

Article

## Spectrophotometric Determination of Iodate in Table Salt

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Iodato de Potássio em sal de cozinha pode ser determinado espectrofotometricamente no UV em dois máximos no espectro de absorção bem definidos (288 e 352 nm) após ser convertido à espécie  $I_3^-$  por reação com iodeto na presença de ácido fosfórico. Curvas de calibração com coeficientes angulares de  $7.320 \times 10^4$  e  $1.103 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$  foram obtidas a 352 e 288 nm, respectivamente a 22°. Resultados de 37.39 ( $\pm 0.15$ ) e 63.67 ( $\pm 0.16$ ) mg de  $KIO_3$  por kg de sal foram obtidos com massas de 0.15-0.21 g, comparáveis aos resultados da titulação iodométrica que utiliza grandes quantidades de amostras (20-50 g). O método tem sido adequado para testar a homogeneidade de distribuição do iodo no sal de cozinha, já que pequenas quantidades de amostras são utilizadas.

Potassium iodate in table salt can be spectrophotometrically determined at two well defined UV absorption maxima (288 and 352 nm), after being converted to  $I_3^-$  by reaction with iodide in the presence of phosphoric acid. Calibration curves with slopes of  $7.320 \times 10^4$  and  $1.103 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$  were obtained at 352 and 288 nm, respectively, at 22 °C. Typical results of 37.39 ( $\pm 0.15$ ) and 63.67 ( $\pm 0.16$ ) mg  $KIO_3$  per kg of salt were obtained with samples of 0.15-0.21 g, comparable with results from a standard but less precise iodometric titration of large samples (20-50 g). The method has been found adequate for checking homogeneity of iodine distribution in table salt, as small weighed samples are normally required.

**Keywords:** *iodized salt, spectrophotometry, salt, iodate*

### Introduction

In order to control the main cause of endemic goitre, specially for inhabitants of mountainous areas in several regions of the world, the addition of some form of iodine to common salt for human consumption became an universal practice. The World Health Organization recommends an addition of 10 mg of the element to 1 kg of table salt (10 ppm). In some countries this procedure is not only optional but a legal obligation. In the U.S.A. iodized salt has 100 mg  $\text{kg}^{-1}$  of iodine, while in Switzerland the value is 5 mg  $\text{kg}^{-1}$ . In Brazil the iodine content is officially controlled in commercial products and should fall in the range of 10-30 mg  $\text{kg}^{-1}$  of the element in table salt, as potassium iodate. It is also desirable that the iodine distribution in salt for human consumption be as homogeneous

as possible. It is not possible to measure the latter parameter using the less sensitive titration method, usually applied for the element determination<sup>1</sup>.

In spite of controversies about such addition, sodium or potassium iodide was formerly added to salt as the source of the element. However, the recognition that the oxidation of iodide to iodine was possible during salt treatments and long storage, with eventual losses of the element, lead to the current use of potassium iodate for this purpose, due to its high chemical stability in a neutral or alkaline medium. In fact, iodide is thermodynamically unstable in sea water, especially in the presence of light and dissolved oxygen<sup>2</sup>. Measurement of the average content of iodate in food grade salt is normally performed iodometrically, by titrating, with  $5 \times 10^{-3} \text{ mol L}^{-1}$  thiosulphate, the iodine released by reaction between iodate and iodide ions in acidic medium, from

large samples of salt (20-50 g)<sup>1</sup>. Alternative sensitive procedures are found in the literature on the basis of mixed techniques involving iodate reduction followed by extraction and spectroelectrochemical measurements<sup>3</sup>, on the basis of the catalytic effect on the classic Ce(IV)/As(III) system<sup>4,5</sup> by ion-pair chromatography<sup>6</sup> and the indirect spectrophotometric method<sup>7</sup>. All these procedures do not seem adequate for routine analysis as they require several cumbersome steps of sample treatments and/or they are not very precise, although sensitive.

A new alternative, sensitive and easy to perform spectrophotometric method is herein presented for determination of iodate in salt. As it requires small amounts of salt in the working solution (0.1-0.2 g), it is particularly useful for determining the homogeneity of the distribution of iodate in a commercial sample.

## Experimental

All reagents were of A.R. specification (Merck, Carlo Erba): sodium chloride, iodine, potassium iodate, sodium hydroxide, sodium tiosulphate and acids. Commercial table salts were tested during the development of the analytical method.

Solutions were prepared with deionized and subsequently distilled water and made up to the desired volume in first class volumetric flasks.

Measurements were carried out using a Hewlett Packard 8452A spectrophotometer with a 1 cm light path quartz cuvette, at room temperature, 22 °C. The Origin 3.5 software from Microsoft was used for developing calibration curves and the regression parameters of the linear plots.

