A Highly Sensitive and Selective Method for the Determination of an Iodate in Table-salt Samples Using Malachite Green-based Spectrophotometry

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A simple, rapid, and sensitive malachite green-based spectrophotometric method for the selective trace determination of an iodate has been developed and presented for the first time. The reaction mixture was specifically involved in the liberation of iodine in the presence of an excess of iodide in an acidic condition following an instantaneous reaction between the liberated iodine and malachite green dye. The optimum condition was obtained with a buffer solution pH of 5.2 in the presence of 40 mg L⁻¹ potassium iodide and 1.5 × 10⁻⁴ M malachite green for a 5-min incubation time. The iodate contents in some table-salt samples were in the range of 26 to 45 mg kg⁻¹, while those of drinking water, tap water, canal water, and seawater samples were not detectable (< 96 ng mL⁻¹ of limits of detection, LOQ) with their satisfied method of recoveries of between 93 and 108%. The results agreed with those obtained using ICP-OES for comparison.

Keywords Iodate, iodide, iodine, malachite green, water, salt

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Introduction

Iodine is a considerably important trace element required for human physiological functions. Along with being essential for healthy efficient metabolism and thyroid function, the roles of the thyroid hormones include growth, development, and the control of some metabolic processes in the body.¹⁻³ Nearly one third of the global population has insufficient iodine intake, and are therefore at risk of developing iodine deficiency disorders (IDDs).⁴⁻⁶ The most well-known of which is goiter, which is characterized by an enlargement of the thyroid gland.

In Thailand, health agencies tend to say that many people are iodine deficient, which is evident from the fact that low iodine status is related to numerous diseases, including thyroid cancer. The safe dietary intake of iodine, as recommended by the World Health Organization (WHO), consists of a daily uptake of about 100 μg day⁻¹ for infants and 150 μg day⁻¹ for adults.⁷ However, iodine is a widespread trace element in the earth’s crust and hydrosphere, which depends on natural sources.⁸⁻⁹ Iodine may not satisfy its requirement by the body, since iodine from these sources may not be in a bioavailable form; also, the concentration of iodine may be less. In fact, the thyroid only transports iodine in its iodide form.¹⁰ Therefore, iodide levels are needed to be optimized for daily diets. The iodide content in drinking water is sometimes checked to decide the amount of supplementation needed.¹¹ Potassium iodate ingested within the human body is captured from the blood into the thyroid gland where it is first deoxidized into iodine to be incorporated in the biosynthesis of different thyroid hormones.¹²⁻¹³ Adequate intake of iodine can be achieved by the consumption of iodized salt by the addition of potassium iodate to salt samples due to its good stability and bioavailability.¹⁴ Therefore, the determination of an iodate in different kinds of water and table-salt samples is of interest and important for routine analytical tasks. There are various analytical methods for determining the content of iodine, iodide, and iodate in various samples, including redox titration using sodium thiosulfate, gas chromatography, ion-chromatography and high-performance liquid chromatography,¹⁵⁻¹⁰ spectrophotometric methods based on methylene blue,¹³ rhodamine B²¹ and variamine blue²² prior to measurement of its absorbance, kinetic spectrophotometric method,²³ spectrofluorometry,²⁴ flow-injection analysis,²⁵ microscale spectrophotometry followed by liquid-phase microextraction,²⁶ capillary ion chromatography,²⁷ inductively coupled plasma-mass spectrometry (ICP-MS),²⁸⁻³² inductively coupled plasma optical emission spectrometry (ICP-OES),³³ and inductively coupled plasma atomic emission spectrometry (ICP-AES).³⁴

This paper describes a simple and sensitive UV-Vis spectrophotometry method for a highly selective trace determination of iodate. Thus, both sensitive and selective iodate determinations were developed utilizing a simple, rapid, and low-cost system. Also, an accurate and precise determination of the contribution of iodate from samples to total dietary intake requires new methods. This selective method is based on the reaction of iodate with a new reagent, malachite green (MG). To the best of our knowledge, no selective study on the trace determination of iodate using MG dye has been reported. The developed method has been successfully employed for the determination of iodate in commercially available drinking water, real natural water, and some iodized table salt samples.

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The kinetics of the method is very fast and has advantages over conventional methods; for example, it is free from losses of iodine, and it is also interference free.

Experimental

Chemicals and reagents

All chemicals and solvents used were of analytical reagent grade (AR grade), and all solutions were prepared by deionized water (Milli-Q Millipore 18.2 MΩ cm–1 of resistivity) from Millipore Corporation (USA). Malachite green (NNN′N′-tetramethyl-1,4,4′-diaminotriphenylcarbenium chloride) was obtained from Sigma-Aldrich (Germany). Sulfuric acid, sodium acetate, and potassium iodate were purchased from QREC™ (New Zealand). Potassium iodide was available from Carlo Erba (Italy).

