DRY SUBSTANCE BY DRYING

versus

DRY SUBSTANCE BY IMMERSION REFRACTOMETER

AS MEASURED IN THE NORMAL WEIGHT SOLUTION

F. R. Bachler

In the course of mutual control analyses of weekly composite samples collected in all the factories of the American Crystal Sugar Company and which were exchanged between, and analyzed by, the different laboratories, the outstanding disagreements were found to exist in the item of "per cent dry substance by drying".

Inasmuch as the true purity based upon dry substance by drying is used as one of the important criteria in judging individual factory efficiency, disagreements between the various laboratories in this item became a serious problem which finally resulted in raising the question as to "how true" the true purity can be when dry substance by drying at 105° C. could not be determined by the different chemists with at least the same degree of accuracy as is the case with the item of per cent sucrose by the Clerget method.

Relief in this respect came about in 1933 with the introduction of the normal weight solution method of analysis by the author in which all determinations are carried out in the same solution which must be prepared for polarization and with the decision, that henceforth in all of the factories of the American Crystal Sugar Company the immersion refractometrically determined dry substance was to replace the dry substance by drying at 105° C.

This move was justified not only because the refractometric dry substance of the control samples checked within even narrower limits than the polarizations but also because we were able to adduce proof that THE WEIGHT LOSS AT 105° C. WAS NOT SOLELY DUE TO LOSS OF MOISTURE BUT WAS ALSO DUE TO PROFOUND CHEMICAL CHANGES THAT OCCUR DURING DRYING WHICH RESULT IN AN APPARENT LOSS OF ACTUAL DRY SUBSTANCE showing, that the heretofore accepted method of dry substance by drying at 105° C. was giving too inaccurate results to warrant their use for the calculation of the "true" purity.

These dry substance losses we established by refractometric measurements and it is the purpose of this paper to describe our method of procedure and report on the results which have been obtained by drying at 105°. Another series of similar analyses comparing drying at 105° C. with drying in vacul at 60° C. with corresponding refractometric measurements will be reported upon their completion.

II.

The method of determining the dry substance of a product by drying rests upon the supposition that under the observance of the ordinary analytical precautions only free moisture is removed and that no weight consuming changes in the dry substance itself do occur.

If this supposition is true in the case of sugar products, then it should be possible within reasonable limits to find the same per cent of refractometric dry substance in a sample before and after drying.

To ascertain this point a series of experiments were made with products of different purity as collected in our different factories in which the following procedure was employed:

The sample was first made homogeneous by thorough mixing and kneading; two portions of 5.200 grams were then weighed out.

Portion A was made up of 100 ml. with distilled water of 20° C. A portion of this solution was refractometered at 20° C. The balance was clarified with a weighed portion of Horne's dry sub lead acetate and then polarized at 20° C.

Portion B was dried under carefully regulated strictly uniform conditions at atmospheric pressure at a temperature of 105° C. Constancy of weight was assumed to have been reached when two successive weighings agreed to within 0.05% dry substance. (In the case of molasses we ran very frequently against the condition that after a certain length of drying time the weight of the dried sample showed an increase rather than a decrease in weight).

The sand used for drying was acid and water washed, strongly heated, again washed and finally screened to uniform size. For each determination exactly 50 grams of sand were taken. In each case we added 5 ml. of boiling hot distilled water to facilitate uniform distribution of the sample within the sand. Thirty minutes of the pre-drying, followed by renewed stirring of the mixture, preceded the actual drying at 105° C. in the electrically heated oven which was automatically controlled to within ± 1° C.

In the case of molasses samples these were first thoroughly mixed, then de-aired by heating in a water jacketted funnel, screened through a fine mesh funnel, allowed to cool to room temperature and then analyzed. All analyses were made in duplicate and if the results did not agree closely, the test was repeated in its entirety.

The dry matter was then dissolved with boiling distilled water. The soluble portion was transfered to the same 100 ml. flask that was used for portion A, made up to 100 ml. at 20° C., refractometered at 20° C., clarified with the same weight of Horne dry lead as used in portion A and then polarized at 20° C.

On Table I are given the detailed results of one group of samples. On Table II are given summary results of analyses of similar products collected in widely separated localities and during different campaigns.

