

# Interference of Nitrite in the Iodometric Determination of Sulfite

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## Introduction

Beet sugar technologists normally employ sulfur dioxide to control color formation in process juices. Sulfitation also reduces alkalinity and improves the boiling properties of the thin juice. Sulfur dioxide when added to thin juice reacts with the excess alkali and produces sulfite ion. The latter is easily oxidized by oxygen of the air to sulfate. Thus, it becomes desirable to determine the amount of sulfite remaining in the thin juice after sulfitation. Quantitation of sulfite is ascertained by direct titration either with iodine or with potassium iodate solution using starch as an indicator. In many instances factory analysts have experienced an abnormal end point and, on occasion, sample solutions have turned dark blue on addition of deKonich starch solution or potassium iodide. Subsequent investigation showed that this phenomenon was caused by the presence of nitrite ion in the process juices.

This paper presents an indirect titration procedure with potassium iodate for the determination of sulfite in the presence of nitrite. The proposed method includes reaction of nitrite with hydrazine sulfate, addition of sample to excess iodine, and back titration with sodium thiosulfate solution.

## Experimental Procedure

### *Reagents*

All chemicals used are of reagent grade.

Standard Potassium Iodate Solution, 0.0200 N. Dissolve 0.7133 g of dry, primary standard grade,  $KIO_3$  with deionized water and dilute to one liter.

Sodium Thiosulfate Solution, 0.02 N. Dissolve 5 g of  $Na_2S_2O_3 \cdot 5H_2O$  plus 0.1 g of  $Na_2CO_3$  with one liter of freshly boiled and cooled distilled water. Allow the solution to stand for a day before standardizing.

Starch Indicator Solution, 0.2%(W/V).

### *Determination of Sulfite in Process Juice Containing Nitrite*

Transfer about 200 ml of cooled process juice into a 250-ml Erlen-

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meyer flask. While the sample is being stirred, add 0.2 g of  $N_2H_4 \cdot H_2SO_4$  and follow by 1 ml of concentrated HCl.

Pipet 10 ml of 0.0200 N  $KIO_3$  solution into a 250-ml Erlenmeyer flask. Add 20 ml of distilled water, 1 g of KI and 10 ml of 6N HCl. With constant stirring, pipet 50 ml of the hydrazine-treated sample into the flask. Quickly titrate with sodium thiosulfate solution until the brown color of the iodine turns to yellow. Add 2 ml of starch indicator solution and titrate to the disappearance of the blue color.

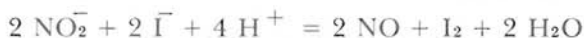
The sodium thiosulfate solution is standardized with  $KIO_3$  solution using the aforementioned procedure by replacing the sample with 50 ml of distilled water.

### Discussion

#### *Interference of Nitrite*

Fresh sugarbeets usually contain no measurable amounts of nitrite. The presence of nitrite in thin juice is attributed to bacterial reduction of nitrate in the beet end of the factory (4).<sup>2</sup>

Nitrite in an acidic medium, even in trace quantity, reacts with iodide producing nitric oxide, iodine, and water (5).



The resulting nitric oxide forms higher oxides of nitrogen by reaction with oxygen of the air, and these oxides then react with iodide producing more iodine and nitric oxide. The cycle repeats itself indefinitely. Consequently, iodine originating from the nitrite-iodide reaction interferes in the iodometric titration of sulfite.

The data in Table 1 demonstrate that a very small amount of nitrite will interfere in the iodometric determination of sulfite. Reaction between nitrite and iodide is practically instantaneous in acidified sugar solution. In the absence of acid no reaction was detected for at least one hour. Also, oxygen of the air slowly oxidizes iodide in acidified sugar solution. Since a titration normally requires 2-3 minutes, oxidation of iodide by oxygen of the air should offer no serious problem. Such an error is relatively constant and can be evaluated with a blank determination.

Table 1.—Reaction between nitrite and iodide in a 14% sugar solution.

$[NO_2^-]$	$[I^-]$	$[H^+]$	Color of Sugar Solution
$4.4 \times 10^{-6}$ M	$1.2 \times 10^{-2}$ M	0	Remained colorless for 1 hr.
$8.7 \times 10^{-6}$	$1.2 \times 10^{-2}$	0	Remained colorless for 1 hr.
0	$1.2 \times 10^{-2}$	0.6M	Turned blue in 4 min.
$4.4 \times 10^{-6}$	$1.2 \times 10^{-2}$	0.6	Turned blue in ca. 1 sec.
$8.7 \times 10^{-6}$	$1.2 \times 10^{-2}$	0.6	Turned blue in ca. 1 sec.

<sup>2</sup>Numbers in parentheses refer to literature cited.

The data appearing in Table 2 were obtained by indirect titration with potassium iodate. The percent recovery of sodium sulfite decreased with increasing amounts of nitrite.

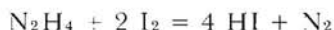
Table 2.—Magnitudes of nitrite interference.

