RP536

THE PREPARATION OF OPTICALLY STABLE SUGAR SOLUTIONS FOR COLORIMETRIC ANALYSIS[1]

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ABSTRACT

The successful application of colorimetry in the sugar industry is dependent upon the development of a satisfactory technique for preparing sugar solutions having a satisfactory degree of transparency. In the present paper existing methods have been revised. The process of clarification has been shortened and the transparency of the solutions improved. These results have been accomplished by increasing the concentration of the dry substance or total solids, dissolving and filtering the sugar products hot, and developing the application of better filters. In addition, other details of manipulation have been improved.

CONTENTS

I. INTRODUCTION

Peters and Phelps[2] in an earlier publication, hereinafter referred to as T338, have described methods used in the preparation of sugar solutions for colorimetric analysis and have discussed the optical properties of sugar solutions, particularly with reference to the effect of turbidity upon color measurement. They found that uncontrollable errors of varying magnitude result from turbidity and that Beer's law does not hold for turbid solutions. In order to secure the necessary degree and stability of transparency, advantage was taken of the protective action of sucrose in concentrated solution toward the turbidity-producing colloids. The solutions were so prepared as to have as high a concentration of total solids or dry substance (d. s.) as was compatible with a reasonably rapid filtration rate with the filtering apparatus then available and at the same time avoid crystalization. The dry substance (d. s.) concentration was placed at about 0.70 g per ml, corresponding to approximately 55 Brix. The solutions were then filtered through pads of purified asbestos.

More recent experience, especially with hard white sugars, has shown that a more satisfactory and more stable degree of transparency is obtainable for this class of sugars if the dry substance concentration be made much higher. In the present paper it is therefore recommended that this never be lower than 60 Brix (about 0.77 g per ml) and without disadvantage may be higher. The samples of sugar product are to be dissolved and diluted with the aid of heat and

[1] Presented in part before the sugar division of the American Chemical Society at Swampscott, Mass., September, 1928, under the title "The Spectrophotometry of White Sugars."
[2] H. H. Peters and F. P. Phelps, B. S. Tech. Paper No. 338, Pt. II, March, 1927.

filtered warm. Filtering apparatus with greater filter area than that formerly used for retaining the asbestos is also described so that the process of clarification is hastened. A method for the dilution of color with dry colorless sugar is also described.

II. FILTERS

Two filters with pads of purified asbestos are to be prepared before the sugar solution is made up. Various forms of filters are suitable. Among these the 25 ml Gooch crucibles fitted with a disk of 200-mesh bolting silk, as recommended in T338, page 211, is convenient and low priced. Greater filter area may be similarly obtained by fitting a 10 cm glass funnel with a 4 cm perforated porcelain plate which is then covered with 200-mesh bolting silk as above. Because of convenience and cleanliness Jena filters in the form of cylindrical funnels, 60 or 120 ml capacity with 4 cm fritted glass filter disks, have been found most satisfactory. The largest pore size, No. 1, is used for preliminary, and No. 3 which is much finer, for the final filtration. The pores of the latter frequently become clogged with fine asbestos which retards filtration. The intermediate pore size, No. 2, allows the passage of fine asbestos which, however, usually ceases after several washings with water and the filtration of 100 ml or less of high density sirup. This size as well as the No. 1, after careful preparation of the pads, has been successfully used for the final filtration.

When forming the pad, regardless of what form of filter is employed, the asbestos is sucked down by means of the aspirator and packed tightly by tamping with a blunt stirring rod to produce a layer about 0.5 cm thick. The pad is then washed several times with water (See T338, p. 271.) Equally good clarification has been obtained with XXX, XX, or A grade asbestos. The finer-fibered grades B and C give satisfactory filtration, but there is greater difficulty in washing out the acid used in purification. A rapid method for purifying asbestos has been described elsewhere.[3]

Diatomaceous earth has been used, especially in Europe, as an aid in clarifying sugar solutions for colorimetric analysis. Mastalir[4] has recently shown that this material has a decided decolorizing effect upon molasses solutions.

