

ive changes when going in one direction would tend to simulate a loss, or, if going into the other direction, indicate a gain. For these reasons the refractometrically determined dry substance losses must, in the meantime, merely taken as proof that the official method of determining dry substance by drying at 105° C. is not dependable and that, therefore, the "true purity" based thereon is in reality quite far from the truth.

Work, which is underway, (but which is not yet supported by a large enough number of analyses of low purity products) indicates, that dry substance determined by drying in vacuo at 60° C., and the refractometric dry substance as determined immersion refractometrically by the Oxnard normal weight solution method, show a very close agreement when checked by the above described method.

Theoretical yield calculations of fillmasses based upon the refractometric dry substance purity agree very closely with actual yields. This feature, we hold, is the best proof for the dependability of the refractometric method of analysis over the double dilution Brix, or the dry substance by drying, method of analysis.

THE RELATIONS EXISTING BETWEEN pH MEASURED IN THE LABORATORY AT 25° C.

AND

THE pH OF THE SAME SOLUTION AT THE EXISTING OPERATING

TEMPERATURES IN THE FACTORY

F. R. Bachler

I.

The occurrence of unseemly high percentages of invert sugar in the final molasses is at times observed in every beet sugar factory. Aside from the accidental possibility now and then of a distinctly acid pH condition during some phase of the process, it often cannot be readily understood why invert sugar should occur in what may be considered to be a safely pH alkaline house.

A clue as to the principal source of such invert sugar occurrences can be had only from a systematic and often very protracted invert sugar survey which must begin with the thin juice and end with the molasses, including all intermediate steps in the process. When invert sugar is found at all it will nearly always show up in the thick juice first, yet practically never will there be any invert sugar in the thin juice entering evaporators. From the thick juice stage on there will, likely, be found relatively little additional invert sugar provided, of course, that the pH of the white fillmass was not allowed to drop below pH 7.5 and that of the succeeding fillmasses not below pH 7.3.

From these observations we conclude that the bulk of the invert sugar found in the molasses originates from thick juice. Since the thin juice entering the evaporators was free from invert sugar it follows that all the invert sugar in the thick juice was formed during evaporation. By further extending our search to the juices of the different evaporator bodies, we find that approximately 78% of the invert sugar in the thick juice originated in the first body, about 20% were formed in the second body and the remainder of 2% was formed in

the third body. Very likely none was formed in the fourth or fifth bodies of evaporators.

We know that the rate of inversion of a pure sugar solution is a function of pH, heat, time, and concentration of same. In the case of an impure sugar solution must be added another, in its effects as yet not so well known but, nevertheless, very important factor, that of the character and the quality of the non-sugars, "buffer substances", that are present. As regards the latter we know that with all other inversion promoting conditions being equal, the rate of inversion in general will become slower the more buffer substances are present; we also know that a given weight of a certain non-sugar, or group of non-sugars, will influence the rate of inversion differently than would be that if a similar weight of another non-sugar or group of non-sugars were present.

Of the five factors which govern the rate of inversion of the thin juice entering the evaporators we can definitely control only alkalinity, respectively, pH. Before the advent of pH control it was considered safe practice that the thin juice entering evaporators should be at least faintly alkaline to phenolphthalein and if the thick juice leaving the evaporators did not show a faint pink, but happened to be colorless to phenolphthalein, then the alkalinity of the thin juice would be raised slightly until the thick juice left the evaporators at least faintly alkaline to thick juice. Experience had shown that under such conditions sugar losses due to inversion during evaporation did either not occur at all, or were so small as to be negligible. If it so happened that either an undue rise, or fall, of alkalinity occurred during evaporation then this was considered a sign that errors had been committed during the purification stages of the process and all efforts were bent toward removing the cause of this unusual behavior.

