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Reprinted from

AMERICAN POTATO JOURNAL, MARCH, 1960, VOL. 37 — No. 3

pp. 102-107

A RAPID METHOD FOR THE DETERMINATION OF SULFUR DIOXIDE IN SULFITED PRE-PEELED POTATOES¹

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The pre-peeled potato industry has become sizable since about 1947. It is estimated that approximately 5 million bushels of potatoes are now processed in central peeling plants for sale as whole potatoes or French fry slices (6). Most of this output is sold for restaurant and institutional use, but some attempts have been made to establish a retail pack.

A series of publications (1, 2, 5, 7, 8, 10, 13) describe the treatment of raw, peeled potatoes to prevent discoloration. A sulfite, such as sodium bisulfite, is usually employed with or without an acid, such as citric, to inhibit the enzymatic oxidation causing discoloration. While a method is available for determining the concentrations of sodium bisulfite and citric acid present in a dipping bath (8), no simple method has been available to the best of our knowledge, for determining the amount of sulfite present in fresh potatoes. Such determination is usually made as sulfur dioxide which is liberated from bisulfite when it is acidified. An easy, reliable method is needed for plant control and for furthering research on factors affecting the sulfur dioxide pickup and retention in peeled potatoes. While it is believed that the residual sulfur dioxide in commercial pre-peeled potatoes is nearly always below the maximum set by the several states having regulations, absence of a simple method has made it difficult for processor and user to establish the sulfur dioxide content of much of the product now on the market.

Much attention has been devoted to methods of determining sulfur dioxide, principally in dried fruits and vegetables. The Monier-Williams method (3) has long been considered as more or less the standard procedure. However, it is rather difficult to execute and is laborious. Ponting and Johnson (11) developed a method for determining sulfur dioxide in fruits in which the sulfur dioxide is extracted in buffered sodium chloride solution and the filtered extract titrated with iodine solution. The various procedures for determining sulfur dioxide were recently considered by Nury and others (9), who modified previous methods to develop a colorimetric procedure for use with dried fruit.

The method described here for determining the sulfur dioxide in sulfited, fresh potatoes can be carried out quickly, easily, without complicated equipment, and by one who has not had formal training in chemical analysis. While this method represents modifications of prior methods for iodometric determination of sulfur dioxide content of dehydrated food products, it employs a set of conditions that have been found to give good results with fresh potato.

¹Accepted for publication October 21, 1959.

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APPARATUS

Blendor—10,000 RPM, 1-liter size, Waring type³.
Graduated cylinders—5, 10, 100, and 500 ml. sizes.
Trip scale or torsion balance capable of weighing 100 grams \pm 0.1 gram.
Timer, watch, or clock with sweep-second hand.
Filter paper, folded, Whatman #14 type.
Beakers—250 and 400 ml. sizes.
Items for stirring—magnetic stirrer with 1½ inch “Teflon”-covered magnetic stirring bars for use with 250 ml. beakers, or 250 ml. Erlenmeyer flasks (if manual stirring is employed in procedure).
Pipette—50 ml.
Burette—50 ml. with 0.1 ml. graduation.
Funnels—5 inch diameter.
Funnel rack.
Bottle—glass-stoppered, dark glass or covered with dark material or paint to exclude light, to serve as container for 0.01 Normal iodine solution.

REAGENTS

Special Buffer Solution. Dissolve 35 grams citric acid monohydrate and 65 grams disodium phosphate hepta-hydrate in distilled water, add 0.5 ml. toluene as preservative, and dilute to 1 liter. This buffer has a pH of 4.4 after dilution to 5 times its original volume, as practiced in the procedure.

Iodine, 0.01 Normal Solution. Dissolve 12 grams iodine and 22 grams potassium iodide in a minimum amount of water, dilute to 9 liters. and standardize against 0.01 Normal sodium thiosulfate or arsenious oxide solution according to the A.O.A.C. method (4). Store the iodine solution in a dark bottle

Hydrochloric Acid. Concentrated, A.C.S. grade.

Formaldehyde. 28 per cent Solution, A.C.S. grade.

Starch Indicator Solution, 1 per cent. Mix 10 grams soluble starch, 25 grams potassium iodide, 10 grams sodium bicarbonate (A.C.S. grade), and 0.01 gram mercuric iodide (preservative) in hot distilled water and dilute to 1 liter with the hot water. Mix for four minutes in the Waring-type blender.

“Santocel C”. Used as a filter aid.

