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## The Determination of Sulfates in Sugar-Factory Products Employing the Tetrahydroxyquinone (THQ) Reagent

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A method for the determination of sulfates in beet sugars and sirups by titration using tetrahydroxyquinone as an indicator was developed by my experiments during the 1939 intercampaign and through experiences with the use of it during the 1939-40 campaign. The method adapted and developed for our use has been successfully

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used for the control of sulfates in several of our Great Western factories during the 1939-40 and 1940-41 campaigns, where sulfate problems were troublesome. Several hundred determinations were made by the THQ method and the sulfates controlled so that very high-grade sugar could be made at all times.

The advantage of the method is that a large volume of work can be accomplished and the results obtained very quickly, making the procedure particularly useful for the control of sulfates in the process of sugar manufacturing. High sulfates in raw sugars are detected in time so that treatment by barium and re-routing through the process prevents the effect on the white sugar. The sample can be weighed, made up to volume, the titration completed, and the result calculated in 20 minutes or less, compared to about 5 hours elapsed time required when the precipitate is allowed to stand for the period recommended in most gravimetric methods. The determination not only can be completed, using the THQ indicator, in a very much shorter period, but the actual total time of the required work is a great deal less.

The tetrahydroquinone indicator generally referred to as THQ is manufactured by the W. H. and L. D. Betz Laboratories. Several papers (1, 2, 3, 4, 5) describing the direct titration of sulfates in boiler water using the THQ method were studied while experimenting, to determine if the procedures could be adapted to the determination of sulfates in beet sugars and sirups.

Preliminary experiments consisted of first determining if the use of ethyl, isopropyl, or methyl alcohol made any difference in the accuracy of the titration. The results obtained when using methyl alcohol were high but results obtained with ethyl and isopropyl were the same. The investigation was continued using the isopropyl alcohol, because it was much lower in cost and it was easier to obtain.

Next by calculation and by experimenting it was determined what was the most satisfactory quantity of sample to use and the best strength of barium chloride to employ.

To cover the determination of all ranges of sulfate concentration, barium-chloride solutions of three different strengths were made up, but most of our determinations were made with a solution containing 10 grams of C. P. barium chloride per liter. Sometimes the sulfates in our high raw sugar were low enough so that the solution containing 2 grams of barium chloride per liter was the best to use. "When we determined sulfates in granulated sugar, the solution that gave the best results contained only 0.2 gram of barium chloride per liter.

For pure granulated sugar an amount of 10 grams of sample was found to be the best. For high and low raw sugar, sirups, and molasses of usual purity, 2.5 grams of sample are used. For very low-purity molasses and other low-purity or dark sirups or sugars it may be necessary to reduce the sample to 1.25 grams.

The method in general for each product is, of course, the same but the detail of the amount of samples, the strength of the standard barium chloride used, and the addition of chemicals to sharpen the end point all vary considerably.

The practice used was to dissolve 10 grams of granulated sugar in 25 ml. of water, but for all other products sufficient quantities of the sample were diluted to 500 ml. so that 25 ml. of the dissolved sample contained the required amount of the original material.

No chemicals are used in the sulfate determination of granulated sugar to sharpen the end point, while both silver nitrate and sodium chloride are used to sharpen the end point of other sugar-factory sugars and sirups, with the amount of silver-nitrate solution being increased as the purity of the product decreases.

On some high raw sugars low in sulfates, it is imperative that the sodium-chloride solution be added, because a purple color develops during the titration and it is impossible to detect any end point. In the THQ method of titration for sulfates in all beet sugars and sirups, except granulated sugar, the addition of a sodium-chloride solution in the proper order of the procedure makes the solution turn a brighter orange color, giving a more definite end point that remains permanent and increasing the accuracy of the titration. When titrating low-purity sugars and sirups without the addition of the sodium chloride solution, the end point was a sort of brownish-orange, Chang-

Table 1.—Comparative sulfates in high and low raw sugar and molasses obtained by the THQ and gravimetric methods.