NO <sub>2</sub> <sup>-</sup> Added (μg)	Na <sub>2</sub> SO <sub>3</sub> Taken (mg)	Na <sub>2</sub> SO <sub>3</sub> Recovered (mg)	% Recovery
0	16.7	16.6	99
100	17.4	16.2	93
200	18.2	15.7	86
500	17.8	11.7	66
1000	16.3	7.9	48

#### *Elimination of Nitrite with Hydrazine Sulfate*

In aqueous solution, hydrazine is both an oxidizing and a reducing agent. Hydrazine reacts quantitatively with nitrite in acid medium (1, 6). Oxidation of hydrazine ordinarily yields nitrogen as a product.

Employment of iodine for the direct titration of hydrazine has been documented (2). The pH is maintained between 7.0 and 7.4 with sodium bicarbonate during the titration. At a pH lower than 7, the reaction is very slow.



Hydrazine should react rapidly with nitrite ion in acid solution, but possibly, the reaction between hydrazine and iodine is sufficiently slow that iodine solution may still be used for the titration of sulfite.

Experiments with 50 to 150 mg of hydrazine sulfate in different concentrations of hydrochloric acid indicated that no detectable reaction occurred between hydrazine and iodine when the concentration of the acid was 0.3 to 0.6 N. When the solution was adjusted to 0.15 N HCl, a very small quantity of iodine, 0.6% of the total amount used, was reduced by hydrazine. Thus, all subsequent titrations were performed in 0.6 N HCl. Solution of hydrochloric acid greater than 0.6 was not investigated.

#### *Determination of Sulfite*

Preliminary studies on recovery of sulfite by direct titration of reagent grade sodium sulfite with iodine yielded results ranging from 90 to 96% recovery. The error was mostly due to air oxidation of the sulfite during the titration. This problem was satisfactorily circumvented by adding the sodium sulfite to an excess iodine solution and back titrating the remaining iodine with sodium thiosulfate solution.

Potassium iodate reacts with excess iodide and acid producing an equivalent amount of iodine. The resulting iodine can then be used to oxidize sulfite. The advantages of employing potassium iodate for

the source of iodine are: (a) potassium iodate is commercially available in a high state of purity and this salt can be used for the direct preparation of standard solution, and (b) dilute iodate solution is more stable than dilute iodine solution.

The accuracy of the described method for the determination of sulfite in the presence of nitrite was established by analyzing small portions of reagent grade sodium sulfite. The sodium sulfite had an assay value of 99.6% and was used without further purification. The results are presented in Table 3.

Table 3.—Determination of sulfite in the presence of 1000  $\mu\text{g}$  of nitrite using the described method.

$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ (mg)	$\text{Na}_2\text{SO}_3$ Taken (mg)	$\text{Na}_2\text{SO}_3$ Recovered (mg)	% Recovery
50	19.5	19.4	99.5
50	18.6	18.5	99.5
50	19.0	19.0	100.0
50	18.5	18.6	100.5
50	18.9	18.9	100.0

To evaluate the accuracy of the described method for the determination of sulfite in thin juice, known amounts of sodium sulfite were added to five separate portions of thin juice. Determinations of sulfite in the original thin juice and samples with added sodium sulfite were made. Each milliliter of the original thin juice contained 66.4  $\mu\text{g}$  of sulfite and 4.9  $\mu\text{g}$  of nitrite. The nitrite content was ascertained using a photometric method described by Buckett et al (3). The results are summarized in Table 4.

Table 4.—Recovery of sodium sulfite added to 50 ml of thin juice using the described method.

$\text{Na}_2\text{SO}_3$ Added (mg)	$\text{Na}_2\text{SO}_3$ Recovered (mg)	% Recovery
17.3	17.1	98.8
20.1	20.0	99.5
19.3	19.2	99.5
18.6	18.3	98.4
18.3	18.2	99.4

The data in Table 3 and 4 demonstrate that the described method is applicable for the determination of sulfite in the presence of nitrite. Interference of nitrite was eliminated with the use of hydrazine sulfate.

Samples of process thin juice containing various quantities of nitrite were analyzed for sulfite by two different methods. Results are

Table 5.—Determination of sulfite in thin juice containing nitrite.

Sample No.	NO <sub>2</sub> <sup>-</sup> $\mu\text{g/ml}$	$\mu\text{g SO}_3^{2-}/\text{g Solids}$	
		Direct Titration With KIO <sub>3</sub>	Described Method
1	45	0	49
2	24	0	414
3	7.0	457	577
4	4.9	250	494

shown in Table 5. As expected, direct titration with potassium iodate solution gave considerably lower sulfite content as compared to that ascertained by the proposed method. In cases where the nitrite concentration is abnormally high, titration of sulfite with iodate without elimination of nitrite is not possible.

### Summary

Nitrite in acid medium, even in trace quantity, reacts with iodide producing nitric oxide, iodine, and water. The resulting nitric oxide combines with the oxygen in the air forming oxides of nitrogen. The latter dissolves in water and produces more nitrite. This reaction is cyclic and continues indefinitely. Iodine originating from the nitrite-iodine reaction interferes in the iodometric titration of sulfite.

A method for the determination of sulfite in thin juice that contains nitrite has been developed. The method is based on elimination of nitrite in the thin juice with hydrazine sulfate, addition of sample to excess iodine, and back titration with sodium thiosulfate solution.

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