With the advent of pH control it was realized that the point at which phenolphthalein changed color was at pH 8.2 - 8.3 and it became the practice for awhile to hold the pH of the thin juice entering evaporators at that figure, or a little higher if a loss of pH occurred during evaporation. Gradually the operators receded from this point and felt justified in doing so because thin juice of a pH lower than 8.2 - 8.3 boiled faster in the evaporators and that the subsequent fillmasses too may have boiled and purged easier; and if it so happened that during such a campaign there was practically no invert sugar produced even though the pH of the thin juice entering evaporators was held as low as pH 7.5 - 7.6, then this was considered by that factory, and maybe a number of other factories, as an example to emulate during next campaign. If in the succeeding campaign in that, or a different factory, the same pH of thin juice resulted in a more or less heavy invert sugar production, then the cause thereof was, as a rule, not assigned to having started out with too low a pH but that "the beets this year were peculiar", which is true in a way, considering what baleful effects a slight change in the character of the non-sugars may produce as regards the physical and chemical behavior of the juices in the house.

The beet sugar factory laboratory technic of determining pH closely followed the scientific development of the art; thus the colorimetric drop method was followed by the likewise colorimetric test tube method which was replaced by methods that measure the electric potential existing between the juice and metal to metal oxide electrodes of the antimony type. The change from one method to another was due to a gradual realization of serious shortcomings inherent to that method. Thus for instance, the colorimetric methods

suffer from serious errors due to temperature, the solvent, salt, protein and colloid effects; that of the calomel half cell antimony electrode types, while free from some of the errors of the colorimetric methods, are fast being recognized of giving inaccurate results due to the presence of chemical substances in the beet juices which react with the antimony oxide such as SO_2 , or certain organic acids or organic salts, which form complexes with the antimonous oxide. This knowledge of the limitation which the various methods of determining pH imposed was acquired in the beet sugar laboratory gradually and by the hard way of an ever widening bitter experience which served to increase the desire for a method, or an instrument, which would not be affected by the limitations above cited. Such an instrument, as every chemist knew, would be one equipped with glass electrodes but in view of the extreme fragility of these electrodes this remained a pious wish until about a year ago when the present rugged Beckman electrodes appeared.

In the meantime some factories had adopted continuously indicating pH instruments of the antimony type, the electrodes of which were immersed in a flow through chamber through which flowed a continuous stream of the hot juice as existing in the house. These instruments did not indicate the pH of the juice at the existing temperature but the pH as would be found had the juice been cooled to 25°C . When the pH indications of this factory instrument were compared with the pH value of the laboratory antimony instrument on the same juice but which had been cooled to 25°C ., then, as a rule, a fairly close agreement was found which served for a time to confirm the faith in the accuracy of the pH value as determined by these antimony instruments.

This faith was due for a rude awakening, for now enters the Beckman Glass Electrode pH Indicator as a house control device. Intending to use the Beckman instrument for the control of pre-defecation, we placed one such instrument at Oxnard side by side with an L&N antimony continuous pH indicator, both instruments using exactly the same juice. It was our original intention to check the pH indicators of the Beckman instrument against those of the L&N. We expected to find a very close agreement and were quite surprised, when we found that a very large difference in the indicated pH values existed. The cause of this difference was found to be due to the basic fact that the Beckman instrument indicated the pH as it exists at the actual factory temperature, while the L&N antimony instrument indicates the pH value corrected by an inbuilt device which checks within fairly close limits with the pH of the laboratory antimony instrument, which measures the pH juice cooled to 25°C . This fact was definitely established by experts of the National Technical Laboratories, who measured the pH of the juice hot and cold with a hydrogen electrode, the results of which were found to check within ± 0.02 pH with those as found by the glass electrode.

The fact that the Beckman factory glass electrode pH as measured on first carbonation juice at a temperature of 85°C . was lower by 1.2 pH than that obtained by the L&N factory antimony instrument was too significant to be overlooked. It led us to a somewhat closer study of the pH conditions as these actually exist at the prevailing elevated temperatures in the house in comparison with those which were found in the laboratory on the same juices cooled to 25°C . and this paper is a resume of the results of this study.

II.

Our initial attempts to measure these differences with our regular antimony laboratory instrument led to no satisfactory results. The answer to our problem was found in using the Standard Industries Model M. Beckman Glass Electrode pH Meter which, by virtue of the chemical inertness of the glass electrodes, is free from the chemical inhibitions that mitigate against the obtaining of accurate results with the antimony electrode. A special Beckman glass electrode, recently developed, suitable for working ranges up to 100° C. was used in conjunction with the standard instrument for the high temperature pH measurements. The comparison calomel electrode employed was the standard Beckman type.

