

bility of calcium phosphate and the *comparatively* large solubility of the borate. I find, however, that in uncooked eggs there is just enough phosphoric acid to account for three cc. tenth-normal sodium hydroxide, when working on five grams of sample, so I now propose to deduct three cc. of sodium hydroxide from the number of cubic centimeters taken by the sample. I scarcely need point out the necessity of proving the acid by the alcohol test. As a rule the presence may be ascertained by simply stirring some of the sample with a drop of sulphuric acid and a little spirits of wine and then setting fire to it.

When dealing with milk I allow one cc. of sodium hydroxide for every ten grams of the sample. If the amount of acid is, as usual, very small, no particular accuracy can be claimed for the process; but if present in larger and, consequently harmful quantity, the results are all that may be desired.

LONDON, ENG., JUNE, 1896.

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## A STUDY OF THE CLARIFICATION OF SUGAR CANE JUICE.<sup>1</sup>

BY J. L. BEESON.

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THE clarification of the cane juice, so important a factor in the manufacture of sugar, is practically the same in method as that in use by the planters of Louisiana one hundred years ago. The method consists in the addition of slaked lime or milk of lime to the cold juice until neutrality or slight alkalinity is reached; then the temperature of the mass is raised nearly to boiling, when a coagulum forms and is carried to the surface by the upward motion of the liquid, and there forms a thick dark green scum called "the blanket." This is removed by skimming, and calcium superphosphate solution (called clariphos), is added until the juice begins to brighten in color. The method is, in the main, an empirical one, the nature of the bodies removed and the chemical changes involved therein not being understood. The practical sugar boiler has virtually no facts to guide him in this important branch of his work. It was therefore the object of this investigation to compare the juice expressed by the mill with that obtained from the same large sample of cane obtained by

<sup>1</sup> This work was done in the laboratory of the Audubon Sugar School, New Orleans, which institution was discontinued last July.

the process of diffusion with hot water. Also to compare these juices before and after clarification, and to study the products so removed. The methods of analyses used were those adopted by the Association of Official Chemists. The total proteids and albuminoids were obtained by multiplying the total and albuminous nitrogen by the factor 6.25, the difference being termed amids. The "gums" or non-nitrogenous solids not sugars, were obtained by subtracting the total proteids and ash from the "solids not sugars." Since the diffusion juice is more dilute than the mill juice, the results of the former were calculated to the same total solids of the mill juice for the sake of easy comparison. These analyses were made in duplicate throughout. Below is given the results of these analyses :

ANALYSIS I.

	Total solids.	Sucrose.	Glucose.	Solids not sugars.	Purity coefficient.	Ash.	Gums.	Total proteids.	Albuminoids.	Amids.
Mill juice.....	14.9	10.8	2.03	2.07	72.5	0.413	1.385	0.292	0.099	0.193
Diffusion juice .....	14.9	11.4	1.87	1.63	76.5	0.448	0.93	0.224	0.065	0.179
Clar'f'd diffu'n juice	14.9	11.3	1.97	1.63	75.9	0.456	0.97	0.204	0.056	0.148

By comparing the juice from the mill with that obtained by diffusion with hot water, it will be seen the latter contains less solids not sugars, less total proteids, less albuminoids and amids than the mill juice. This would indicate that the hot water had, during the process of diffusion, coagulated and left behind in the begasse about one-third of both the albuminoids and gums, in which case analyses of the begasse from these two sources should show more albuminoids and gums in the diffusion sugars. Estimation of the gums was not attempted, but estimation of the total proteids in the two bagasses showed an excess in that from the diffusion, as will be seen below :

ANALYSIS II.

	Per cent.
Bagasse from mill, proteids .....	1.146
Bagasse from diffusion process, proteids.....	1.731

This analysis was repeated with mill and diffusion bagasse of another variety of cane, showing as before a larger percentage of proteids in the latter.

