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Ascertainment of iodization of iodine through kinetic parameter and its strategic

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Abstract
Lack of Iodine causes various abnormalities qualified as 'disorder due to iodine deficiency (endemic griters, hypothysodism, cretinism and anemia. Iodization of edible salt is recommended by WHO to prevent iodine deficiency disorders. The kinetic study of dietary iodized salt proves to be of interest not only for the determination of the conditions of production of iodine, but also for a good knowledge of the kinetic and thermodynamic parameters fo the reaction. In this work, two salt brands were studied and one of them was used for the kinetic study. The kinetic study showed that the reaction proceeded slowly at a medium rate. Since the reaction admits a global order equal to 1, potassium iodide has no influence on this reaction rate. The concentration of iodate ions introduced in the dietary salt is a kinetic parameter that affects the reaction rate. Calculated rate constant was inversely proportional to time. The study has therefore determined experimentally kinetic parameters of the reactions between iodate and iodide ions.

Keywords: Edible iodized salt, Reaction Rate, Reaction Order, Rate Constant

1. Introduction
Salt is used in many households as a source of iodine as well as an effective way to distribute iodine to the population [8]. Salt is the ideal vehicle for iodine because it is an essential nutrient [2]. Iodine is an essential substrate for the body and for the synthesis of thyroid hormone [9, 10]. It is used in pharmaceutical and chemical industries. Aqueous solutions of di-iodine used in various assays are generally obtained in acid medium between iodate and excess of iodide. Iodine is found mainly in anionic form (iodide and iodate). The reaction between iodate and iodide is important because it allows the extraction of iodine from the liquid effluent for its industrial preparation. However, iodine is an unstable product which sublime slowly at room temperature. A hot and humid climate is a factor contributing to the impoverishment of food iodized salts [15].

Many studies on the determination of iodine in salt exist [2, 8], but none has studied the kinetic approach of iodine quantification. Given these observations, this work aims to follow the kinetic of iodine quantification in dietary salts. Various kinetic parameters such as reaction rate, reaction order and rate constant were determined.

2. Materials and Methods
2.1. Sampling
Samples of iodized salt were chosen from two distinct trademarks, a selection has been made on the basis of their high selling frequency. These salts were Salina and Enasel, respectively in the form of unit packet of 907 g and 1000 g.

2.2. Reagents
The reagents used were of analytical grade and were purchased from various suppliers. Sulfuric acid for analysis (Normapur®, $d = 1.83$, purity = 95%); potassium iodide (Sharlau®), woluble starch (Merck®), sodium thiosulfate pentahydrate (Normapur®) and distilled water. Working solutions consist of 1 M sulfuric acid, 1% (w/v) soluble starch, 10% (w/v) potassium iodide and 2.5 mM sodium thiosulfatepentahydrae. The last two solutions were stored in brown bottles.

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2.3. Kinetic Parameters Determination
Iodine was measured by titrimetry and required a magnetic stirrer (Fisher brand); a precision balance (Denver Instrument, 0.0001) and a stopwatch (Casio). The experimental device was a traditional burette which consists of glass tube of constant bore with a graduation scale etched on it and a stopcock at the bottom.
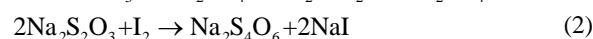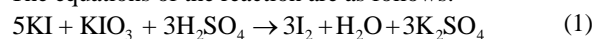
Iodine content of the two types of salt was determined. The mark containing a high amount of iodine was used for the kinetic study. The determination of the reaction rate was assessed by the progress of the reaction over time requires. The time taken to perform the assays was determined, which was carried out by the time which allowed the titration of di-iodine formed. The partial orders of the reaction were calculated according to the assumptions of order 0, 1 and 2. The rate constant was calculated from the knowledge of the reaction rate and the partial orders. Three tests were performed for the determinations of iodine content while five (5) were necessary for the kinetic study.

2.3.1. Assays Principle
In the presence of sulfuric acid (H_2SO_4) and potassium iodide (KI), iodate ion (IO_3^-) contained in the salt is reduced.

The released di-iodine is analyzed using sodium thiosulfate in the presence of starch as a color indicator. The volume of sodium thiosulfate used is proportional to the amount of di-iodine released by the salt.

The equations of the reaction are as follows:

$$5KI + KIO_3 + 3H_2SO_4 \rightarrow 3I_2 + H_2O + 3K_2SO_4 \qquad (1)$$

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI \qquad (2)$$

2.3.2. Sampling Preparation
Prepare 200 mL of salt solution by dissolving 40 g of salt in an Erlenmeyer flask of 200 mL. Introduce into a beaker variable volumes of salt solution according to Table 1. Then successively add other reagents in the order listed in Table 1. The final solution turns yellow, a characteristic of the released di-iodine.

2.3.3. Released di-Iodine Determination
Add 2-5 drops of starch solution into the beaker, the solution turns to dark purple. Continue stirring and titrate the solution of the beaker with sodium thiosulfate [16]. Start the timer when the first drop of sodium thiosulfate in the beaker falls. Continue the titration until the purple color disappears and the solution becomes colorless. Note the equivalent volume (V_E) and the time (T_E) taken to perform the assay.