		Sulfates (SO <sub>4</sub> )					
High raw sugar		Low raw sugar		Molasses produced			
THQ method	Gravimetric method	THQ method	Gravimetric method	THQ method	Gravimetric method		
.87	.85	.90	.89	1.19	1.11		
.34	.34	.68	.70	1.41	1.45		
.94	.96	.65	.69	1.06	1.03		
1.35	1.25	.81	.77	1.02	1.08		
.67	.72	1.12	1.12	1.17	1.37		
.55	.55	.74	.77	1.23	3.24		
1.00	3.09	.66	.66	1.21	1.19		
.44	.42	.87	.87	1.14	1.27		
.63	.62	.91	.90	1.02	1.16		
.47	.45	.86	.86	1.37	1.48		
.44	.43	.68	.64	1.24	1.22		
.23	.20	.64	.65	1.16	1.16		
.27	.31	.65	.64	1.00	1.12		
.30	.30	.79	.75	1.01	1.08		
.40	.41	.72	.71	1.27	1.27		
.60	.63	.63	.64	1.31	1.34		
Average							
.598	.596	.769	.766	1.176	1.223		

Detailed specifications of the reagents required and the specific methods employed for various sugars and sirups are given at the end of this paper.

ing slowly, and is hard to recognize, usually causing high results. Consistent results could not always be obtained until sodium chloride was used, after the silver nitrate in the procedure.

The method is more accurate on high-purity products, being extremely accurate on granulated sugar, and with care and experience the method is reasonably accurate on all products. However, when used as a control method, we are not interested in extremely high precision.

It can be observed in the comparative results in table 1 that the average accuracy of the THQ method and the gravimetric method differs only in the third decimal place on high and low raw sugar, and the averages on molasses produced differ by less than 4 percent.

#### Determination of $\text{SO}_3$ by the THQ Method

The general procedure for the THQ method for the determination of  $\text{SO}_3$  in various sugars and sirups is the same, but as the details differ considerably the procedure will be described for each one.

Reagents.—1. "THQ", tetrahydroxyquinone (50 to 100 grams required for a campaign supply.

2. Barium-Chloride Solutions. — I. Dissolve 10.00 grams of C. P. barium chloride in water and make up to 1000 ml. 1 ml. of solution = 3.277 mg. of  $\text{SO}_3$ . (For use with low raw sugar, low raw massecuite, molasses and products with high  $\text{SO}_s$  content.)

II. Make 200 ml. of solution I up to 1000 ml. 1 ml. of solution = .6554 mg. of  $\text{SO}_3$ . (For use with high raw sugar.)

III. Make 100 ml. of solution II up to 1000 ml. 1 ml. = .06554 mg. of  $\text{SO}_3$ . (For use with white sugar.)

3. Isopropyl alcohol. (2 gallons sufficient for a campaign supply.)

4. N/50 sodium hydroxide.

5. N/100 hydrochloric acid.

6. Saturated C. P. sodium-chloride solution.

7. 0.1 N silver-nitrate solution.

Determination: 1. White Sugar.—Transfer 10 grams of white sugar to a 250-ml., wide-mouth, Erlenmeyer flask. Dissolve in 25 ml. of water. Make alkaline to phenolphthalein with N/50 NaOH. Neutralize carefully with N/100 HCl. The temperature of the solution must be below  $35^\circ$  C. and preferably between  $20^\circ$  and  $25^\circ$  C. Add 25 ml. of isopropyl alcohol. Introduce 1 dipper of the THQ indicator (approximately 0.15 gram) and mix completely by swirling the flask. Add the standard barium-chloride solution III at a slow, steady dropping rate with constant swirling of the flask until the brown color changes to a rose. From the number of ml. of the standard barium-chloride solution used, calculate the percentage of  $\text{SO}_3$  in the sample.