Working with a 60 Brix solution of washed raw sugar rendered transparent by two filtrations with asbestos, the present writers twice repeated the filtration with purified standard filter cel (1 per cent by weight of dry substance) and observed the following decrease in $-\log t$ at wave length 560: Asbestos filtrate, $-\log t=0.236$; first filter cel filtrate, $-\log t=0.216$; second filter cel filtrate, $-\log t=0.166$. A corresponding decrease was observed at four other wave lengths. Because of this decolorizing action, diatomaceous earth, even in the improved forms now available, is not regarded as being suitable for the clarification of sugar solutions that are to be subjected to colorimetric analysis. Peters and Phelps (T338, p. 269), after trying the best grades of Kieselguhr then available, rejected this material because it not only decolorized but also acted selectively, causing a change in the slope of the absorption curve.

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[3] J. F. Brewster and F. P. Phelps, J. Ind. Eng. Chem. (Analyt. ed.), vol. 2, p. 373, 1930.
[4] V. Mastalir, Zeit. Zuckind. Cechosl. Rep., vol. 56, p. 337, 1931–32.

III. CALCULATION OF WEIGHTS

A generous supply of turbid solution should be available, the amount to be prepared depending upon the capacity of the optical cells employed. Time is saved by preparing a definite weight of solution having a definite, predetermined Brix which may be satisfactorily approximated by using a rough balance. No fractional gram weights are used except in the case of very dark products that require dilution of color. These will be considered in a later section. The required weights of sample and water may be calculated as follows:

$$\frac{\text{Weight of solution required} \times \text{Brix of solution}}{\text{Brix of sample}} = \text{weight of sample to be taken.}$$

Weight of water to be added = weight of solution − weight of sample. The Brix of dry sugars may be assumed to be 100. In the case of nearly dry products of relatively high purity such as 96 test raw sugars, a sufficiently close approximation results if polarization be substituted for Brix of sample in the denominator of the above fraction.

The transparency of thin liquors may be improved by the addition of an amount of sucrose, previously tested and found to be colorless, sufficient to increase the Brix to 60 or higher. The weight of water in this case remains constant and the formula for calculation may be written:

$$\frac{\text{Weight of solution required} \times (100 - \text{Brix of solution})}{100 - \text{Brix sample}} = \text{weight of sample.}$$

Weight of solution − weight of sample = weight of sucrose to be added.

IV. PREPARATION AND FILTRATION OF THE SAMPLE

The calculated amount of sample to provide a solution of 60 to 65 Brix is weighed in a tared flask and weights equivalent to the required amount of water are added to the pan. The flask with contents is placed in a water bath heated to 80° to 90° C. and hot distilled water is added in small quantities at a time, the flask being shaken to promote quick solution and to insure a high concentration. To guard against over dilution the flask dried on the outside is occasionally placed on the balance pan.

When solution is complete and the required amount of water has been added, purified asbestos (grade A) in amount equal to about 0.5 per cent of the solution is added. The flask is then closed with a clean rubber stopper, and vigorously shaken. The flask is returned to the warm bath and the preliminary filter is heated by rinsing with hot distilled water which is drawn off as thoroughly as possible by suction. A few milliters of the warm solution are poured on the pad and drawn through to displace water. The main portion of the solution, or as much as the filter will hold, is added and after a few drops have filtered the suction is stopped and a clean receiver is substituted. The pads are to be kept covered with solution during filtration, at the end of which the suction is stopped before the pad becomes uncovered. The receiver is detached and returned to the bath while the second filter is being rinsed with hot water and drained.

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The second filtration is performed exactly as the first, no asbestos being added to the first filtrate. The main portion of the filtrate is collected in a clean receiver. This filtrate is cooled and adhering water wiped from the neck of the bottle which is then closed with a clean, dry stopper and shaken to mix the contents thoroughly. The refractometric Brix of the optically clear filtrate is determined and c (=g dry substance per ml) obtained by reference to Table 2 (Appendix). The solution is now ready for colorimetric examination. With properly prepared solutions and filters further filtration is of doubtful value unless some scattered particles of asbestos have passed through. If the second filtrate appears turbid the best practice is to prepare a new solution with increased dry substance concentration. Jena filters are easily cleansed by removing the pads and drawing water and air through the pores by means of the aspirator connected alternately to the mouth and the stem of the funnel. This dislodges asbestos fibres, which may be poured out. Treatment of the glass filters with chromic-sulphuric acid mixture removes waxy or greasy film deposited by sugar solutions.