Table I

Comparing Refractometric Dry Substance with Dry Substance by Drying

A. Refractometric Dry Substance and Direct Polarization

	Item No.	White Fillmass			Intern.Fillmass			Raw Fillmass			Molasses		
		a	b	Avg.	a	b	Avg.	a	b	Avg.	a	b	Avg.
Grams of original product	1	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2
Refract. Scale Reading at 20°C	2	17.70	17.71	17.70	17.78	17.80	17.79	18.25	18.25	18.25	16.40	16.43	16.42
Grams of Refractometric dry substance	3	4.730	4.732	4.731	4.756	4.760	4.758	4.880	4.880	4.880	4.390	4.395	4.392
% Refractometric Dry Subst. on original product	4			90.98			91.50			93.84			84.47
% Direct Polarization	5	16.94	16.96	16.95	15.68	15.70	15.69	14.13	14.15	14.14	9.48	9.50	9.49
Gms. of direct polarization sucrose	6	4.404	4.410	4.407	4.077	4.082	4.079	3.674	3.679	3.676	2.465	2.490	2.467
Apparent Purity	7			93.15			85.72			75.32			56.16

B. Dry Substance by Drying and Direct Polarization

Grams of original product	8	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2
Grams of dry substance	9	4.694	4.702	4.698	4.714	4.726	4.720	4.826	4.818	4.822	4.262	4.274	4.268
% Dry substance by drying on original product	10			90.34			90.77			92.73			82.04
% Direct Polarization(See note)*	11			16.95			15.69			14.14			9.49
Gms. of direct polarization sucrose	12			4.407			4.079			3.676			2.467
Apparent purity	13			93.80			86.41			76.23			57.80

C. Refractometric Dry Substance and Direct Polar. of Re-Dissolved Dry Subst.

Refractometric Scale Read.20°C.	14	17.57	17.55	17.56	17.58	17.60	17.89	17.92	17.95	17.93	16.02	16.05	16.03
Gms. of Refractometric dry subst.	15	4.696	4.690	4.692	4.706	4.710	4.708	4.797	4.800	4.798	4.282	4.290	4.286
% Refractometric Dry Substance as if in original product	16			90.23			90.54			92.27			82.42
% Direct Polarization	17	16.74	16.78	16.76	15.34	15.36	15.35	13.65	13.70	13.69	9.10	9.15	9.12
Gms. of Direct Polarization Sucrose	18	4.352	4.363	4.358	3.998	3.994	3.991	3.549	3.562	3.554	2.366	2.379	2.371
Apparent Purity	19			92.88			84.77			74.07			55.31

Note: Items 11 and 12 same as 5 and 6

The difference between items 3 and 15 and items 6 and 18 afford a measure of the changes that occur during drying.

Oxnard, Cal. December 1939 (F.R.Bachler)

Table II - Comparison of Refractometric Dry Substance with Dry Substance by Drying

A. Refractometric Dry Substance and Direct Polarization

	Steffens House Raw Fillmass					Straight House Raw Fillmass					Steffens House Molasses					Straight House Molasses				
	Oxnard	Rocky Ford	Grand Island	Mason City	Average	Clarksburg	Missoula	E. Grand Forks	Chaska	Average	Oxnard	Rocky Ford	Grand Island	Mason City	Average	Clarksburg	Missoula	E. Grand Forks	Chaska	Average
	8	3	8	4	23	3	2	6	8	19	8	3	8	4	23	3	2	6	8	19
	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2
	18.23	18.07	18.06	18.08	18.11	18.43	18.42	18.22	18.21	18.32	15.61	16.27	16.17	16.07	16.03	16.26	16.37	16.11	16.17	16.23
	4.872	4.825	4.824	4.836	4.839	4.927	4.919	4.876	4.867	4.897	4.183	4.356	4.326	4.300	4.290	4.352	4.373	4.314	4.322	4.340
	93.70	92.80	92.77	93.00	93.06	94.75	94.60	93.77	93.60	94.48	80.45	83.77	83.20	82.70	82.53	83.7	84.10	82.96	83.12	83.47
	14.20	14.81	14.36	14.21	14.39	14.63	14.83	14.27	14.11	14.46	9.56	10.65	10.28	9.60	10.02	9.90	10.12	9.65	9.33	9.75
	3.692	3.850	3.734	3.695	3.725	3.804	3.857	3.710	3.670	3.760	2.486	2.769	2.673	2.499	2.606	2.572	2.631	2.509	2.426	2.534
	75.7	79.7	77.4	76.4	77.0	77.2	78.4	76.1	75.4	76.8	59.4	63.5	61.7	58.1	60.7	59.1	60.1	53.1	56.1	58.4