“REGULAR” PROCEDURE

Weigh out approximately 100 grams of sulfited potatoes, to the closest 0.1 gram, and place the sample in a 500 ml. graduated cylinder. This size of sample represents approximately 20 pieces, with French fry slices ¾" x ¾" x 2". With whole, peeled potatoes, take slices from about 10 potatoes and weigh out the approximately 100 grams. Add 100 ml. of the buffer solution and dilute to 500 ml. with tap water. To compensate for the volume occupied by the insoluble material in 100 grams of potato, add an extra 12 ml. of water. Transfer the contents of the graduated cylinder to

³Mention of specific manufacturers or products in this paper does not imply endorsement by the U. S. Department of Agriculture over others not mentioned.

the blender, add 1 heaping teaspoonful of "Santocel C" as a filter aid, note the time, and mix for exactly 2 minutes. Filter through the folded filter paper into a 400 ml. beaker. If excessive turbidity is encountered in the first portion of the filtrate, return this portion to the funnel for a second pass.

With employment of magnetic stirring in the titration, place a stirring bar in a 250 ml. beaker and pipette 50.0 ml. of the filtered sample into the beaker. Titrate the iodine solution into the periphery of the liquid to prevent holdup in the foam in the center of the vortex. Erlenmeyer flasks of 250 ml. capacity are convenient for swirling manually the 50 ml. sample during titration. Place 10 ml. of the starch indicator solution in the titration vessel and fill the burette with the standardized 0.01 Normal iodine solution. Begin the titration exactly 5 minutes after homogenization was started in the blender. The titration must be carried out rapidly and continuously to prevent less rapid side reactions from becoming significant. Use of a magnetic stirrer greatly facilitates execution of a fast titration. A few practice titrations will enable the analyst to perceive accurately the end point, which is the first medium blue color that persists for 20 seconds.

The blank or control value is determined promptly on a 50 ml. aliquot of the same filtrate from which the sample was taken. Add 2.5 ml. of the hydrochloric acid and 10 ml. of the formaldehyde solution, stir, and let stand for 10 minutes to bind the free sulfur dioxide (12) and permit determination of the reducing power of the potato substances only. Add 10 ml. of starch indicator and titrate in a manner similar to the aliquot under determination. Occasionally, blank titrations produce an off-color end point. This difficulty can be remedied by the use of an additional 20 ml. of starch indicator when necessary. With only a slight loss in accuracy, time may be saved by running only one set of duplicate blanks for each batch of samples.

Calculation. Subtract the blank titration ml. from the sample titration ml. to get the corrected ml. of iodine solution to be used in the computation. Multiply the corrected ml. of iodine solution by the normality factor to obtain a measure of the iodine used; this is further multiplied by 0.03203 to obtain the weight of sulfur dioxide in grams equivalent to the iodine used. This weight of sulfur dioxide is to be expressed in parts per million of potato. The sample weight of potato is multiplied by 0.1 since a one-tenth aliquot of the extract was taken for titration.

$$\text{Then, SO}_2 \text{ in P.P.M.} = \frac{\text{corr. ml. I}_2 \times \text{Normal. I}_2 \times 0.03203 \times 1,000,000}{\text{sample wt.} \times 0.1}$$

OPTIONAL LABORATORY PROCEDURE FOR MAXIMUM ACCURACY

The "regular" procedure given above is intended for use in a peeling plant for ordinary control of the sulfur dioxide content of the finished product. While the simplicity makes it possible for a person with little or no chemical training to use this procedure after some practice, it also gives acceptable results for research purposes. If, however, one desires greater accuracy than permitted by the blank correction in the regular procedure, then a correction curve may be plotted.

More specifically, the procedure for determining sulfur dioxide with maximum accuracy is as given below:

Standardize 0.01 Normal sodium bisulfite solution against 0.01 Normal iodine solution. This standardized bisulfite solution is used to introduce known amounts of sulfur dioxide. Prepare for sulfur dioxide determination the following mixture in a 500 ml. graduated cylinder: 100 grams of unsulfited potatoes (from same lot from which the sulfited unknown is taken), 100 ml. of standardized sodium bisulfite solution, and 100 ml. of the buffer solution. Dilute to 500 ml. with water (adding 12 ml. extra water to compensate for the volume of insoluble solids in the 100 g. potato sample), transfer to blender as described under the "regular" procedure, and homogenize. Filter, and titrate 50 ml. aliquots of filtrate every 5 minutes with standard iodine solution. Run correction controls, containing formaldehyde and hydrochloric acid as under the "regular" procedure, along with each aliquot and correct the titres accordingly. The optimum time to be used for the waiting period before making the titration of the unknown is found by taking the point on the time-iodine-titration curve where the corrected ml. iodine solution used equals that used in titrating 10 ml. of the sodium bisulfite solution alone.