In working the comparative tests between the pH of the hot and the cold juice it was not practical to use a single set of electrodes for both sets of measurements. A more practical way was to use two sets of electrodes, the special high temperature electrode for hot and the regular standard electrode for cold pH measurements with a separate calomel electrode for each. It was thus a simple matter, necessitating merely withdrawing the plugs of one set of electrodes and inserting those for the other electrodes in order to change from a hot to a cold pH measurement. While making a series of determinations, the particular electrode set not in use was kept immersed in either water, juice or buffer solution of a temperature corresponding to that of the juices to be measured. In this manner both sets of electrodes were at all times instantly ready and in proper temperature equilibrium.

The pH meter was standardized with the electrodes against a pH 7.0 phosphate buffer. Since this particular buffer solution changes but very slightly with temperature (less than 0.05 pH over the entire range between room temperature and 100° C.) it was particularly well adapted to this investigation as the same buffer could be used as a reference standard for the instrument with both the high and the low temperature electrodes at their working temperatures.

Two series of tests were always made in which the pH of the juice at high temperatures, approximately that prevailing under actual operating conditions, was determined and compared directly to that as determined on identically the same sample after cooling same to 25° C. The pH at the high temperature IS THE ACTUAL pH OF THE JUICE IN THE PROCESS AT THE EXISTING TEMPERATURE, whereas the pH of the second test, that of the cooled juice, corresponds to the pH obtained at the usual laboratory test which, so far, WE HAVE PRESUMED TO BE INDICATIVE OF THE ACTUALLY EXISTING OPERATING pH.

(Incidentally with the studies on temperature effect here reported another study is in progress comparing the results obtained in the laboratory by measuring the pH of the same juice at room temperature, using the glass and the antimony electrode instruments. While this study is far from being complete, the results obtained so far throw a dark shadow of doubt on the dependability of the pH values obtained from the antimony electrode system. We mention this here because the need of investigating these two methods of pH determination originated from our early, though futile, attempts to study the effects of pH by high and low temperatures with our laboratory antimony instrument).

Knowing that large pH differences existed, we were desirous of finding out first of all whether or not a constant relationship existed between the pH of the juice at its working and at its laboratory temperature and, if such a relationship did exist, to find out if it were possible to apply to the laboratory determined pH value a constant correction factor so as to correct it to the pH as existing at the actual working temperature; also to determine, if it were possible to do so, if inversion of sucrose would occur in a juice that was pH alkaline when cold but pH acid when hot.

All measurements were made during the latter half of 1939 campaign in the Oxnard Laboratory of the American Crystal Sugar Company by Mr. F. W. Weitz and Mr. Arthur Lorenz. While the data presented are by no means complete, being more in the nature of a preliminary survey, these do reveal highly significant facts of which immediate cognizance had to be taken in the interest of better factory control.

The first series of tests was devoted entirely to thin juice entering evaporators. An overflow type electrode chamber was connected with the sample line of juice to evaporators and a constant flow of juice was allowed to flow through. The temperature of the juice at this point averaged 96° C. During these tests the high temperature electrodes were inserted in the flow-through electrode chamber and kept immersed in the stream of juice. Hence the set was available and ready for a test at any time merely by plugging into the instrument.

Whenever a reading was made on the hot juice, a portion of the juice overflowing at that moment was collected in a small bottle, quickly cooled in a water bath, and then used for the corresponding comparative cold test. In this manner a considerable number of tests were made and compared at frequent intervals. The results of this group of tests, made on several successive days, are tabulated and shown in the accompanying table headed "Comparative Tests of pH of Thin Juice at 96° and 25° C.