Iodine content is given by the Equation (3) as follows:
Iodine (ppm)

$$= \frac{N \times V \times 21.15 \times 1000}{m} \qquad (3)$$

N: normality of sodium thiosulfate (eq.g.L^{-1}).
V: volume of sodium thiosulfate (L).
m: mass of the test portion of dietary salt (g).
21.15 factor: equivalent to 1/6 of the atomic mass of iodine (one mole of iodate reacted with 6 moles of sodium thiosulfate, atomic mass of iodine = 126.9).
ppm (part per million) = 1 mg/Kg = 1 µg/g.

Table 1: Preparation of different samples.

	Beaker 1	Beaker 2	Beaker 3	Beaker 4	Beaker 5
Salt solution (mL)	50	35	25	15	50
Distilled water (mL)	0	15	25	35	0
KI 10% (mL)	5	5	5	5	2.5
H_2SO_4 1 M (mL)	1	1	1	1	1

3. Results and Discussion
3.1 Iodine Content in Dietary Salts
Iodine was present in all samples salts. The average content (ppm) was 1.533 ± 0.165 for Salina* and 45.374 ± 0.987 for Enasel*. Enasel* contains iodine in an amount much higher than Salina*. The World Health Organization (WHO) recommends at least 15 to 20 ppm of iodine in salts. Iodine content in Enasel* is less than what is specified on the package (from 50.55 to 84.25 ppm) but it remains within the recommended standards (WHO). Taking into account environmental conditions and in order to provide a sufficient quantity of iodine to each individual, the national program of nutrition identified a normal range of 30-50 ppm of iodine in households salts [2]. Since all salts on the market are not properly iodized, the prevention of iodine-deficient diseases cannot be avoided. Efforts still need to be made to strengthen the control of marketed salts. For the kinetic study, Enasel* has been chosen, due to its high salt content.

3.2. Kinetic Parameters Determination
3.2.1. Average Rate of Iodate Ions Disappearance
Monitoring the progress of the reaction over time requires the determination of the reaction rate. The calculation of this rate is presented in Table 2.

The time taken to perform the assays is extended to several seconds, which allowed applying the titration to determine the reaction rate. The formation of di-iodine from iodate and iodide is a slow reaction. The iodate disappearance rate increases when its concentration increases. The concentration is therefore a kinetic factor which has an influence on the rate.

Table 2: Average rate of iodate ions disappearance.

	Beaker 1	Beaker 2	Beaker 3	Beaker 4
t (s)	211	167	100	66
$\left[IO_3^-\right]$ (10^{-5} mol/L)	25.580	17.830	10.500	7.910
Rate (10^{-5} mol/L/s)	1.2144	1.0679	1.050	1.194
Average rate	$(113.14 \pm 8.28) \times 10^{-8}$ mol.L^{-1}.s^{-1}

3.2.2. Determination of Reaction orders
1. Partial order with respect to iodate ions $\left(IO_3^-\right)$

The results of partial order calculations from the assays are shown in Table 3.

Table 3: Partial order with respect to IO_3^- according to the assumptions of order 0, 1 and 2.

	Beaker 1	Beaker 2	Beaker 3	Beaker 4
t (s)	211	167	100	66
C (mol/L)	0.0002557	0.0001783	0.000105	0.000791
lnC	−8.2713	−8.6319	−9.1616	−9.4440
I/C (Lmol^{-1})	3910.0684	5607.4871	9523.8095	12631.6853

$C = \left(IO_3^-\right)$.

According to the three assumptions of a single order, only a line is obtained when plotting the logarithm of iodate concentration as a function of time. The partial order of reaction with respect to iodate is 1.

2. Partial order with respect to iodide ions (I⁻)
The results of partial order calculations from the assays are shown in Table 4.
The reaction rate with respect to iodide ions (I⁻) remains substantially constant despite the variation in iodide concentration. The ratio of the reaction rate expressions of experiments 1 and 5 leads to a partial order equal to 0 after calculation. The partial order of the reaction relative to iodide is therefore 0. the formation of di-iodine admits a global order equal to 1. Only the concentration of iodate affects the reaction rate. The order of a reaction is an experimental characteristic that cannot be measured directly.

Table 4: Partial order with respect to I⁻ according to the assumptions of order 0, 1 and 2.

	Beaker 1	Beaker 5
$\left[IO_3^-\right]$ (mol/L)	0.0002557	0.0002541
t (s)	211	204
Rate (10^{-6} mol/L/s)	1.21	1.24
[I⁻] (mol/L)	0.0602	0.0301

3.2.3. Rate Constant Determination
The rate law is the relation which binds the rate of reaction to the concentrations of all the substances present in the reaction medium, as well as all the factors likely to have an influence on the rate. The general rate law takes into account only reagents.
Knowing the partial orders for each reagent, the expression of the reaction rate was determined as follows:

$$v = k\left[IO_3^-\right]^1\left[I^-\right]^0 \tag{4}$$

$$v = k\left[IO_3^-\right] \tag{5}$$

The average value of the rate constant is $k = \left(8.14 \pm 3.88\right) \times 10^{-3} \text{s}^{-1}$. This rate constant depends only on IO_3^-. The rate constant of a reaction of order 1 has the dimension of the inverse of time.

4. Conclusion
This work was intended to allow the kinetic of iodine quantification in food iodized salts. Iodine content of the two brands of salts allowed us to retain one brand for the kinetic study. Some kinetic parameters including average rate, global order of the reaction and rate constant have been assessed. It is apparent that the reaction between loaded and iodide takes place at a slow rate, admits a global order equal to 1, and the reaction rate is dependent on the concentration of the reactants. This reaction can be used profitably to clean and extract iodine from waste and soil.

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