DISCUSSION

Achievement of quantitative extraction of the sulfite was the greatest single difficulty encountered. Oxidation of the sulfite and reaction of the free sulfite with the interior of the potato exposed during disintegration had to be minimized. Homogenizing the potato sample with water in a Waring-type blender to extract the sulfite proved superior, in our experience, to distilling the sulfur dioxide (after acidification) or pressing out the juice under a carbon dioxide blanket. Still, the air bubbles stirred in by the blender caused much oxidation of the sulfite under ordinary conditions. It was found that adjustment of the pH to 4.4 with a buffer would permit 2-minute mixing in the blender without any detectable oxidation of the sulfite. This mixing time proved to be adequate to extract the sulfite.

The use of a time-titration curve in connection with the maximum-accuracy, alternative procedure was decided upon as a result of the following reasoning. Because of the several side reactions involving sulfur dioxide, the iodine required to reach the end point is not initially the theoretical value that would be obtained due to the sulfur dioxide alone. With some lots of potatoes, titres made soon after homogenization of the potato sample in the buffer solution are greater than theoretical; with other lots, they are less. However, it was found in every case that the titre-time curve eventually crossed the line of the theoretical titre value. This point of crossing, which gives the optimum time (after homogenization) should be determined on a representative sample from each lot of potatoes to be tested. Then a representative sample of the sulfited potatoes from the same lot can be assayed for sulfur dioxide, titrating the unknown at the optimum time after homogenization.

The usual filter aids gave slow filtration of the dilute potato macerate and absorbed some of the sulfite. Rapid, clear filtration without sulfite loss was attained by use of "Santocel C".

Precision. Table 1 presents a set of data that establish the "regular" sulfur dioxide determination as satisfactory from the standpoint of reproducibility. Nine samples were taken from the same lot of potatoes, and sub-samples were then selected to provide replication within a sample. In Table 1, mean values of sulfur dioxide content are calculated in parts per million and the standard deviations are expressed in parts per million sulfur dioxide. The percentage coefficient of variation ranged from 2.28 to 5.56, with a mean of 3.55.

Accuracy. The accuracy of the determination of sulfur dioxide in sulfited, pre-peeled potatoes by the "regular" procedure described here was ascertained by establishing that values obtained for known amounts of sodium bisulfite added to potato were near the true values when the titres were corrected for the blank titres. Table 2 presents data on the sulfur dioxide found in several samples of potatoes, to which specified amounts of sulfur dioxide had been added as sodium bisulfite.

TABLE 1.—Parts per million of sulfur dioxide found in sulfited, pre-peeled potatoes.*

	Sample Numbers								
	1	2	3	4	5	6	7	8	9
Replicates A	440	387	330	318	266	214	197	158	112
B	431	376	342	298	264	222	187	153	125
C	420	358	358	300	278	203	196	..	117
Mean	430.3	373.7	343.3	305.3	269.3	213.0	193.3	155.5	118.0
Std. Dev.	10.02	14.64	14.05	11.02	7.57	9.54	5.51	3.54	6.56
Per cent Coef. Var.	2.33	3.92	4.09	3.61	2.81	4.48	2.85	2.28	5.56
Mean per cent Coef. Var. = 3.55									

*All the potatoes used in these determinations were from a single lot (Katahdin, L. I., New York); sulfur dioxide determinations were made by "regular" procedure, with blank titres used for corrections.

TABLE 2.—Accuracy of sulfur dioxide determinations by "Regular" method on potato samples containing known parts per million of sulfur dioxide.

Sample	Determinations Averaged	P.P.M. SO ₂ Added	P.P.M. SO ₂ Found	Per cent Error
1	4	163	171	+4.9
2	5	120	128	+6.7
3	4	248	243	-2.0

SUMMARY

A simple method has been developed for determining the sulfur dioxide content of sulfited, fresh potatoes. A 100 gram sample of potato is homogenized in a buffer solution at pH 4.4, which was found to reduce the oxidation of the sulfite to a negligible amount during the extraction and subsequent filtration. An aliquot of the filtered extract is then titrated with iodine solution, using starch indicator.

Moderate accuracy was obtained by titrating an unknown 5 minutes after the potato was homogenized in the buffer solution, and correcting for the effect of the potato constituents by subtracting the titre of the blank. Maximum accuracy was obtained by plotting a time-titration curve and selecting the optimum time (after homogenization) for titrating the unknown. The optimum time varied from lot to lot of potatoes.

The sulfur dioxide content is computed as parts per million of potato.

ACKNOWLEDGMENT

The authors wish to acknowledge with thanks certain suggestions made by E. G. Heisler during the course of this study .

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