The dye solution of malachite green was prepared in deionized water at a concentration of 1.0 × 10–4 M and diluted to a mark in a 50-mL volumetric flask with deionized water. A 1 M of sulfuric acid was prepared by diluting 5.45 mL of conc. H2SO4 to the mark in a 100-mL volumetric flask with deionized water. A stock solution of the iodate (100 mg L–1) was prepared by dissolving 0.0122 g of KIO3 in 100 mL of deionized water. A solution of iodide (250 mg L–1) was prepared by dissolving 0.032 g potassium iodide in 100 mL of deionized water. A 2 M sodium acetate solution was prepared by dissolving 16.4 g of sodium acetate in 100 mL of deionized water.

Apparatus

An iodate analysis was carried out using an Agilent Technologies Cary 60 UV-visible spectrophotometer (Germany) for an absorbance measurement with a 1.0-cm path length quartz cell. The UV-visible spectrum was recorded from 200 – 800 nm. The iodate content was compared by a Perkin-Elmer OPTIMA 2100 DV inductively coupled plasma-optical emission spectrometer (ICP-OES) (Wellesley, MA, USA) with a standard ICP torch and peristaltic pump. The operational system was controlled with PE Winlab software. The instrument and operating conditions for ICP-OES are described in Table 1.

<table>
<thead>
<tr>
<th>Analytical emission line/nm</th>
<th>182.976 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF power/W</td>
<td>1300</td>
</tr>
<tr>
<td>Peristaltic pump flow rate/mL min–1</td>
<td>1.5</td>
</tr>
<tr>
<td>Plasma flow rate/L min–1</td>
<td>15.0</td>
</tr>
<tr>
<td>Auxiliary flow rate/L min–1</td>
<td>0.20</td>
</tr>
<tr>
<td>Nebulizer flow rate/L min–1</td>
<td>0.8</td>
</tr>
<tr>
<td>Nebulizer/spray chamber</td>
<td>Sea Spray/Gas cyclonic</td>
</tr>
<tr>
<td>Purge</td>
<td>Normal</td>
</tr>
<tr>
<td>Resolution</td>
<td>Normal</td>
</tr>
<tr>
<td>Replicate read time/s</td>
<td>20</td>
</tr>
<tr>
<td>Sample uptake delay time/s</td>
<td>14</td>
</tr>
<tr>
<td>Wash time/s</td>
<td>1</td>
</tr>
<tr>
<td>Number of replicates</td>
<td>3</td>
</tr>
</tbody>
</table>

Statistical analysis

Data results are given as the mean ± standard deviation (SD)

Samples

Drinking water samples were purchased from a local supermarket in a retail shop at Khon Kean University Complex and Services. Canal water samples were collected from canal sites near the Khon Kean University campus. Tap-water samples were taken directly from our chemical laboratory. The surface seawater was collected at Sucha beach, M. P. Y. beach and Lam Chareon beach, Rayong province around the east beach of Thailand in a 250-mL bottle. The sample was stored in ice until it could be filter through a filter paper. All of the water samples were centrifuged to remove any precipitate formed and filtered (Whatman™, No. 1) prior to use, then stored in a refrigerator (4°C). Nine commercial brands of some table salts were purchased from convenient stores in the Khon Kaen province, Thailand. These samples were stored in a dry atmosphere before use.

Ultrasound-assisted extraction

Due to the fact that the ultrasound-assisted extraction (UAE) allows for the release of target analytes in a short time, the operation conditions involve atmospheric pressure and room temperature. Therefore, UAE was selected for iodate extraction. At first, the sample (0.1 g of table salt) was accurately weighed and extracted with 5 mL of deionized water by an ultrasound energy corresponding to ultrasonication at 35 kHz for 5 min to leach out the target analyte. After sonication, the obtained extract was separated from the remaining solid materials using centrifugation for 5 min at 5000 rpm (3075g). Three replicates of each alternative sample and blank were used to optimize the analytical parameters of the extraction procedure.

The alternative method was also mineralized using an ICP-OES for comparison. Briefly, 0.1 g of samples were accurately weighed and extracted with deionized water by an ultrasonic-assisted extraction (UAE) method for 5 min under a constant frequency of 35 kHz. The extract in the supernatant was immediately determined after centrifuging at 5000 rpm for several minutes. The ICP-OES was used as a reference method for iodine determination under its optimal conditions with a reliable method efficiency.

