ANNEX 1

Titration method for determining salt iodate and salt iodide content

A1.1 Titration method for determining salt iodate content

The iodine content of iodated salt samples is measured using the iodometric titration method (*16*,*23*,*37*). The method consists of preparing the reagent solutions, which may last for variable periods of time, and then using these reagents in the titration procedure.

Usually, salt samples of 10 g each are dissolved in a measured amount of water for the titration analysis. However, in the case of coarse salt and in salt containing impurities, a bigger sample weight of 50 g salt will yield more accurate results. A chemical analyst will be able to advise on the appropriate glassware, preparation of reagents (including adjustments to the concentrations of some of the reagents), and the necessary calculations to obtain the correct results.

For community or population surveys, 10 g salt samples are sufficient; however, for monitoring the iodine content at the production level, 50 g salt samples are preferred for the titration procedure.

A1.1.1 Description of the reaction

The reaction mechanism includes two steps:

- **Liberation of free iodine from salt:** The addition of H_2S_4O liberates free iodine from the iodate in the salt sample. Excess KI is added to help solubilise the free iodine, which is quite insoluble in pure water under normal conditions.
- **Titration of free iodine with thiosulfate:** free iodine is consumed by sodium thiosulfate in the titration step. The amount of thiosulfate used is proportional to the amount of free iodine liberated from the salt. Starch is added as an external (indirect) indicator of this reaction and reacts with free iodine to produce a blue colour. When added towards the end of titration (i.e. when only a trace amount of free iodine is left) the loss of blue colour, or end-point, which occurs with further titration, indicates that all remaining free iodine has been consumed by thiosulfate.

Reaction steps for iodometric titration of iodate

1.	IO_3	+	$5I^-$	+	$6H^+$	→	$3I_2$	+	$3H_2O$	
	(from salt)		(from KI)		(from H_2SO_4)					
2.	$2Na_2S_2O_3$	+	I_2	→	2NaI	+	$Na_2S_4O_6$			
	Sodium thiosulfate		Iodine		Sodium iodide		Sodium tetrathionate			

A1.1.2 Reagent preparation

The preferred water for this method should be boiled distilled water, which requires provision of a distillation unit. As a simpler alternative, regular tap water treated with a mixed bed deionizing resin can be used, thus avoiding the need for an expensive distillation unit. Many reputable chemical and pharmaceutical companies supply deionized, double-distilled, and purified water which is iodine-free.

- **0.005 M Sodium thiosulfate ($Na_2S_20_3$):** Dissolve 1.24 g $Na_2S_20_35H_20$ in 1000 ml water. Store in a cool, dark place. This volume is sufficient for 100 to 200 samples, depending on their iodine content. The solution is stable for at least one month, if stored properly. Standardization of sodium thiosulfate with a volumetric solution of potassium iodate is recommended. The concentration of the sodium thiosulfate could be adjusted to accommodate the analysis of larger sample weights (e.g. 50 g or 100 g salt samples).

- **2 N Sulfuric acid (H_2S0_4):** Slowly add 6 ml concentrated H_2S0_4 to 90 ml water. Make to 100 ml with water. This volume is sufficient for 100 samples. The solution is stable indefinitely. Always add acid to water, not water to acid, to avoid excess heat formation and spitting of acid. Stir solution while adding acid.

- **10% Potassium iodide (KI):** Dissolve 100 g KI in 1000 ml water. Protect reagent from direct light. Store in an amber/brown bottle and in a cool, dark place. Properly stored, the solution is stable for six months, provided no change occurs in the colour of the solution. This volume is sufficient for 200 samples.

- **Starch indicator solution:** Dissolve reagent-grade sodium chloride (NaCl) in 100 ml double-distilled water. While stirring, add NaCl until no more dissolves. Heat the contents of the beaker until excess salt dissolves. While cooling, the NaCl crystals will form on the sides of the beaker. When it is completely cooled, decant the supernatant into a clean bottle. This solution is stable for six to 12 months. Dissolve 1 g chemical starch in 10 ml double-distilled water. Continue to boil until it completely dissolves. Add the saturated NaCl solution

to make 100 ml starch solution. This volume is sufficient for testing 20 to 45 samples. Preferably, prepare fresh starch solution every day since this solution deteriorates easily.

A1.1.3 Titration step

Sampling of salt

Prior to taking a 10 g or 50 g salt sample for analysis, salt should be thoroughly mixed, preferably in zip-lock bags or appropriate containers to ensure that the iodine is homogeneously distributed in the salt. Usually 10 g iodated salt is dissolved in 50 ml distilled water. Optional: 50 g iodated salt could be thoroughly dissolved in 250 ml distilled water, from which an aliquot of 50 ml could be analysed as mentioned in the titration step below, without adjusting the concentrations of the reagents or calculation.

