

Three iodized salt formulations were prepared. The first two contained only KIO_3 or KI at the 100 ppm level. A third sample was prepared with a formulation typical of commercially available Canadian iodized salt: a KI and invert sugar solution (1 and 6 % respectively) was added to refined salt to produce final concentrations of 50 ppm iodine. Calcium silicate powder was then added (0.5 % level) as a free-flowing agent.

At 40°C, 60% RH (relative humidity), the KIO_3 control batch retained 93 % of the iodine after 6 months of storage. The KI control batch retained 88 % of the iodine. The KI control batch with CaSiO_3 and dextrose retained all of its original iodine. All samples remained white in colour throughout the six month storage period.

Double fortified salt samples containing ferrous sulphate and KI retained no iodine after one month of storage under any of the three storage conditions tested. Samples made with KIO_3 and ferrous sulphate were equally unstable, losing 93% of their iodine content. Most of the iodine had disappeared after only a month of storage in the batch containing ferrous sulphate, and the salt had turned yellow.

Samples containing ferrous fumarate retained more iodine than those fortified with ferrous sulphate. Salt fortified with KIO_3 and ferrous fumarate retained 80.9 and 79.7 % of its iodine after 7 months at room temperature and at 40°C, 60% RH, respectively. While KI was reasonably stable at room temperature, (79 % remaining after 6 mo) at 40°C, 60 and 100% RH it retained only 27 and 23% of the original iodine, respectively. The fumarate fortified salt darkened somewhat with storage, turning to a brown tinge, from the original light pinkish-tan colour.

We tested the double fortification composition reported by Narasinga Rao (1994). SHMP representing 0.5% and 1 % by weight was added directly to salt fortified by ferrous sulphate heptahydrate and either KI or KIO_3 .

Several batches were made using KI as the iodine compound. KI was added either as a powder, or as an aqueous solution. Ferrous sulphate was added either as a powder, or as an aqueous solution.

Batches containing SHMP made with the addition of iodide in solution were pale yellow in colour due to slight oxidation of the ferrous ions. This colour, due to the presence of Fe^{+++} , reverted to white after extended storage at high temperature and humidity, due perhaps to the formation of white ferric phosphate. All dry mixed batches were initially white in colour.

At room temperature, the batch containing 1 % SHMP with iron retained 77 % of the iodine after 6 months of storage, while the batch with 0.5 % SHMP and iron retained only 45 %.

At 40°C, 60%RH, in all of the batches drastic declines in iodine levels were observed after two months of storage. At 40°C, 100% RH, the iodine content dropped rapidly. After 6 months, no iodine was left in either of the two batches containing 0.5 % SHMP, while 26 % iodine was retained in the batch containing 1 % SHMP. Clearly 0.5 % SHMP has insufficient chelating power to prevent the loss of iodine under tropical storage conditions.

We repeated the test with commercial salt obtained from India. The samples discoloured within one week at high temperature and humidity and lost most of their iodine in the first two months.

The results indicate that the formulation developed by Narasinga Rao et al. is suitable for providing acceptable iodine and iron levels through salt double fortification, but only if the salt is highly purified, and it is stored for periods not exceeding three months during distribution, retail and consumption. While this is encouraging, clearly a more stable system is required in much of the area where double fortification is justified.

It was suggested by Venkatesh Mannar et al. (1982) that KI or KIO_3 , in combination with ferrous fumarate would be a more stable formulation, due to the stability and bioavailability of the ferrous fumarate. They suggested that the improved organoleptic properties and improved stability will more than offset the extra cost associated with using the fumarate instead of the sulphate.

Initial tests with potassium iodate resulted in the rapid discolouring of the salt. Double

fortification with ferrous fumarate and potassium iodide was much more effective. Using SHMP as a stabilizer in the presence of dextrose and calcium silicate the formulation retained 90% of its iodine under low humidity conditions, but lost some 50% under high humidity after 4 months. The organoleptic properties, i.e. colour, flavour and odour were stable. No hint of "rusty" flavour developed in these samples.

The results of the tests confirmed that the double fortified salt systems are susceptible to major losses of iodine, when stored at high temperature and humidity. Although SHMP significantly increases the stability of the iodine, the effects of impurities normally present in the salt seem to preclude the use of double fortified salt containing ferrous sulphate and either KI or KIO₃ without purification beyond current local practice.

As iodine loss was shown to be due to chemical reactions with salt components and air, the protection of the iodine by providing a physical barrier between it and its immediate environment should result in stable double-fortified salt formulations. This physical barrier must remain intact from manufacture, through to home usage, but must release the iodine in the digestive system. Microencapsulation using food-grade, digestible ingredients were therefore investigated.

We selected encapsulating agents representing broad chemical categories: a modified starch, sodium hexametaphosphate, gelatin, and purified salt.

Dextrin with limited solubility at the target storage temperature of 40°C represented a good compromise, as an inexpensive, stable food ingredient. Sodium hexametaphosphate, chelates iron, thus preventing its reaction with iodine. Gelatin has the capacity to retain large quantities of water, and is readily digested. Finally, we also wanted to test salt itself as the encapsulant, as unless sufficient moisture is present to dissolve the salt, a crystal which includes the iodine at its centre will protect the iodine as a physical barrier to all other components in the system.

Spray drying was selected as the microencapsulation technique. In this technique the

encapsulating agent, and the encapsulated reagent are both dispersed in a solvent as a true solution. As droplets of the solution are sprayed into a stream of hot air the water evaporates, leaving behind the two solid components. The dextrin-iodide system, for example consists of spherical particles, each of which contains 0.5-2% KI, evenly distributed throughout the particle. While the iodide remaining on the surface of the particle remains vulnerable to oxidation, and iodine loss, this represents a very small fraction of the total iodide present. It was hoped, that the iodide entrapped deeply in the particles would be unavailable to chemical attack or leaching.