In the second series the scope of the tests was expanded to take in other juices. In this group of tests the pH at high and low temperatures was compared on first and second carbonation juices, thin juice, thick juice, and first liquor. Unlike the previous series, in which the tests were made directly at the station, the tests in this group were made entirely in the laboratory. Portions of the regular routine test samples brought to the laboratory were used for these special tests. The test portions, in groups of five, were first heated on the hot plate to a uniform temperature of 98° C. The electrodes, which in the meantime, and during the interval between tests, had been brought to and kept at the proper working temperature by being suspended in buffer solutions of pH 7.0 at 98° C., were immersed into the test solution and the readings of the five samples in the group being taken consecutively. The samples were then quickly cooled and the corresponding cold pH measurement made. This series of tests, too, was extended over a number of days to obtain varying juice conditions and several groups of tests were made on each of these days. The samples thus tested probably covered a representative range of average juices produced during that period. The results of these tests are given in the second table.

Before entering into a discussion of the results obtained in these tests, we will briefly describe another series of exploratory tests in which we attempted to ascertain if a thin juice of a given cold and hot pH would show signs of inversion if kept boiling for a measured period of time. For this purpose we determined pH hot and cold at the commencement of the boiling period and again after thirty minutes of continuous boiling on the hot plate. We also determined the invert sugar at the beginning and at the end of the boiling period.

The following results were obtained:

	<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>
pH at 25° C. at beginning of boiling period	8.3	7.8	7.5	7.3
pH at 25° C. at end of boiling period	8.2	7.6	7.3	6.9
pH at 98° C. at beginning of boiling period	7.4	7.0	6.6	6.4
pH at 98° C. at end of boiling period	7.3	7.0	6.4	6.1
				Strong
Invert sugar before boiling - % on Dry Subst.	None	None	Trace	Trace
Invert sugar after boiling - % on Dry Subst.	None	Trace	0.22	0.39

Crude as was the arrangement of those tests, they do show, nevertheless, that inversion does occur if the pH of the hot juice is on the acid side and that inversion becomes the greater the lower the pH. Similar results were obtained in the house. In these laboratory tests, in reality, the pH of the boiling just must have been lower still, because the measurements were made at 98° C., while the juice was boiling at 101.5° to 102° C. In the first body of evaporators, where temperatures as high as 115° C. exist, the actual pH will be still lower and the inversion losses be very likely even higher. A systematic survey needs to be made on the changes in pH, measured hot and cold, on the juices as these enter and leave the various evaporator bodies. Much could be learned from such a study if the pH values were plotted against evaporation time in each body, changes in temperature and concentration as these occur in the different bodies.

We will now briefly discuss the results reported on the two tables. A study of the data reveals at once that a distinct and measurable difference exists between the pH of the juice at its process temperature and that of the same juice cooled to 25° C. The pH at the high temperatures is appreciably lower than that of the cold juice. It would be very convenient if this difference were a constant, because this would enable us to correct observed readings at room temperature to obtain the pH of the same juice at actual working temperature. Unfortunately, however, our observations show that such a simple and convenient relation does not exist but that rather, at different times, as the character of the juice changes, the pH difference due to temperature also changes.

In the case of our observations on thin juice, covering 98 tests, we found that the pH as measured at 96° C. was fairly constant, varying only between 7.2 and 7.45. When the pH of the same juice was measured at 25° C., more and larger fluctuations were shown and the pH varied from 7.7 as a minimum to 8.45 as a maximum, or a total spread of 0.75 pH.

This spread on the cold pH, however, only partially reveals the actual pH differences, as in many instances the maximum cold pH was obtained on tests in which the pH hot was on the low point. In such cases a difference in pH at the two respective temperatures of as much as 1.15 was shown. On the other hand, a difference as low as 0.5 pH was obtained in other tests. The average difference of all tests made on thin juice was 0.9 pH. With extreme variations from 0.5 to 1.5 pH it would hardly be feasible to safely apply the average difference as a correction factor to convert observed readings at room temperature to what may be the true pH at operating temperatures.

The second series of tests, which was extended to cover other juices in addition to thin juice, corroborated the findings in the first series. Again we found that the higher temperature the pH of the juice was lower than when determined after cooling, with the difference varying from as little as 0.5 to as much as 1.6 pH.

