Determination of Floc in Refined Sucrose by Coagulation with Quarternary Amines

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Introduction

The various methods of measuring the amount of floc material present in refined sugar have not been entirely satisfactory. A control method is needed which is rapid and which has a means of quantitatively assigning a value of the amount of floc material present. Older methods for laboratory control were based on visually estimating the amount of floc and required a reaction period of at least twenty-four hours.

There have been some very good methods devised through which the floc material can be extracted quantitatively and identified (1), (2)[2]. These methods require a considerable amount of technique and require the time of the analyst to the point where they are out of the scope of an ordinary control laboratory.

The Quaternary Amine method has been developed. It is not time consuming and can readily be used for control purposes. It is rapid and does not rely upon the operators visual estimation of floc actually present, since the measurement is taken on a spectrophotometer or on a colorimeter capable of measuring transmittance at 720 $m\mu$.

Floc material extracted from refined sugar has been identified as saponins or a glycoside consisting primarily of glucuronic and oleanolic acids or their salts (1). Saponins are largely removed by carbonation but a small amount does at times get past the purification steps and hence into the sugar crystal itself. Saponins present in crystallized sugar are of colloidal size when the sugar is dissolved. These colloids are negatively charged and hence can be coagulated by cationic compounds. Hyamine 10-X No. 1622 or Roccal will bring about coagulation under the proper conditions. This characteristic is the basis of the method developed.

This method is a modification of Dr. Galvin's preliminary quaternary amine titration and Holly's preliminary method of excess Roccal addition. The method is placed on a quantitative basis through use of curves based on sugars with a known amount of saponin added.

Preparation of Saponin for Basic Standardization.

Several procedures for extracting a saponin material from sugar beets were investigated. The method recommended produced a material which is easily reproduced and which, when used in the floc method, is comparable to saponin material supplied by the Western Utilization Research Laboratory for our preliminary work. The product extracted is not a pure compound but a mixture of compounds which is representative of the actual floc material in sugar beets. It also has characteristics which should make it suitable for analysis of cane sugars as well as beet sugar. It is light brown or tan in color and is easily pulverized to make handling easy.

Procedure.

Select one or more sugar beets which are in good condition. Peel the outer skin from the beet. This peeling should be at least one-eighth inch

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[2] Numbers in parenthesis refer to literature cited.

thick but avoid peelings which are over one-fourth inch. Discard the peeled beet. Cut the peelings into small pieces and place them in a Waring Blender. Add water equal to about one-fourth the weight of the peelings and blend for five minutes.

Extract the blended material with water in a Soxhlet Extraction apparatus for three to four hours. Extraction must be carried out in batches until one or two liters of liquid is obtained. The pulp is discarded. The extract contains sugar, glycosides, and other soluble non-sugars which are contained in the skin of the beet. Since the saponin is concentrated in the skin of the beet this procedure is preferable to using diffusion juice as the starting point.

Acidify the liquid to 1.5 pH with HCl and heat to 90°C. for one hour. Allow the acidified liquid to stand overnight. Filter the juice through a Buchner funnel, using a small amount of filter-aid to speed up filtration. Wash the cake with acidified water to remove sugars. Discard the filtrate and washings. Dry the cake with infra-red lamps. Do not heat the cake too much or decomposition of the material may cause trouble.

Extract the dried cake with ethanol or with special denatured ethyl alcohol for six hours. This also must be a batch operation. Concentrate the extract to a small volume (50 ml. or less) and pour into a larger volume of acidified water (3000 ml.). Let this solution stand overnight. A white flocculent precipitate will form.

Filter the solution through a white filter paper which is tight enough to retain the precipitate but which has good flow rates. Do not use filter-aid.

Dry the precipitate carefully and dissolve it with hot alcohol by pouring the alcohol through the paper. Use only enough alcohol to dissolve the precipitate and wash the paper slightly. Evaporate the alcohol solution slowly in an evaporating dish. The brown material remaining can be readily scraped from the dish after it is dried. This material is pulverized and bottled for use. This is the saponin material for standardization.

From one beet of average size about 500 to 1000 mg. of material can be obtained.

Standardization of Floc Method.

(1) Accurately weigh out 0.0250 grams of the saponin material. Dissolve the saponin in alcohol (heat slightly if necessary) and make up to a total volume of 250 ml. with alcohol (Bakers Reagent Alcohol, Denatured No. 3A). 1.0 ml. of this solution contains 0.1 mg. of saponin.