We successfully produced encapsulated potassium iodide and/or iodate using each of these wall materials. Dextrin, SHMP, gelatin and salt all produced stable particles of encapsulated iodine. Gelatin produced sticky particles, that created some difficulty in producing a free-flowing double fortified salt. The physical characteristics of the other systems were suitable for mixing with salt, except for their small particle size. The size of a spray dried encapsulated particle depends on the droplet size and the concentration of solids in the droplets. The limited solubility of dextrin limits the size of the dried particles to about 100µm in our laboratory apparatus. To obtain a stable mixture, we had to use very fine salt.

Double fortified salt prepared by mixing dextrin encapsulated KI and ferrous fumarate was stable for 12 months even at 40°C and 100% RH, although some darkening of the sample occurred due to oxidation of the fumarate. The encapsulation process was tested on a pilot scale at the POS Pilot Plant Corporation in Saskatoon, and the material was used for double fortification of finely ground, purified salt. Field tests in Ghana have demonstrated both the consumer acceptance and the effectiveness of this approach for the simultaneous elimination of iodine deficiency, and maintenance or improvement of the hematological status of pregnant women and children respectively

5. CONCLUSIONS

The results of extensive stability tests under controlled temperature and humidity clearly demonstrated the vulnerability of both iron and

iodine to interaction with air, moisture and salt impurities.

Ferrous sulphate was less stable than ferrous fumarate, and imparted undesirable colour and taste to the salt, while reducing the iodine content through reaction with potassium iodate.

Although sodium hexameta phosphate (SHMP) improved the stability of the system, addition levels of 1% were required under most storage conditions. While refined, double fortified salt stabilized with 1% SHMP was stable for at least 3 months at 40°C 60% RH, in unrefined salt, with typical impurities, the salt discoloured and lost its iodine content within two months. The refining and drying of salt is a prerequisite for stable double-fortified salt, prepared by conventional mixing technology.

The stability of iodine was significantly improved by microencapsulation. The best results were obtained by spray-drying potassium iodide in dextrin to provide a stable additive representing 0.1-0.4% of the weight of salt.

The process was tested on a pilot plant scale, and the effectiveness of double-fortified salt prepared with ferrous fumarate and microencapsulated potassium iodide was demonstrated in field tests in Ghana.

REFERENCES

- Clydesdale, F.M., Weimer, K.L. (editors), (1985) *Iron Fortification of Foods*. Food Science and Technology: A Series of Monographs, Academic Press Inc., Harcourt Brace Jovanovich, Publishers, 1-176.
- Diosady, L.L., Alberti, J.O., Venkatesh Mannar, M.G. and Stone, T (1997) - Stability of Iodine in Iodized Salt Used for Correction of Iodine Deficiency Disorders - Food and Nutrition Bulletin **18(4)** 388-96.
- Diosady, L.L., Alberti, J.O., Venkatesh Mannar, M.G. and FitzGerald, S. (1998) - Stability of Iodine in Iodized Salt Used for Correction of Iodine Deficiency Disorders II Food and Nutrition Bulletin **19(3)** 239-49.
- Hancock, R.G.V. (1978) Some aspects of the Analysis of Ancient Artifacts by Neutron Activation, J. International Institute of Conservation - Canadian Group **3(2)** 21-27.
- Harvey, A.E., Smart, J.A., Amis, E.S., (1955) Simultaneous Spectrophotometric Determination of Iron (II) and Total Iron with 1,10-Phenanthroline. *Analytical Chemistry*. **27(1)**, 26-29.
- Nadiger, H.A., Krishnamachari, K.A.V.R., Nadamuni Naidu, A., Narasinga Rao, B.S., Srikantia, S.G., (1980) The Use of Common Salt (Sodium Chloride) Fortified with Iron to Control Anemia: Results of a Preliminary Study. *British Journal of Nutrition* **43**, 45-51.
- Narasinga Rao, B.S., Prasad, S., Apte, S.V., (1972) Iron Absorption in Indians Studied by Whole Body Counting: a Comparison of Iron Compounds Used in Salt Fortification. *British Journal of Haematology* **22**, 281-286.
- Narasinga Rao, B.S., Vijayasathy, C., (1975) Fortification of Common Salt with Iron: Effect of Chemical Additives on Stability and Bioavailability. *The American Journal of Clinical Nutrition*, **28**, 1395-1401.
- Narasinga Rao, B.S., (1994) Fortification of Salt with Iron and Iodine to Control Anemia and Goitre: Development of a New Formula with Good Stability and Bioavailability of Iron and Iodine. *Food and Nutrition Bulletin*, **15(1)** 32-39.
- Report of the Working Group on Fortification of Salt with Iron, (1982) Use of Common Salt Fortified with Iron in the Control and Prevention of Anaemia--A Collaborative Study. *The American Journal of Clinical Nutrition*, vol. **35**, 1442-1451.
- Venkatesh Mannar, M.G. (1987) Control of iodine deficiency disorders by iodization of salt: strategy for developing countries. The prevention and control of iodine deficiency disorders. B.S. Hetzel, J.T. Dunn and J.B. Stanbury, eds. Elsevier.
- Venkatesh Mannar, M.G., Jayapal, S. and Pandav, C.S. (1989) Double fortification of salt with iron and iodine. *Proceedings of the Sixth International Nutrition Congress, Seoul*.
- Williams, S Ed. (1984)- *Official Methods Of Analysis of the Association of Official Analytical Chemists* 14th Edition;