

RAPID DETERMINATION OF PHOSPHATE IN CANE JUICES

B. E. BEATER.

With the exception of analyses conducted on phosphatic fertilisers, or other materials very rich in phosphates, all phosphoric acid determinations at the Experiment Station are carried out colorimetrically. The method at present in use for cane juices is that reported by the writer in 1933 (1), and by this method, roughly three thousand five hundred determinations have been made to date. The technique of this method, however, seems a little too lengthy for the factory laboratory, which is not always fortunate enough to have the necessary equipment.

The procedure outlined below is far more rapid and easy to carry out, though it does not take into consideration the total phosphate content of the cane juice. Some remarks on the value of such a determination are, however, appended in the discussion.

Procedure.

Unless the juice is first cleared in some way, difficulty will be experienced in matching the blue colour developed with that of the standard. In order to effect this, filter a portion of the juice through a close grade analytical filter paper, previously adding a quantity of kieselguhr. Kieselguhr normally contains no phosphate, and was found to have no sorptive properties when working with a soluble phosphatic salt. The small amount of sorption brought about by the filter paper can be largely overcome by discarding the first droppings of the filtrate.

Take 2 ml. of the filtrate and dilute to 100 ml. with distilled water. Mix well and pipette off 5 ml. into a 100 ml. stoppered measuring cylinder. Add 1 ml. of the molybdate reagent and make to the mark. Shake, and add six drops (0.25 ml.) of freshly prepared stannous chloride reagent. Treat similarly a standard solution containing 0.02 m.g. P_2O_5 and after both have stood a few minutes, match the colours in a Schreiner colorimeter, using Hehner tubes. If no Schreiner colorimeter or Hehner tubes are available, the colours can be matched by any suitable method. McRae (2) gives a method for doing this.

Suppose the reading in the standard tube to be 80 while the reading of the unknown is 100. Then m.g. P_2O_5 in 100 ml. cane juice is estimated as follows:—

$$(0.02 \times \frac{80}{100}) \times 1000 = 16.0$$

A single determination can be made in little over five minutes.

Below are given a number of comparisons between total P_2O_5 determined by ashing and the P_2O_5 determined by the above method:

Variety	Total P_2O_5 (m.g. per 100 ml. juice)	P_2O_5 by present method (m.g. per 100 ml. juice)	P_2O_5 by present method per
			cent. of Total
Co. 281	44.0	29.9	68.0
Uba	38.0	22.0	57.9
Co. 290	10.5	10.4	99.0
Co. 281	24.2	17.8	73.6
P.O.J. 2878	37.2	26.0	69.9
Co. 270	37.8	28.6	75.7
P.O.J. 2714	15.8	11.0	69.6
Co. 281	59.0	40.0	67.8
Uba	22.6	16.0	70.8
P.O.J. 2727	56.0	44.4	79.3
P.O.J. 2725	16.5	14.0	84.8
Uba	32.6	20.0	61.3
Co. 270	32.2	20.8	64.6
P.O.J. 2878	43.4	26.7	61.5
			Mean 71.7

It will be noticed from these figures that on an average, 70 per cent. of the total phosphate of the juice is estimated by this method, which suggests that the remaining 30 per cent. is perhaps *unavailable for defecation*. Kean & Hill (3) came to the conclusion that much of the phosphate found by ashing was of little or no significance in juice purification. It is possible that we may be justified in assuming that the phosphate estimated by the above procedure is a measure of the amount available for juice purification. No experimental work has been done on this, however, and it would not be safe to draw any final conclusions.

Reagents.

Standard Phosphate Solution: Dissolve 0.7668 gm. pure dry monopotassium phosphate (KH_2PO_4) in distilled water and transfer quantitatively to a litre flask. Add 10 ml. 1:3 sulphuric acid and make to mark. This standard keeps indefinitely. 5 ml.

of the solution contain 2 m.g. P_2O_5 . In order to obtain the required concentration, take 10 ml. of the above solution and dilute to one litre with distilled water. 5 ml. of this solution contain 0.02m.g. P_2O_5 .

Ammonium Molybdate Reagent: Mix 100 ml. of 10 per cent. ammonium molybdate solution with 300 ml. of 50 per cent. (by volume) sulphuric acid. The reagent is best kept in the dark. A slight reduction of the molybdate itself may be found to take place on standing, resulting in the reagent turning blue. The reagent need not necessarily be discarded for this reason as the results will not be materially affected.

Stannous Chloride Reagent: Dissolve 0.1 gm. of pure tin foil in 10 ml. conc. HCl, warm to complete action, and make to 10 ml. with distilled water. This can conveniently be done in a test tube with the 1 ml. and 10 ml. marks scratched on the side. The stannous chloride solution must be prepared fresh each day. The reagent is sometimes preserved under liquid paraffin.

Discussion.

To discuss at any length the relation of juice clarification to phosphate content would be beyond the scope of this paper. Nevertheless, it has to be stressed that from the point of view of factory control it seems that a knowledge of total phosphate, as determined by ashing, would be less instructive than that determined by the above rapid procedure. Carrero (4), for example, states that "apparently the determination of total phosphorous after destruction of organic matter (ashing) is valueless for mill control purposes, the amount present in the juice as phosphoric acid being the deciding factor in efficient defecation."