Analytical procedures

The proposed method is based on a dye bleaching of malachite green in a 10-mL volumetric flask. One milliliter of the standard or sample extract was mixed with 2 mL of 200 mg L–1 potassium iodide (final concentration is 40 mg L–1) to generate free iodine; 1 mL of 2 M sulfuric acid was added, and then the reaction mixture was gently shaken; 1.4 mL of 1.0 × 10–4 M malachite green was added to the reagent solution followed by 2 mL of 2 M sodium acetate. This was diluted to volume with deionized water. After about 5 min, the absorbance of the reaction solution was measured at 620 nm with respect to a blank solution. The sample measurements were calibrated to the standard curve of an iodate concentration ranging from 0.5 to 1.5 mg L–1.

Selectivity study

For the effect of selectivity, anions and cations in aqueous samples including Cl–, Br–, NO3–, CO32–, SO42–, PO43–, Na+, K+, Ca2+ and Mg2+ were studied. Each concentration of the interference ions was fixed at 0.7 mg L–1 as the same concentration of KIO3 used. These reaction solutions were carried out in the same manner as mentioned above.
Results and Discussion

Mechanism of the dye decolorization

When an oxidizing agent (the analyte target) is added to an excess of iodide in an acidic medium in order to produce free iodine, which can be monitored by titration, it is called iodometry. The iodometry provides a simple and rapid method of analysis. It also provides chemical amplification of signals. However, the conventional iodometric titrations suffer from several limitations, such as the loss of iodine, titration error, lack of suitable indicators, and poor detection limits. These limitations can be overcome by converting the liberated iodine into an appropriate signal, so as to prevent the loss of iodine.

Besides, the reaction system of the dye decolorization is introduced. The present method involves the reduction of iodate to iodine, which is liberated in an excess of KI in an acidic medium and is directly proportional to the iodate concentration, as shown following the redox reaction, in Eq. (1):

\[ \text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O}. \]  

Iodate is a well-known oxidizing agent. It oxidizes many inorganic and organic compounds. Most of the oxidizable organic compounds have functional groups, such as amino, imino, carboxyl or diol on adjacent carbon. The reaction between iodate and these functional groups is also known as the Malaprade reaction, and has been used for indirect determination of 1,2-diols and related compounds.

In this work, the liberated iodine selectively bleaches the blue color of malachite green (MG) dye, and its absorbance is measured at 620 nm. The decrease in the absorbance is directly proportional to the iodate (IO\text{3}^-) concentration. The result of the stoichiometry showed that one mole of MG\text{+} cation was consumed by one mole of IO\text{3}^-, which is consistent in Scheme 1.

Optimization for the liberated iodine

This method involves the liberation of iodine (I\text{2}) by the reaction of iodate ion with potassium iodide in an acidic medium, and then the liberated I\text{2} reacts with the malachite green (MG) dye solution. The absorbance spectrum of MG dye in deionized water is shown in Fig. 1 with the maximum absorption at 620 nm. It was found that the liberated iodine selectively bleached the blue-green color of MG. The trace content of iodate was determined by measuring the decrease in the absorbance of a solution containing an increased IO\text{3}^- concentration. The linear quenching graph was obtained by plotting the absorbance against an appropriate range of several parameters. In particular, a plot of A_0-A against its concentration measured was made, where A_0 is the absorbance of the mixture solution without iodate as a control, and A is the absorbance of the mixture solution with iodate (dye-iodine complex) in the presence of various parameters.

Effect of either iodide or iodate concentration on the dye decolorization

The effect of the iodide concentration was evaluated by increasing the KI concentrations from 1 to 40 g L\text{–}1 in the dye solution. As shown in Fig. 2(a), the absorbance increased with an increasing concentration of KI up to 40 g L\text{–}1. The absorbance increases at very high concentrations of the iodide solution, indicating that only I\text{–} ion is not enough to liberate the iodine into the reaction system. The effect of the iodate concentration was also evaluated by increasing the KIO\text{3} concentration from 0.01 to 40 g L\text{–}1 in the dye solution. As shown in Fig. 2(b), the IO\text{3}^- concentrations in the solution had no effect at all on the absorbance of the dye solution, despite the higher concentrations.

Effect of the iodide concentration coupled with a certain amount of an iodate on the dye decolorization

In this study, a certain amount of IO\text{3}^- was fixed at 0.7 mg L\text{–}1 with various concentrations of 2.0 - 60.0 mg L\text{–}1 I\. As shown in Fig. 2(c), the absorbance of the dye solution increased with increasing I\text{–} concentrations up to 40 mg L\text{–}1, and then remained constant. Thus, an iodide excess of about 40 mg L\text{–}1 was used as its coupling reagent in the absorption quenching of the dye solution; consequently, it was also used for further experiments.