The following solutions were used in the spectrophotometric procedures:

**Solution 1:** 0.2140 g of the primary standard potassium iodate (dried in an oven to 110 °C) were made up to 100 mL in a volumetric flask in order to obtain a 0.0100 mol L<sup>-1</sup> solution. This solution was diluted in order to obtain a final standard iodate solution of 1.000 x 10<sup>-5</sup> mol L<sup>-1</sup>, to be used in the calibration curve.

**Solution 2:** 5.00 g of sodium chloride were made up to a volume of 50 mL.

**Solution 3:** 3.32 g of potassium iodide (iodate free as checked by acidification) were made up to a volume of 100 mL, including 1 mL of 0.1 mol L<sup>-1</sup> sodium hydroxide.

**Solution 4:** 11.5 g of phosphoric acid (85%) were made up to a volume of 100 mL to obtain a 1.0 mol L<sup>-1</sup> solution.

**Solution 5:** (Blank 1 solution) 2.0 mL of solution 2 plus 1.0 mL of solution 4 were made up to a volume of 10 mL in a volumetric flask.

**Solution 6A:** (Sample solution) About 1 g of the salt was made up to a volume of 25 mL, for checking homogeneity of the product.

**Solution 6B:** (Sample solution) About 100 g of the salt were made up to 500 mL for analysing the average iodate content, and comparing of methods.

**Solution 7:** (Blank 2 solution) 4-7 mL of solution 6A or 6B plus 1.0 mL of solution 4 were made to a volume of 10 mL in a volumetric flask.

**Procedure 1. Calibration curve.** 1-6 mL of the standard iodate solution (1.000 x 10<sup>-5</sup> mol L<sup>-1</sup>) were pipetted into 10 mL volumetric flasks with 1 mL of solution 3, 2.0 mL of solution 2 and finally 1 mL of phosphoric acid. The volumes were made up and the absorbances at the desired wavelength (288 and/or 352 nm) vs. the blank, solution 5, were measured. 1 cm light path cuvettes were used. The parameters of the linear plot of A vs. [IO<sub>3</sub><sup>-</sup>] or [I] were determined.

**Procedure 2. Sample analysis.** 4-7 mL of solution 6A or 6B, or 0.2 g of the salt, plus 1 mL solution 3 and 1 mL solution 4 were made up to 10 mL. Absorbances at 288 or 352 nm vs. blank 2 (solution 7), containing the same salt solution were measured.

C is the concentration of potassium iodate or iodine in mg kg<sup>-1</sup> of salt and was calculated by the following formula:

$$C = \frac{1000 A W V_1 V_3}{b \varepsilon V_2 m}$$

where A is the absorbance at the desired wavelength with the corresponding molar absorptivity  $\varepsilon$  (see Table 1); W is the mol of potassium iodate, 214.0 g or the mol of iodine, 126.9 g, b is the light path, 1 cm; m in g is the sample of salt weighed out and made up to a V<sub>1</sub> mL volumetric flask (see solutions 6A and 6B); V<sub>2</sub> is the volume of 4-7 mL pipetted into the V<sub>3</sub> volumetric flask, usually 10 mL, in order to prepare the working solution.

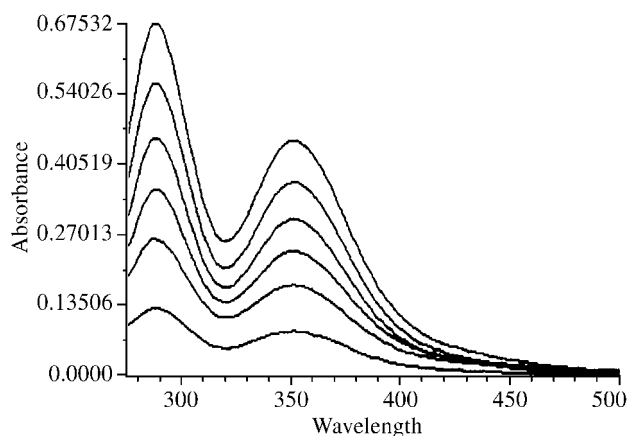
**Titration Procedure.** For the conventional procedure<sup>1</sup>, 40 g of the salt or 50 mL of a solution containing 200 g L<sup>-1</sup> of the salt (6B) were used. The salt solution was treated with 10 mL of solution 3 and 10 mL of solution 4. The released iodine was titrated with a 0.005 mol L<sup>-1</sup> standard thiosulphate, with addition of 1 mL of starch indicator, 1% solution, near the end point.