COMPARATIVE TESTS OF pH OF TEIN JUICE AT 96° AND AT 25°

pH				pH				pH			
Time	96°	25°	Diff- erence	Time	96°	25°	Diff- erence	Time	96°	25°	Diff- erence
(Date)	October 1, 1939			11:35	7.3	8.15	.85	(Date)	October 2, 1939		
10:02	7.3	7.9	.6	39	7.4	8.25	.85	9:15	7.2	8.2	1.0
04	7.2	7.7	.5	42	7.45	8.3	.85	17	7.2	8.2	1.0
06	7.2	7.75	.55	45	7.45	8.3	.85	20	7.2	8.3	1.1
08	7.2	7.8	.6	47	7.45	8.35	.9	23	7.2	8.3	1.1
10	7.25	7.85	.6	50	7.4	8.3	.9	25	7.25	8.35	1.1
12	7.25	7.8	.55	53	7.35	8.25	.9	29	7.25	8.35	1.1
14	7.2	7.75	.5	56	7.35	8.25	.9	32	7.2	8.3	1.1
16	7.2	7.8	.6	59	7.4	8.25	.85	35	7.2	8.3	1.1
22	7.2	7.85	.65	12:35	7.4	8.25	.85	38	7.2	8.3	1.1
26	7.2	7.95	.75	37	7.4	8.25	.85	40	7.2	8.3	1.1
30	7.25	8.0	.75	40	7.4	8.3	.9	46	7.2	8.3	1.1
33	7.25	8.1	.85	43	7.4	8.3	.9	49	7.2	8.25	1.05
35	7.3	8.2	.9	45	7.4	8.3	.9	53	7.25	8.3	1.05
38	7.3	8.15	.85	47	7.4	8.35	.95	56	7.25	8.4	1.15
41	7.3	8.15	.85	50	7.4	8.35	.95	10:00	7.35	8.45	1.1
44	7.25	8.05	.8	53	7.4	8.3	.9	05	7.35	8.45	1.1
47	7.2	7.9	.7	56	7.4	8.3	.9	09	7.35	8.45	1.1
50	7.2	7.75	.55	1:00	7.4	8.25	.85	13	7.3	8.45	1.15
53	7.2	7.8	.6	04	7.4	8.25	.85	17	7.3	8.45	1.15
55	7.2	7.8	.6	07	7.4	8.25	.85	20	7.3	8.4	1.1
58	7.2	7.85	.65	09	7.4	8.25	.85	25	7.3	8.4	1.1
11:00	7.2	7.9	.7	11	7.4	8.25	.85	(Date)	October 3, 1939		
03	7.2	7.9	.7	13	7.4	8.25	.85	10:15	7.2	8.2	1.0
05	7.2	7.95	.75	15	7.4	8.25	.85	19	7.25	8.3	1.15
08	7.25	8.0	.75	18	7.4	8.3	.9	22	7.3	8.35	1.05
11	7.25	8.0	.75	20	7.4	8.3	.9	25	7.3	8.4	1.1
13	7.3	8.1	.8	25	7.4	8.3	.9	28	7.25	8.4	1.15
16	7.3	8.15	.85	32	7.4	8.35	.95	31	7.25	8.4	1.15
18	7.35	8.15	.8	34	7.45	8.4	.95	35	7.35	8.4	1.05
22	7.35	8.2	.85	39	7.45	8.45	1.0	39	7.35	8.4	1.05
26	7.35	8.25	.9	43	7.45	8.45	1.0	42	7.35	8.4	1.05
30	7.4	8.25	.85	45	7.45	8.45	1.0	45	7.35	8.4	1.05
33	7.35	8.15	.8	48	7.45	8.45	1.0				

Average of above 98 tests
 pH at 96° 7.3
 pH at 25° 8.2

Maximum difference 1.15
 Minimum difference .5
 Average difference .9

Tests made with Beckman Industrial Model M pH meter glass electrode.
 Special high temp. electrode used for tests at 96°. The above tests were made
 at the evaporator station.

Oxnard, Calif.
 1939 Campaign.