By comparing the clarified with the unclarified diffusion juice it will be seen that there was a further, but much smaller, removal of the albuminous bodies by the action of lime and heat in the process of clarification. But there was a slight increase in ash and what is estimated as gums, attended by a lowering of the coefficient of purity of the juice. The increase in ash doubtless accounts for the increase in what is termed gums, for the lime had combined with the free acids in the juice, most of which acids identified in the juice form soluble compounds with lime. Then it is a well known chemical fact that hot alkaline solutions will decompose amids with the liberation of ammonia, forming the alkaline salts of the acid of the amid. This would further augment the lime salts in the juice. The decrease in amids in the clarified juice in this case would indicate that this decomposition of the amids had taken place during the heating and skimming. If the juice were sufficiently alkaline and the heating prolonged, we should expect the albuminoids to be broken down into their constituent compounds, reducing sugars, amids, etc., and the latter broken up into ammonia and lime salts of the acid of the amid. This would decrease the albuminoids, as is true in the above case, as well as increase the lime salts in solution. It is clear that excessive use of lime and heat would decrease the purity of the juice, as is noticed in this case. These analyses were repeated with five different kinds of cane, each time showing results similar to the above. This lowering of the purity of the juice by clarification was doubtless due to the presence of an excess of lime due to the solution of the larger particles of lime during the heatings and skimmings, for an analysis of the settlings in the bottom of the clarifying tanks showed about fifty per cent. of lime. This trouble, of course, could be remedied by using lime which had been ground to an impalpable milk with water in a mill. This would approximate a true solution. Lime-water cannot be used on account of the dilution it effects. The amount of ash in the clarified juice depends upon the original acidity of the juice and the amount of calcium superphosphate added after skimming. If more be added than is required to remove the free lime, there might be a lessening of the ash, but this would again set free the acids in the juice,

which might cause considerable inversion during the subsequent heatings and evaporations.

Below is given the analysis of the products removed by the clarification:

## ANALYSIS III. OF SKIMMINGS.

	Per cent.
Ash .....	26.84
Proteids.....	15.52
Gums and acids .....	57.52

The relatively small quantities of albuminoids in this coagulum would indicate that some of these bodies had been broken down by the clarification, as was previously suggested, and the presence of so large quantities of ash and non-nitrogenous bodies would indicate the formation of lime compounds. Upon comparing the three juices in Analysis I it is clear that the greatest purging of the juice was effected by heat alone during the process of diffusion, removing a third of the albuminoids and gums in the juice, the lime or heat in the clarification removing a further portion of the albuminoids, but increasing the non-nitrogenous bodies of the juice. What would be the relative effect if lime were added first and then heat applied? Which is the clarifying agent, lime, or heat, or both? In order to throw light upon these questions the following experiment was performed: To one liter of cold mill juice, clear lime-water was slowly added. After the acidity of the juice had disappeared (about ten cc. were required), a dark greenish precipitate appeared and continued to form as the lime-water was added until a faint alkalinity was reached, requiring 190 cc. more of the lime-water. This precipitate was carefully collected, dried at 100° C., weighed and analyzed. Then a few drops of calcium superphosphate solution were added until the juice began to brighten, in order to remove the small quantity of free lime. The juice was then heated for twenty minutes to 90°-95° C., when a small coagulum was formed. This was collected, dried, weighed and subjected to analysis. Many sugar houses pass sulphur dioxide into their juices before clarifying with lime and heat. In order to see if sulphur dioxide removed any bodies which lime and heat would not, a portion of the above juice was saturated with sulphur dioxide gas and heated. The juice was bleached, but no further

precipitate was formed. But this does not show that sulphur dioxide will not reduce certain organic bodies to compounds removable by lime and heat which would not otherwise have been removed by these agents. No experiments could for lack of time be made to settle this important point. Below is given the analysis of the juice before and after the lime-heat clarification :