## Results and Discussion

Figure 1 shows the spectral characteristics of iodine with maxima at 288 nm and 352 nm and a minimum at 320 nm, in the presence of excess iodide and in acidic medium in order to avoid disproportionation of the halogen by reaction with water. In spite of the higher sensitivity presented, this strong spectral band appears only in the presence of iodide and can be attributed to the formation of I<sub>3</sub><sup>-</sup>. Although the peak observed at 288 nm presents greater sensitivity, the peak at 352 nm has been used to measure the iodine released from the reaction of ozone with iodide ions<sup>8,9</sup>. Other spectrophotometric measurements of the species I<sub>3</sub><sup>-</sup> are based on the blue color developed in the presence of starch<sup>10,11</sup>. In spite of the possibility of measuring the deep blue iodine/starch mixed species at the

**Table 1.** Comparison between spectrophotometric and titrimetric methods for the analysis of two commercial iodized salts. Average results in mg kg<sup>-1</sup> from seven determinations; 95% confidence level are shown.

SALT I	288 nm	352 nm	288 + 352 nm	Iodimetric titration
Fine crystals	$\epsilon = 1.103 \times 10^5$ L mol <sup>-1</sup> cm <sup>-1</sup>	$\epsilon = 7.320 \times 10^4$ L mol <sup>-1</sup> cm <sup>-1</sup>	$\epsilon = 1.835 \times 10^5$ L mol <sup>-1</sup> cm <sup>-1</sup>	
Potassium iodate	37.79 ± 0.09	37.93 ± 0.21	37.85 ± 0.16	37.80 ± 0.26
Iodine	22.41 ± 0.09	22.50 ± 0.12	22.44 ± 0.10	22.42 ± 0.15
Absorbances				
1 cm light path	0.3894 ± 0.0015	0.2595 ± 0.0014	0.6390 ± 0.0028	
SALT II				
Coarse crystals				
Potassium iodate	63.55 ± 0.12	63.67 ± 0.16	63.59 ± 0.09	63.60 ± 0.37
Iodine	37.68 ± 0.06	37.75 ± 0.10	37.71 ± 0.05	37.71 ± 0.22
Absorbances				
1 cm lighth path	0.6549 ± 0.0012	0.4355 ± 0.0011	1.0904 ± 0.0016	

**Figure 1.** Spectral characteristics of released iodine with maxima at 288 nm and 352 nm and a minimum at 320 nm in the presence of 0.020 mol L<sup>-1</sup> of iodide and 0.010 mol L<sup>-1</sup> phosphoric acid. Iodate concentrations from 1 to 6 μmol L<sup>-1</sup>.

visible part of the spectrum (588 nm), some preliminary experiments led us to discard this procedure for iodate/iodine determination in salt. In fact, the color development and color stability of working solutions depend on several parameters such as the starch sample, the concentration and stability of the solution, the acidity, the salting out effects of electrolytes and a number of unexpected factors that can markedly affect the precision of measurements. Thus, it has been found more convenient to develop the procedure on the basis of the more favorable ultra violet measurements of the released iodine.

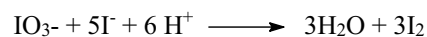
Figure 2 shows that in the range of 0.01-0.025 mol L<sup>-1</sup> of iodide, the absorbances at the peaks reach virtually constant values, due to the well known I<sub>3</sub><sup>-</sup> formation. Thus,

the 0.020 mol L<sup>-1</sup> iodide concentration was used in the development of calibration curves for analytical purposes. Iodide solution in the presence of 10<sup>-3</sup> mol L<sup>-1</sup> sodium hydroxide is highly stable, even in the presence of air: virtually no free iodine was found from spectrophotometric measurements made after 1 month, vs the freshly prepared solution after acidification. However the neutral iodide solution is less stable and should not be used in the working solutions, after storing for more than one week.

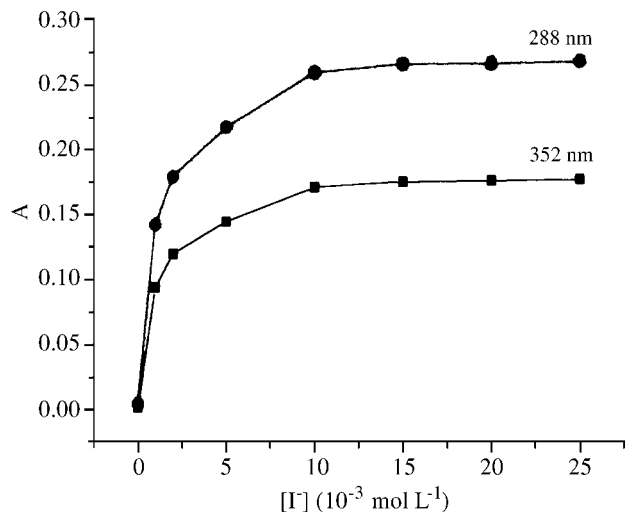
Preliminary experiments have also shown that the presence of chloride has a slight suppressing effect on the measured absorbances, which has been found to be constant in the range of 0.180-0.500 mol L<sup>-1</sup> sodium chloride.