(2) Dissolve 2.0 grams of Hyamine 1622 (10-X) in distilled water and dilute to one liter (0.2 percent solution).

To each of the eighth 100 ml. Kohlrausch flasks add 10.0 grams of sugar which is known to be floc free. Dissolve the sugar in a small amount of water and add reagents according to the following schedule.

Flask Number	ml. Saponin Solution	ml. 10-X	p.p.m. Saponin Present
1	0	0	0
2	0	10	0
3	1.0	10	10
4	2.0	10	20
5	4.0	10	40
6	6.0	10	60
7	8.0	10	80
8	10.0	10	100

Complete all volumes to 100 ml. with distilled water. Mix solutions in each flask by inverting them 8 to 10 times. Be careful not to use a vigorous action as air bubbles will be formed.

Place flasks No. 1 through No. 8 inclusive in an 80°C. water bath for one hour.

Cool the flasks to 20°C. and adjust volumes to 100 ml. to make up for evaporation. Mix the contents of the flasks by inverting them 10 times. The mixing procedure must be carefully done and it must be exact as the coagulation of the saponin does not come to an equilibrium unless adequate mixing has been achieved. The same technique must be followed when determining floc in an unknown sugar.

The solution in flask No. 1 is the reference solution. Read the percent transmittance at 720 $m\mu$ for all flasks. Check each reading carefully and make an average of at least three readings. The entire procedure of standardization should be repeated two or three times and the average taken for a more accurate standardization.

Results are then plotted on regular graph paper. (Figure 1). The graph should be a straight line if all of the work was carefully done. From the graph a table may be prepared for use in the subsequent analysis.

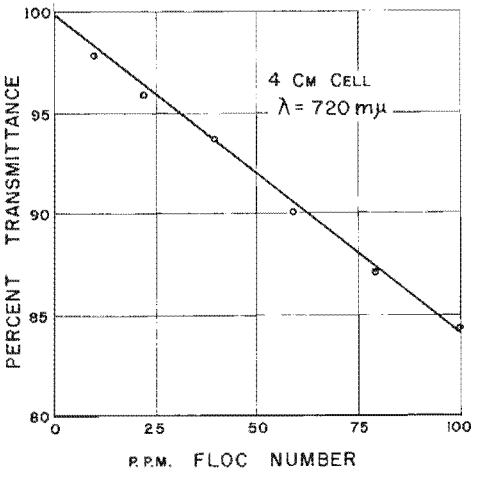

Figure 1.

Analytical Procedure.

After having previously constructed a standardizing graph or table as above the actual analysis is simple.

(A) Weigh 10.0 grams of the sugar under test into each of two 100 ml. sugar flasks. Dissolve the sugar in about 50 ml. distilled water.

(B.) To the first flask add distilled water up to the 100 ml. mark, mix the solution by inverting the flask 10 times carefully.

(C.) To the second flask add 10 ml. of the 4.2 percent Hyamine 1622 solution. Fill to the mark with distilled water. Mix contents by inverting 8 times and place the flask in a water bath at 80°C. for one hour. Cool the flask and re-adjust the volume. Mix the contents by inverting 10 times.

(D.) Find the percent transmittance of the solution at 720 m_μ against the reference solution. From the table or graph find the floc number of the sugar.

Remarks.

In developing the procedure we stated previously that several methods of extracting the saponin material were employed. We used both ether and alcohol as extracting solutions and obtained materials from both extractions on the same acid precipitated material, alcohol followed by ether and vice-versa.

All substances recovered were found to act in a similar manner when their alcoholic solutions were used as standardizing reagents. A statistical analysis did point out that the transmittance values found were significantly different when all of the various extracted substances were compared.

We found, however, that our straight alcoholic extraction was comparable to saponin material furnished by Western Utilization Laboratory. The differences were not significant at 90 percent confidence levels.

We also found that the straight alcoholic extracted material could be duplicated. This led to the procedure adopted for the floc method presented.

Since the standardizing material produced in this manner compares with saponin produced under different conditions in a different laboratory when checked by our proposed method we feel that we can recommend the method for routine laboratory control of floc in sugar.