Effect of an iodate concentration coupled with an excess iodide on the dye decolorization

In this case, the experiment was performed with an excess I\text{–} concentration of 40 mg L\text{–}1 and varying the IO\text{3}^- concentrations between 0.1 and 5.0 mg L\text{–}1. As shown in Fig. 2(d), the absorbance increased with increasing IO\text{3}^- concentrations up to 2 mg L\text{–}1, and then remained constant. Consequently, the developed method gives a linear curve that is highly sensitive and selective for the trace determination of an iodate.

Effect of the reaction time

The effect of the reaction time (0 - 40 min) on the absorbance of a malachite green solution was investigated. The obtained results are shown in Fig. 2(e). The time required for the complete reaction was 5 min; and after that the absorbance remained constant. The reaction time was shorter than a previous related work. Thus, a reaction time of about 5 min is reasonable to obtain the highest yield.
Effect of pH

Besides those optimization parameters, the pH value of the reaction mixture was also varied between 1 and 11. As shown in Fig. 2(f), it was found that the absorbance of the dye solution was maximized at pH 5. The optimal pH of the solution was thus about 5.2. From these results, pH adjustments were approximately performed in the subsequent experiments. The oxidation of iodide to iodine by iodate was effective at a pH of 5.2. The liberation of iodine from potassium iodate in an acid medium was quantitatively obtained. The appearance of a yellow color indicates the liberation of iodine. Although any excess of iodide in the solution would not interfere, it was found that 40 mg L–1 of I– and 1 mL of 2 M H2SO4 were sufficient for the liberation of iodine from iodide by iodate. The present
study was based on the decolorization of MG with a known amount of iodate (0.5 – 2.0 mg L\(^{-1}\)) under an acidic condition, and the determination of iodate was accomplished by the coupling reaction between iodine and MG. As shown in Fig. 2(h), the absorbance significantly decreased while increasing the IO\(_3^-\) concentrations up to 2.0 mg L\(^{-1}\). Consequently, the developed method was highly sensitive and selective for the determination of an iodate ion.

Analytical figures of merit

The trace content of iodate was determined by measuring the decrease in the absorbance of the dye solution containing a range of KIO\(_3\) concentrations. The linear calibration curve was obtained by plotting the absorbance against an appropriate range of the KIO\(_3\) concentration. The absorbance (A) of the dye solution decreased with increasing concentrations of iodate, as shown in Fig. 2(h). The reaction was carried out using an iodate amount in the range of 0.5 to 1.5 mg L\(^{-1}\) with a final volume of 10 mL. Then, the addition of an excess iodide was done followed by a sequential addition of acid, malachite green, and sodium acetate solutions. A calibration plot, \(Y = 0.4589x – 0.0593\), was obtained with a linear regression coefficient of 0.9981. A good linear relationship between the absorbance and the amount of iodate was found, suggesting that the proposed method was selective for the trace analysis of iodate in aqueous samples. The limits of detection (LOD) and quantification (LOQ) calculated at three and ten times the standard deviation of an absorbance signal of 10 reagent blanks were found to be 29 and 96 mg mL\(^{-1}\), respectively, which is lower than previously reported values (LOD = 47.1 mg mL\(^{-1}\)).\(^1\) The precisions of 0.5 mg L\(^{-1}\) iodate \((n = 15)\) were demonstrated within the acceptable ranges as RSDs of 4.65 and 9.30% for an intra-day and an inter-day analysis, respectively.

Selectivity for an iodate/iodide of the proposed method

The effect of different ions on the determination of iodate is described. The selectivity of the analytical method is the key feature of a chemical reaction for iodate determination because the proposed method must ideally respond to only one target species when other related species do not respond in the same direction. The interference of other ions to our proposed method must be investigated by measuring the absorbance change in the presence of various anions and cations, including Br\(^-\), Cl\(^-\), NO\(_3^-\), CO\(_3^{2-}\), SO\(_4^{2-}\), PO\(_4^{3-}\), Na\(^+\), K\(^+\), Ca\(^{2+}\), and Mg\(^{2+}\). The corresponding absorbance and color changes upon mixing each ion are shown in Fig. 3. The absorbance of the MG dye at 620 nm was significantly increased only in the presence of IO\(_3^-\). On the other hand, other studied ions did not have any significant effect on the absorbance. Our proposed method can be used in a quantitative analysis for IO\(_3^-\) and interfering studies confirmed that the proposed method possesses the highest selectivity toward IO\(_3^-\).