B. Dry Substance by Drying and Direct Polarization

	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2
	4.782	4.735	4.732	4.731	4.745	4.803	4.809	4.672	4.729	4.753	4.029	4.273	4.229	4.103	4.158	4.169	4.216	4.120	4.126	4.158
	91.96	91.05	91.00	90.98	91.25	92.36	92.48	89.84	90.94	91.40	77.48	82.17	85.33	78.90	79.96	80.17	81.07	79.23	79.34	79.96
	14.20	14.81	14.36	14.21	14.39	14.63	14.83	14.27	14.11	14.46	9.56	10.65	10.28	9.60	10.02	9.90	10.12	9.65	9.33	9.75
	3.692	3.850	3.734	3.695	3.725	3.804	3.857	3.710	3.670	3.760	2.486	2.769	2.673	2.499	2.606	2.572	2.631	2.509	2.426	2.534
	77.2	81.3	78.9	78.1	78.5	79.2	80.2	79.4	77.6	79.1	61.7	64.8	63.2	60.9	62.7	61.7	62.4	60.9	58.8	60.94

tric Dry Substance and Direct Polarizati on, Determined on Above Re-Dissolved Dry Substance by Drying

	17.97	17.66	17.67	17.82	17.75	18.12	18.07	17.94	17.90	18.02	15.17	15.52	15.57	14.44	14.44	15.67	15.93	15.45	15.73	15.71
	4.803	4.725	4.726	4.766	4.755	4.841	4.829	4.788	4.786	4.811	4.063	4.154	4.172	4.131	4.130	4.193	4.267	4.141	4.206	4.207
	92.41	90.85	90.95	91.68	91.47	93.12	92.83	92.15	92.05	92.53	78.12	79.85	80.25	79.45	79.41	80.85	82.12	79.65	80.85	80.86
	13.80	14.03	13.78	13.77	13.79	14.17	14.34	13.85	13.70	14.01	8.90	9.73	9.44	8.80	9.22	9.18	9.39	8.88	8.59	9.01
	3.588	3.648	3.583	3.580	3.600	3.684	3.728	3.601	3.561	3.643	2.316	2.530	2.453	2.289	2.397	2.382	2.441	2.310	2.233	2.341
	74.7	77.2	75.8	75.1	75.7	76.1	77.2	75.2	74.4	75.7	57.0	60.9	58.8	55.4	58.0	56.8	57.2	55.8	53.1	55.7

as items 5 and 6
ems 3 and 15 and items 6 and 18 afford a measure of the changes that occur during drying.

(F. R. Bachler)

III. Discussion of Results

Had no loss of dry substance or decomposition changes occurred during drying, then the average refractometric weight of dry substance as determined in portion A (Table I, Item 3) and that of the re-dissolved dry substance of portion B (Table 1, Item 15) should have been very nearly equal. We find, however, that during drying at 105° C. happened, a decided loss of refractometric dry substance as is shown by the following figures:

	Total grams of Refractometric Dry Sub. lost	Loss in % on Refr. Dry Sub. of Sample A
White Fillmass	0.039	0.82
Intermediate Fillmass	0.050	1.05
Raw Fillmass	0.082	1.68
Molasses	0.106	2.42

At the present stage of these investigations, we are looking upon these refractometric dry substance losses as a closely approximate measure of the sum total of actual dry substance losses which occur during drying at 105° C.

In regular analytical procedure we would ordinarily compare the refractometric dry substance of the original product with the dry substance by drying of the original product and in doing so obtain the following comparisons:

	White Fillmass	Inter. Fillmass	Raw Fillmass	Molasses
Grams of Refrac. Dry Subst(item 3)	4.731	4.758	4.880	4.392
Grams Dry Subst. by drying (item 9)	4.698	4.720	4.822	4.268
Dry Subst. by drying is smaller	.033	.038	.058	.124
Diff. in % on Refr. Dry Subst.	0.69	0.79	1.18	2.82

These differences are large enough to cause appreciable variations in purity as seen in the following comparison:

	White Fillmass	Inter. Fillmass	Raw Fillmass	Molasses
Appar. Purity by Refr. (item 7)	93.15	85.72	75.32	56.16
Appar. Purity Dry Subst. (item 13)	93.80	86.41	76.23	57.80

The analyses show that the removal of moisture by drying at 105° C. is accompanied by a far reaching decomposition of original solid matter which becomes manifest by appreciably lowered polarimetric and refractometric readings.

These losses appear smallest in the white fillmass and are greatest in the final molasses. Taken as a whole, they are lower in non-Steffens than in Steffens houses.

It cannot be gainsaid that the effects of heat and time during drying become manifest in two directions; the one resulting in a direct loss of dry matter due to volatilization of some of the solid constituents, the other of causing changes in the refractive indices of some of the solids. These refract-

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 by some 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