Average values (transmittance) found by using a few of the various materials are shown in Table 1. Statistically there is no significant difference between Alcohol Ex. 55-1, Alcohol Ex. 55-2 and WR-54.

Table 1.—Transmittance Values for Various Extracted Materials.

(4 Cm. Cell Depth)						
p.p.m. Saponin	Alcohol Ex. 55-1	Alcohol Ex. 55-2	WR 54	AX 54	Ether Ex. 55	Ether Alk. Ex. 55
10	97.75	98.33	97.83	98.10	98.13	98.60
20	96.63	96.50	96.33	96.75	96.75	97.90
40	92.88	92.33	92.67	93.88	93.63	95.70
60	89.13	88.50	89.50	90.63	90.63	94.20
80	87.00	84.67	86.83	87.50	87.75	92.00
100	84.50	82.00	84.50	85.38	84.75	90.00

Correlation of the acid-reflux method with the method presented here is difficult. Visual estimation of floc depends upon size and number of particles but does not allow for density. Table 2 illustrates this lack of correlation.

Table 2.—Lack of Correlation Between Two Methods.

Sample	1	2	3	4	5
Visual Grade	2	4	4	1	1
Floc Number (Colorimeter)	12	23	20	27	6

The floc grade of Sample No. 4 was of very fine, evenly diispersed floc. According to instructions it could only be given a grade of 1, however, the colorimetric method shows a fairly heavy concentration of floc.

It is interesting to note that the turbidity developed in the new method does not vary in particle size. It varies only in the number of particles and is stable for long periods of time.

Mixtures of two samples of sugar, known to have a marked difference in floc content, show a promise of accuracy in the colorimetric method (3).

Figure 2 shows the results of this test.

Analysis made on cane sugars also indicate the presence of colloids. Dissolved cane wax behaves in a manner similar to sugar beet saponin.

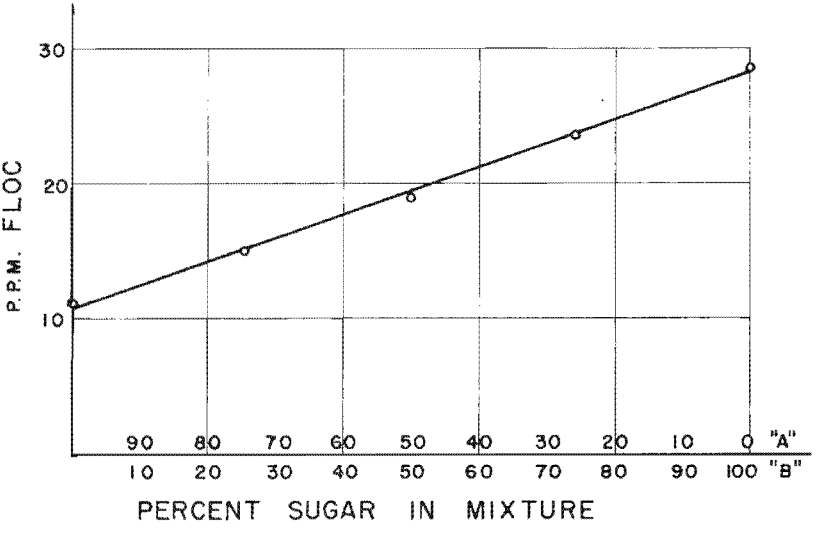

Figure 2.

Conclusions

This method is readily adopted to refinery control. It is rapid and places the floc or saponin content of granulated sugar on a quantitative basis.

Analysis of sugars produced this season show a range of floc from 5 to 27 p.p.m. We have not set a maximum allowable floc value for specific trade sugar as yet. However, sugar produced for bottling purposes has been found to be suitable which has a floc value as high as 12 p.p.m. Generally speaking, floc under 10 p.p.m. will be graded as "O" floc by the older methods.

Acknowledgment

In developing this method many useful suggestions and aid in evaluation were made by Spreckels Sugar Company, Holly Sugar Corporation, and the Western Utilization Research Laboratory.

References

(1) McGinnis, R. A. Alston, P. W., Clark, L. W., and Eis, F. G. 1952. Floc in carbonated Beverages. Ind. & Engr. Chem. 44: 2844.

(2) Correspondence with Western Utilization Laboratory.

(3) Correspondence with R. A. McGinnis, Oct. 1954.