### Table 2

Comparative results (mean ± standard deviation) for the determination \((n = 3)\) of iodate in some table salts and water samples by malachite green-based spectrophotometric method and ICP-OES

<table>
<thead>
<tr>
<th>Sample</th>
<th>ICP-OES/ mg kg(^{-1})</th>
<th>MG method/ mg kg(^{-1})</th>
<th>Recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brand 1</td>
<td>44.06 ± 3.39</td>
<td>44.16 ± 4.47</td>
<td>105.8</td>
</tr>
<tr>
<td>Brand 2</td>
<td>47.16 ± 2.88</td>
<td>43.02 ± 0.73</td>
<td>92.88</td>
</tr>
<tr>
<td>Brand 3</td>
<td>46.65 ± 1.85</td>
<td>45.17 ± 0.95</td>
<td>108.4</td>
</tr>
<tr>
<td>Brand 4</td>
<td>49.89 ± 1.31</td>
<td>44.15 ± 1.08</td>
<td>96.00</td>
</tr>
<tr>
<td>Brand 5</td>
<td>29.89 ± 1.43</td>
<td>26.08 ± 3.45</td>
<td>97.15</td>
</tr>
<tr>
<td>Brand 6</td>
<td>28.92 ± 1.44</td>
<td>29.31 ± 0.84</td>
<td>92.47</td>
</tr>
<tr>
<td>Brand 7</td>
<td>25.91 ± 1.76</td>
<td>26.47 ± 4.56</td>
<td>87.64</td>
</tr>
<tr>
<td>Brand 8</td>
<td>27.38 ± 0.96</td>
<td>27.71 ± 2.70</td>
<td>86.85</td>
</tr>
<tr>
<td>Brand 9</td>
<td>n.d.</td>
<td>n.d.</td>
<td>87.48</td>
</tr>
<tr>
<td>Drinking water</td>
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<tr>
<td>Brand 1</td>
<td>n.d.</td>
<td>n.d.</td>
<td>93.17</td>
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<tr>
<td>Brand 2</td>
<td>n.d.</td>
<td>n.d.</td>
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</tr>
<tr>
<td>Brand 3</td>
<td>n.d.</td>
<td>n.d.</td>
<td>100.5</td>
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<tr>
<td>Tap water</td>
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<tr>
<td>Tap water 1</td>
<td>n.d.</td>
<td>n.d.</td>
<td>100.5</td>
</tr>
<tr>
<td>Tap water 2</td>
<td>n.d.</td>
<td>n.d.</td>
<td>105.7</td>
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<tr>
<td>Canal water</td>
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<tr>
<td>Khon Kaen water</td>
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<td>82.85</td>
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<td>Maha Sarakham water</td>
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<td>n.d.</td>
<td>105.4</td>
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<tr>
<td>Seawater</td>
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<tr>
<td>Sucha beach</td>
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<td>M. P. Y. beach</td>
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<tr>
<td>Lam Chareon beach</td>
<td>n.d.</td>
<td>n.d.</td>
<td>107.2</td>
</tr>
</tbody>
</table>

n.d. = not detectable (< LOQ).

Analysis of real samples

This developed method was successfully applied for the trace determination of iodate in drinking water, natural water, and some table salts. When necessary, the samples were pretreated by ultrasonication before they were used to remove any CO\(_2\) bubbles. The iodate concentrations found in these samples are given in Table 2. The contents of iodate ranged between 26.08 ± 3.45 and 45.17 ± 0.95 mg kg\(^{-1}\) in some table salts. For drinking water, tap water, canal water, and seawater samples were not detected since the iodate content was lower than its LOQ. These results are in agreement at the 95% confidence level (paired \(t\)-test) with those obtained by using ICP-OES. Further, to complement and evaluation of the proposed method and/or to check matrix effects, an addition and recovery test was also performed. For the addition of the analysis, aliquots of iodate standard stock solutions were spiked to real samples containing of 0.7 mg L\(^{-1}\). The spiked samples were subjected to the optimized method; method recoveries of 83 to 108% were obtained, indicating that the dye-based-spectrophotometric method was well developed and free of matrix interferences.
Conclusion

Malachite green was introduced as a chromogenic reagent for the dye-based spectrophotometric determination of an iodate under optimal conditions. The proposed method represents the first attempt to determine iodate using the liberal of iodine method. The developed method was easily applied for trace amounts of iodate analysis in water and table salt samples. It is selectively suitable and useful for the trace determination of iodate species in the presence of iodide in drinking water (if supplementing with iodine), tap water, natural water, and also in commercial iodized salt samples.

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Conflicts of Interest

The authors have declared no conflict of interest.

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