Sulfuric acid step

Once the salt is dissolved in the measured amount of water, sulfuric acid (1–2 ml) and potassium iodide (5 ml) is added to the salt solution, which in the presence of iodine will turn yellow. The reaction mixture is then kept in a dark place (with no exposure to light) for five to 10 minutes to reach the optimal reaction time, before titrated with sodium thiosulfate using starch (2 ml) as the indirect indicator. The concentration of iodine in salt is calculated based on the titrated volume (burette reading) of sodium thiosulfate according to the formula mentioned below, or alternatively it could be read off a pre-calculated table for the specific method (e.g. method: 10 g salt titrated with 0.005N sodium thiosulfate).

Calculation

Mg/kg (ppm) iodine = titration volume in ml x 21.15 x Normality of sodium thiosulfate x 1000 / salt sample weight in g

Precaution

The 10% potassium iodide reagent stock needs to be protected from direct light, and the reaction mixture (after the addition of sulfuric acid and potassium iodide) should be kept in the dark before titration to prevent a side reaction which may occur when these solutions are exposed to light, causing iodide ions to be oxidized to iodine.

A1.2 Titration method for determining salt iodide content

While the use of potassium iodide (KI) is not common for salt fortification in many developing countries, basic details of a titration method (*23*) suitable for analysing salt iodized with KI are provided here.

A1.2.1 Description of the reactions

In the iodometric titration for salt fortified with potassium iodide:

- **Liberation of iodine:** Bromine water oxidizes iodide ions to free iodine. Sodium sulfite and phenol are added to destroy excess bromine so that no further oxidation of I- can occur before KI solution is added.
- **Titration:** The titration reaction with thiosulfate is the same as that described in the iodometric titration method for iodated salt mentioned earlier.

A1.2.2 Reagent preparation

Reagents for oxidization of iodide to free iodine:

- **Methyl orange indicator:** Dissolve 0.0l g methyl orange in l00 ml water.
- **Bromine water:** Place 5 ml in a small flask (keep in fume hood due to dangerous fumes and wear appropriate personal protective clothing, e.g. masks, gloves and goggles). Safety precaution in case of spills: neutralize bromine water of its halogen component by sprinkling sodium metabisulfite, sodium sulfite or even domestic baking soda (bicarbonate of soda).
- **Sodium sulfite solution:** Dissolve 1 g sodium sulfite in l00 ml water. Prepare fresh sodium sulfite solution regularly, since the solution deteriorates easily.
- **Phenol solution:** Dissolve 5 g phenol in l00 ml water.

All reagents prepared and used in the iodate method are also applicable to the iodide method for the titration step.

A1.2.3 Titration steps

Sampling

As described in the iodate method.

Oxidation step (Iodide method)

Once the salt (10 g) is dissolved in the measured amount of water (50 ml), a few drops of methyl orange indicator are added, followed by a few drops of sulfuric acid until the orange colour turns to pink, resulting in

the neutralization of the reaction mixture. With the addition of bromine water (0.5 ml), the reaction mixture changes to yellow. To consume the excess bromine, the reaction mixture is titrated with sodium sulfite until the solution turns to pale yellow, followed by the washing down of the sides of the flask with small amounts of water, and the addition of three drops of phenol, resulting in a clear reaction mixture.

Titration step (Iodide & Iodate method)

Sulfuric acid (1–2 ml) and potassium iodide (5 ml) are added to the reaction mixture, which is kept in a dark place (with no exposure to light) for five to 10 minutes to reach optimal reaction time, before titrated with sodium thiosulfate, using starch (2 ml) as the indirect indicator. The concentration of iodine is calculated based on the titrated volume (burette reading) of sodium thiosulfate according to the formula mentioned below or alternatively could be read off a pre-calculated table for a specific method (e.g. method: 10 g salt titrated with 0.005N sodium thiosulfate).

Calculation:

Mg/kg (ppm) iodine = titration volume in ml x 21.15 x Normality of sodium thiosulfate x 1000 / salt sample weight in g

Precaution

The 10% potassium iodide reagent stock need to be protected from direct light, and the reaction mixture (after the addition of sulfuric acid and potassium iodide) should be kept in the dark before titration, to prevent a side reaction which may occur when these solutions are exposed to light causing iodide ions to be oxidized to iodine.