The necessity of a good supply of available phosphate in cane juices is continually emphasised by writers. Not only is the excess addition of lime avoided, making the juices easier to handle, but the filterability of the final product is improved. Much interesting information could be obtained by sugar laboratories in co-operation with estate workers with regard to the available phosphate content of cane varieties as affected by soils, climatic conditions and fertiliser treatment.

Particularly would it be of interest to know whether phosphate estimated by the above procedure can truly be termed available or not. By an examination of the clarified juice, computing results on some fixed basis such as the sugar content or Brix, it would be possible to ascertain what percentage of the total phosphate has been precipitated. The correlation, if any, between the degree

of juice purification and phosphate content estimated by the above procedure could thereby be ascertained.

The slight refractory nature of P.O.J. 2878 juice, noticed in some other countries, has been attributed to its low phosphate content by Caminha (5). This writer concludes that in order to obtain a satisfactory precipitate in the defecators, not less than 30 m.g. P_2O_5 per 100 ml. of juice should be present. We do not, however, notice at the Experiment Station that P.O.J. 2878 is any lower in phosphate content (total) than other varieties. As a matter of fact the second highest phosphate content on record (102 m.g. per 100 ml. juice) was obtained on a P.O.J. 2878 juice sample.

Information on the phosphate content of the variety canes crushed at the factories is still lacking. The rapid method outlined in this paper should facilitate the accumulation of data, which it is anticipated may assist in throwing some further light on the relative properties of the different cane juices entering the factory.

References.

- (1) Beater, B. E. The Determination of Phosphorus by the Coeruleo-molybdate Reaction. Proc. S. African Sugar Tech. Assoc. (1933) 7th Ann. Congr., pp. 87 - 93.
- (2) McRae, Donald. The Phosphate Content of Cane Juice. Proc. S. African Sugar Tech. Assoc. (1929) 3rd Ann. Congr., pp. 54 - 57.
- (3) Keane, J. C. and Hill, H. G. Filterability of Raw Cane Sugars. Ind. and Eng. Chem. (1931) 23: pp. 421-427.
- (4) Carrero, J. O. Phosphoric Acid in Sugar Canes. Rept. Agr. Exp. Stn., Puerto Rico, Mayaguez (1931) p. 11.
- (5) Caminha, A. Handling Juices of P.O.J. 2878. Int. Sug. Jour. (1935) 37: p. 315 (Abs.).

South African Sugar Association,
Experiment Station,
Mount Edgecombe,
February, 1937.



Mr. CUTLER: With regard to the stannous chloride method, Mr. Beater did not state that the blue colour obtained by the addition of stannous chloride is a very transitory one. It develops to its maximum in five minutes, and at the end of about 15 minutes begins to fade fairly rapidly, and that limits the determination to the time factor. As far as we are concerned, the method has been

discarded for the use of hydroquinone instead of stannous chloride, which gives a darker blue colour—considerably darker—and the colour is permanent, so permanent that you can actually put the tubes away, retain them, and they will last for weeks, so that your determination becomes a more simple matter from the time point of view. We, in Pretoria, have discarded this method, and are now using the old titration method, using caustic soda, and we are now using it in the centrifuge, whereby we can carry out about 100 determinations straight off. We wash our precipitates in the tube, keep them in the tube, and titrate in the tube, simply involving one operation, so to speak, continuously in one piece of apparatus, and the method is giving satisfactory results. I think it would be quite useful, especially in regard to the use of these new canes, if not only the determination of the phosphate but the determination of the calcium and possibly potassium could be carried out at the same time, because I cannot help thinking that there might be found to be a correlation between calcium, potassium and phosphorus. In regard to the procedure, I cannot help thinking that the relationship might be followed out as far as the content of the sugar in your final molasses; it would be interesting to follow it up.

Mr. BEATER: I did not think it would be necessary to give all the details of the coeruleo-molybdate method. There have been two or three papers read before this Association in past years which have made mention of the precautions necessary in the development of the blue colour. With regard to the use of hydroquinone, I have used this as a reducing agent, but since it requires a different strength of molybdate reagent to that used with

stannous chloride, I thought some confusion might result. We, at the Experiment Station find the stannous chloride reduction method quite satisfactory, since the preparation of a new standard takes very little extra time. The titration method mentioned by Mr. Cutler requires a centrifuge and this is not always obtainable in a sugar factory laboratory.

Mr. CUTLER: No, I still maintain that if you follow it out in the centrifuge, titrating in the same glass that you actually do your precipitation in, the method is a very rapid one.

Mr. DODDS: The extreme deficiency of South African soils in phosphorus in their original condition, and the importance of phosphate in the juice as a factor in clarification makes the analysis of phosphorus in soils and sugar cane and its products of the greatest importance. It has, therefore, been one of the principal analytical studies at the Experiment Station ever since we began, to arrive at the most accurate and rapid methods of analysis for phosphorus and phosphate, and we have, as far back as 1929, two papers, by McRae and Draeger on this subject, and I am very glad that the work has been carried on so ably since by Mr. Beater and others.

The PRESIDENT: If there is no further discussion, I would ask you to join me in a vote of thanks to Mr. Beater for his interesting paper.

(Applause).

South African Sugar Association,
Experiment Station,
Mount Edgecombe,
February, 1937.