The iodide/iodine system has been found to follow the Lambert-Beer's law at three wavelengths with the following indirect molar absorptivities for iodate in L mol<sup>-1</sup> cm<sup>-1</sup> in the presence of 0.020 g L<sup>-1</sup> potassium iodide, 0.200 mol L<sup>-1</sup> phosphoric acid and 20 g L<sup>-1</sup> sodium chloride: 1.103 × 10<sup>5</sup> at 288 nm, 7.320 × 10<sup>4</sup> at 352 nm and 3.980 × 10<sup>4</sup> at 320 nm, the latter being the minimum between the two peaks. The sum of spectral measurements at 288 and 352 nm provides an even higher sensitivity for iodate, with a slope of 1.835 × 10<sup>5</sup> L mol<sup>-1</sup> cm<sup>-1</sup> for the calibration curve.

The high sensitivity for the indirect determination of iodate is three times that expected for the I<sub>3</sub><sup>-</sup> species due to the following redox reaction:



As the added element in salt now occurs only as potassium iodate, the above redox reaction and calibration curves are adequate for the determination of the iodine



**Figure 2.** The effect of iodide concentration on the absorbance of  $7.4 \mu\text{mol L}^{-1}$  iodine in  $0.010 \text{ mol L}^{-1}$  phosphoric acid.

element in the commercial product without the need for previous oxidation of iodide.

The best condition for analytical work with the above calibration curve is to measure at 288 nm. However, other analytical calibration curves can be used depending on the sensitivity required for the sample. In fact, the best analytical results are obtained from measuring absorbance near the most precise condition, about 0.43 (36.7% transmittance). Thus, these calibration curves at 288 and 352 nm (and 352 plus 288 nm) with diverse slopes (molar absorptivities) encompass a wide range of iodate concentrations in salts. The identification limit is estimated as being  $2.0 \times 10^{-7} \text{ mol L}^{-1}$  for iodate, with 1 cm light path cuvettes. Many experiments have shown that, for the range of 30–70  $\text{mg kg}^{-1}$  potassium iodate, 10 mL working solutions containing about 0.2 g of salt are adequate for analytical work.

Preliminary studies with acidification with sulphuric, phosphoric and acetic acid, gave virtually the same results. The preference for the use of phosphoric acid in the working solutions is that it can complex traces of iron(III), possibly present in salt samples, thereby reducing the tendency to oxidise iodide to iodine. However, the presence of iron(III) in commercial products of the present study was not detected in qualitative tests with thiocyanate.

Table 1 presents the average of seven analytical results for the iodate/iodine content from solutions prepared with two table salts normally sold in Brazilian supermarkets. Salt I is a higher quality finely ground product and contains some solid additives such as silica and calcium silicates to make it less hygroscopic. When dissolved in water it presents some turbidity which is compensated for in the spectrophotometric measurements with the blank; the filtered solution gave virtually the same analytical result. Salt II is a less refined product, in the form of coarse crystals, without solid additives. In order to make comparisons with the

less sensitive titrimetric procedure, large 500 mL solutions were prepared with a salt content of  $200 \text{ g L}^{-1}$ ; 50 mL aliquots of these solutions were used in titrations with thiosulphate. A normal procedure for the average iodate content was performed with 20–50 g of salt.

The final results in Table 1 show very good agreement between the spectrophotometric measurements and the iodometric titrimetric method, with higher precision for the former method, using three different calibration curves.

It is interesting to show that the distribution of iodate in the commercial products is not homogeneous. The analysis of iodate from 1 g random samples (see Experimental section, solution 6B) shows a relative standard deviation of 3.3% for salt I and 16% for salt II. These deviations are considerably larger than those for these salts shown in Table 1 and are related to the salt refining process. During the salt treatment an iodate solution is sprayed onto huge amounts of the wet salt, followed by mixing and drying. The fine ground salt I has a more homogeneous iodate distribution due to an additional milling process, which enhances the iodate distribution. The titration procedure makes this lack of homogeneity less evident due to the fact that it requires samples of at least 20 g in order to analyse the iodate content.

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