Comparative Tests of pH at 98° and at 25°

Date	First Carb. Juice After Filters			Second Carb. Juice After Filters			Thin Juice Entering Evaporators			Thick Juice Leaving Evaporators			First liquor to Pan Storage		
	98°	25°	Diff- erence	98°	25°	Diff- erence	98°	25°	Diff- erence	98°	25°	Diff- erence	98°	25°	Diff- erence
Oct. 28	9.8	10.7	.9	7.9	9.1	1.2	7.2	8.1	.9	6.6	7.3	.7	6.7	7.3	.6
	9.7	10.5	.8	7.7	8.9	1.2	7.2	7.7	.5	6.7	7.4	.7	6.5	7.2	.7
	9.7	10.6	.9	7.7	8.9	1.2	7.0	7.9	.9	6.5	7.3	.8	6.5	7.2	.7
Oct. 29	9.3	10.7	1.4	7.6	8.9	1.3	7.0	7.9	.9	7.0	7.5	.5	6.8	7.3	.5
	9.4	10.7	1.3	7.5	8.7	1.2	7.1	7.9	.8	6.9	7.6	.7	6.6	7.3	.7
	9.5	10.7	1.2	7.4	8.8	1.4	7.1	8.0	.9	7.0	7.9	.9	6.8	7.6	.8
	9.2	10.5	1.3	7.6	8.9	1.3	7.1	7.8	.7	6.6	7.2	.6	6.6	7.1	.5
Oct. 30	9.0	10.6	1.6	7.6	9.0	1.4	6.9	8.0	1.1	6.6	7.3	.7	6.4	7.2	.8
	9.1	10.7	1.6	7.4	8.9	1.5	6.9	7.9	1.0	6.7	7.7	1.0	6.5	7.3	.8
Oct. 31	9.2	10.6	1.4	7.6	9.1	1.5	7.0	8.0	1.0	6.8	7.5	.7	6.7	7.6	.9
	9.3	10.7	1.4	7.6	8.9	1.3	6.9	7.9	1.0	6.6	7.2	.6	6.5	7.3	.8
	9.2	10.6	1.4	7.6	8.9	1.3	7.0	8.2	1.2	6.7	7.3	.6	6.5	7.5	1.0
Nov. 1	9.4	10.9	1.5	7.6	9.0	1.4	6.9	7.4	.5	6.7	7.4	.7	6.6	7.4	.8
	9.4	10.7	1.3	7.7	8.9	1.2	6.9	7.6	.7	6.5	7.3	.8	6.4	7.2	.8
	9.4	10.6	1.2	7.7	8.9	1.2	7.2	8.0	.8	6.6	7.4	.8	6.5	7.0	.5
Nov. 8	9.2	10.7	1.5	7.4	8.7	1.3	7.2	8.2	1.0	6.9	8.0	1.1	6.5	7.6	1.1
	9.1	10.6	1.5	7.4	8.6	1.2	6.8	8.1	1.3	7.0	8.2	1.2	6.7	7.9	1.2
Nov. 9	9.2	10.5	1.3	7.5	8.6	1.1	7.0	7.7	.7	6.9	7.7	.8	6.8	7.6	.8
	9.3	10.8	1.5	7.6	8.7	1.1	7.1	8.0	.9	6.9	7.8	.9	6.9	7.6	.7
	9.3	10.7	1.4	7.6	8.8	1.2	6.9	7.8	.9	6.9	7.8	.9	6.8	7.7	.9
	9.4	10.8	1.4	7.6	8.8	1.2	7.1	8.2	.9	6.9	7.9	1.0	6.9	7.8	.9
	9.3	10.6	1.3	7.6	8.8	1.2	7.0	7.9	.9	6.8	7.5	.7	6.6	7.4	.8
Max.Diff.(22 tests)			1.6			1.5			1.3			1.2			1.2
Min.Diff. " "			.8			1.1			.5			.5			.5
Av.of 22 tests	9.3	10.7	1.4	7.6	8.9	1.3	7.0	7.9	.9	6.8	7.6	.8	6.6	7.4	.8

Tests made with Beckman Industrial Model M pH meter, glass electrode.
 Special high temperature glass electrode used for tests at 98°.
 For high temp. tests the samples were heated on laboratory hot plate.

Oxnard, Calif.
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It was noted further that in the higher average pH ranges the spread between the pH of the hot and the cold juice was greater than in the lower ranges. Thus, on first carbonation juice with an average pH of 9.3 determined hot and pH 10.7 determined cold, the average difference was 1.4 pH. On second carbonation juice the average difference was slightly less, 1.3 pH. In the lower pH products, thick juice and first liquor averaged respectively 6.8 and 6.6 pH while hot, and 7.16 and 7.4 pH while cold, the average difference for temperature change being 0.8 pH. The tests on thin juice gave an intermediate difference of 0.9 pH, which, it is interesting to note, substantiated the average difference found in the first series of tests on thin juice alone.