2. High Raw Sugar.—Weigh 50 grams of the sugar, dissolve in water, transfer to a 500-ml., Kohlrausch flask, and make to volume at 20° C. Mix the contents of the flask thoroughly. Transfer a 25-ml. sample of the sugar solution to a 250-ml., wide-mouth, Erlenmeyer flask. Make alkaline to phenolphthalein with N/50 NaOH. Neutralize carefully with N/100 HCl. The temperature of the solution must be below 35° C. and preferably between 20° and 25° C. Add 25 ml. of isopropyl alcohol. Introduce 1 dipper of the THQ indicator and mix completely by swirling the flask. Then add slowly at a steady dropping rate, with constant swirling of the flask, approximately % of the standard barium-chloride solution II that it is estimated will be required for the final titration. Introduce 1 ml. of the silver-nitrate solution from a pipette by slowly dropping it into the mixture while rapidly twirling the flask. Then add 5 ml. of the saturated sodium-chloride solution to the mixture while continuing to twirl the flask. Complete the titration to the end point as recognized by the change of color from brown-to-light red or bright orange. Make a blank test on 25 ml. of water and the reagents used. From the ml. of barium chloride used subtract the ml. of the blank and from the net result calculate the percentage of  $SO_3$  in the original sugar.

3. Low Raw Sugar and Massecuite.—Follow the procedure for "high raw sugar" with the following exceptions: Use 2 ml. of the silver-nitrate solution and 10 ml. of the sodium-chloride solution. Titrate with solution I.

4. Dark and Low-Purity Sugars and Sirups.—Weigh 50 grams of the sugar or sirup (use only 25 grams of extremely low-purity or dark sugars or sirups) dissolve in water, transfer to a 500-ml. Kohlrausch flask, and make to volume at 20° C. Mix the contents of the flask thoroughly. Transfer 25 ml. of the sugar solution to a 250-ml., wide-mouth, Erlenmeyer flask. Make alkaline to phenolphthalein with N/50 NaOH. Neutralize carefully with N/100 HCl. The temperature of the solution must be below 35° C. and preferably between 20° and 25° C. Add 25 ml. of isopropyl alcohol. Introduce 1 dipper of the THQ indicator and mix completely by swirling the flask. Then add slowly at a steady dropping rate, with constant swirling of the flask, approximately % of the standard barium-chloride solution I that it is estimated will be required for the final titration. Introduce a silver-nitrate solution from a pipette by slowly dropping it into the mixture while rapidly twirling the flask. Continue adding the silver nitrate in this manner until the solution turns slightly pink. Then slowly drop 10 ml. of the saturated sodium chloride into the mixture while continuing to twirl the flask. Complete the titration with the standard barium-chloride solution to the end point as recognized by the change of the color of the solution from milky-brown to a bright

orange. Subtract the ml. of barium chloride used in a blank test from the ml. used in the titration and calculate the result.

5. Precautions.—It is of the greatest importance to follow the order and manner of introducing the reagents in order to obtain consistent and reliable results. Adding a portion of the barium chloride before the silver nitrate is introduced produces a sharper and brighter end point. The sodium-chloride solution makes the end point perceptible, in that there is a quicker and definite change of color from milky-brown to bright orange.

Note: The most distinct end point is obtained if the volume of barium chloride used is not more than 10 ml. If titration requires more than this volume, with the No. I barium-chloride solution, use a more dilute sample.

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## Some Regional Effects on Beet-Sugar Quality<sup>1</sup>

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Our 1940 report on beet sugars included tables of average data for different regional groups of factories. The grouping used was based on juice purities combined with general geographical location. Ten groups were made so that the individual factory could compare its product with the average of a relatively small number of factories of corresponding location and similar juice purities. They were not intended for comparing the group averages themselves. Therefore, for the study reported in this paper, with the specific object of comparing the sugars of beets from different producing areas, it was found more satisfactory and simpler to group the data representing

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