## ANALYSIS IV.

Mill juice.	Total solids.	Sucrose.	Glucose.	Solids not sugars.	Purity coeffi- cient.	Ash.	Gums.	Total proteids.	Albuminoids.	Amids.
Unclarified ....	14.9	11.32	2.54	1.04	75.9	0.309	0.602	0.131	0.109	0.0224
Clarified .....	14.9	11.91	2.37	0.72	79.4	0.301	0.365	0.062	0.041	0.021

## ANALYSIS V. OF THE PRODUCTS REMOVED BY CLARIFICATION.

	Ash.	Albumi- noids.	Gums.
Precipitate with lime, weight in 100 grams juice, 0.266 gram .....	20.6	18.06	61.54
Coagulum from heating afterwards, in 100 grams juice, 0.025 gram ..	11.5	37.28	51.25

The clarified juice was much clearer and lighter in color than the unclarified. By comparing the constituents of the two juices one by one it will be seen that there is a marked improvement, due to clarification when the process is carefully carried out. The lime-heat clarification has removed over half of the albuminoids, and nearly half of the gums, resulting in a loss of about one-third of the solids not sugars, and an increase in the coefficient of purity of about four per cent. of the juice. By applying the results in Analysis V to those in Analysis IV, it will be seen that the lime alone, when added first, has removed about forty-eight per cent. of the entire albuminoids, and about thirty-six per cent. of the entire gums in the juice, whereas heat alone applied first (Analysis I) removed about thirty-five per cent. of the albuminoids and forty per cent. of the gums. From this it would appear that lime is in general the more effective purging agent, removing decidedly more of the albuminoids, but less of the gums than heat. From Analysis V it will be seen that of the total organic matter removed, nearly ten-elevenths were removed by the lime. Of the albuminoids removed, four-fifths were removed by the lime, and of the gums nine-tenths, the remaining portions of both the albuminoids and gums being removed

by the heat. It is quite clear that the lime has formed insoluble compounds with both the gummy bodies and the albuminoids, the latter forming calcium albuminates, probably similar to the better known copper albuminates. But the lime does not combine with all of these bodies in the juice, or if it does the compounds are soluble. The lower percentage of ash in the coagulum would indicate that if such soluble but coagulable compounds were formed, they were of a different nature, containing less lime. The albuminoids and gummy bodies in cane juice may then be divided into three classes: (*a*) Those which form insoluble compounds with lime, (*b*) those which are precipitated by heat, and (*c*) those which are not rendered insoluble by both lime and heat, the gummy bodies of class *c* being precipitable by nitrate of mercury and the albuminoids by copper hydroxide. Class *c* constitutes nearly one-half of these bodies in the cane juice. It is the further work of the sugar chemist to discover some cheap non-poisonous agent which will remove this class of bodies from the cane juice.

### A NEW FORM OF PYKNOMETER.<sup>1</sup>

BY J. C. BOOR,<sup>2</sup>

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Of all the different forms of pyknometers, Fig. 1 represents the one that is probably most generally used.

Working with this form in a room where the temperature is much higher than the normal, there is one difficulty to contend with, which is, that in the time it takes to dry and weigh the pyknometer the liquid is continuously running out of the capillary tube in the stopper.

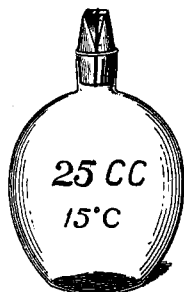


Fig. 1.

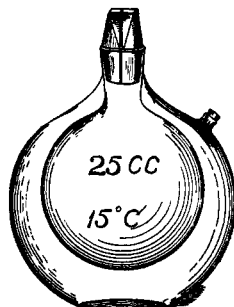


Fig. 2.

For the purpose of making accurate specific gravity determi-

<sup>1</sup> *Chem. Ztg.*, 1896, 20, 63.

<sup>2</sup> Read before the New York Section of the American Chemical Society, Nov. 6, 1896.