As noted before in the case of thin juice, the difference in pH between hot and cold test on any one product is not a constant. The difference varies from hour to hour, and even more so from day to day, as the nature and the character of the juice changes. The difference, therefore, can be considered in a rough way as an approximate correction factor to estimate from the cold pH as determined in the laboratory what the actual pH may be in the process.

The fact that the difference in pH between the hot and the cold test on any one kind of juice is not a constant factor is explainable on the grounds of changes in character of the juice itself. As the beets from different localities, and even from different fields in the same locality, change in composition, so must the juice also change in character. The amount and the nature of both the organic and inorganic constituents are constantly changing. To this we must add the widely varying quality of the first carbonation juice as is obtained from the Dorr continuous carbonation process, which is a mixture of perfectly carbonated, over-carbonated, and raw juice, the proportions of which are constantly changing, and even though these juices show what appears to be the desired pH, are, nevertheless, quite widely differing in quality. Since the effect of temperature on the potential difference set up between the electrodes varies with different salts, the change in pH due to temperature differences in the juice constantly changing in character, must necessarily be a pH fluctuation-causing factor.

Those pH fluctuations in the juice as observed at Oxnard are not necessarily wholly applicable to conditions in other houses, especially if those be non-Steffens houses using batch (instead of continuous) carbonation, just as a certain set of conditions existing in a previous campaign may not necessarily be successfully applicable to other campaigns or in other factories.

This leads us to a consideration of the point as to what real value we can attach to the laboratory records of pH measurements at 25° C. when we now positively know that the real operating pH at the existing house temperature is radically different.

Undoubtedly, a better understanding of these conditions will lead to a more rational work in the house by helping us to fight adverse conditions more intelligently than we have been able to do thus far under the assumption that the laboratory determined pH of the cold juice was a dependable criterion.

It seems that the solution of the problem will be found in the installation at various strategic points in the house of Beckman Glass Electrode continuous pH Indicators for the immediate guidance of the operators and in the laboratory by substituting the presently used colorimetric or the potentiometric antimony pH instruments with the Beckman type Glass Electrode pH Instruments.

The matter of cost of replacing these laboratory instruments should not be looked upon as an insuperable item, for it is **easy** to see that inaccurate or faulty equipment may lead to errors in the manufacturing process which could on any one day be far more expensive than the cost of such an instrument. Neither can there be an argument on the ground that if the antimony electrodes have been found to give faulty results, that there is no assurance that the same may not happen with the glass electrode instruments, for today the industry at large knows positively that the glass electrode is the logical first choice because of its wide pH range, freedom of scale errors, freedom of poisoning and for the easy reproducibility of its results, and that its pH indications check under all working conditions within extremely narrow limits with the pH values as determined with the hydrogen electrode which, after all, is the ultimate standard against which the values found by all other pH instruments, or methods, are referred to.

SUMMARY

Report is made of an investigation undertaken in the Oxnard factory laboratory of the American Crystal Sugar Company during campaign 1939 on the pH values of various beet sugar factory products if these are measured, as is customary, at room temperature or at the actually existing factory temperatures.

Method of procedure and description of equipment used is given.

It was found that the actual pH of the juices at, or near, the process temperatures is very appreciably lower than that of the same juices if measured at 25° C.

It was found experimentally at first and later confirmed under factory conditions, that when the laboratory pH value seemed to be well above pH 7.0, that such juices at boiling temperatures may be well below pH 7.0 and may suffer serious inversion losses.

The hope of finding a constant correction factor to be applied to the laboratory determined pH values so that a measure be had as to what the actual operating pH may be, did not materialize.

The results obtained so far throw a heavy shadow of doubt on the reliability of the pH results as presently determined at room temperature as to their value of being a dependable guide to the operators.

The recommendation is made that glass electrode pH indicating instruments be placed into strategic positions in the house and that the laboratory control be carried out with similar instruments.