V. DILUTION OF COLOR

Directions are given in T338, pp. 277 and 285–286, for the dilution of very dark sugar solutions with colorless sirup in order that good photometric readings may be made and to insure a high degree of transparency. Instead of employing for this purpose a stock sirup, which may be subject to decomposition and change in storage, a high-grade, nearly colorless solid sugar may be used in the following manner: One hundred grams of the solid sugar are weighed in a tared flask. A small amount of the colored sample whose dry substance content has been determined is introduced and the whole reweighed. All these weighings should be accurate to the nearest milligram in order that the proportion of colored dry substance may be calculated. The mixture is dissolved and diluted to 60 to 65 Brix exactly as described in the foregoing section. Sugar of the quality of the highest grade refinery tablets may be used as diluent and for accurate results its absorbancy may be deducted. The specific absorptive index of good tablet sugars is less than 0.005 at wave length 560 and in many cases this may be ignored as not affecting the final results. The reference at the head of this section is to be consulted for methods of calculating colored dry substance in the mixture.

VI. COMPARISON OF PROCEDURES

In Table 1 are given for comparison results obtained by varying the dry substance concentration and the temperature at which the samples were dissolved and filtered. Four types of sugar products were used, each diluted to three different d. s. concentrations designated in column 2 as A, B, and C, corresponding, respectively, to 55, 60, and 65 Brix, the approximate concentration before filtration. The final concentration after filtration and cooling is given as refractometric Brix in column 3, and as the corresponding c in g per ml in column 4. In column 5 is given the specific absorptive index, $-\log t$, at λ 560 mμ of each solution. In column 6 are shown the differences $(-\log t\ \mathrm{A})-(-\log t\ \mathrm{B})$ and $(-\log t\ \mathrm{C})-(-\log t\ \mathrm{B})$ expressed as per cent $-\log t$ B. In column 7 the approximate temperatures at which the solutions were prepared are given. The solutions prepared at 40° were filtered at room temperature, while those prepared at 70° were filtered at 70°.

The influence of dry substance concentration is to be seen by reference to columns 5 and 6. Regardless of the temperature at which the solutions were prepared, the highest absorption value for any given product occurs in the solution having the lowest density and is attributed to the presence of turbidity in these solutions that is not removable by the filtration method used. (Compare T388, p. 280.)

Samples 8 and 9 were prepared by dispersing the molasses in very pure sucrose solution as described in Section V. The proportion of molasses dry substance in total dry substance varied from 0.88 to 1.13 per cent and the general agreement among the results demonstrates the effectiveness of sucrose in preventing turbidity. Optical disturbance due to crystallization in 70 Brix sugar solutions has never been encountered and it is therefore inferred that many high density refinery or factory liquors may be prepared for colorimetric analysis without further dilution.

TABLE 1.—*Comparison of procedures*

I. PLANTATION GRANULATED SUGARS

Sample No.	Designation of solution	Brix by refractometer	c in g/ml	−log t λ 560	Difference per cent on −log t B	Approximate temperature of solution
1	2	3	4	5	6	7
						° C.
1	A	55.2	0.6948	0.0213	+10.40	40
	B	61.3	.7933	0.0193		70
	C	66.4	.8800	.0199	+3.11	70
2	A	56.0	.7074	.0458	+3.62	40
	B	61.4	.7940	.0442		40
	C	66.3	.8780	.0440	−.45	40

II. WASHED RAW SUGARS

Sample No.	Designation of solution	Brix by refractometer	c in g/ml	−log t λ 560	Difference per cent on −log t B	Approximate temperature of solution
3	A	55.1	0.6533	0.349	+26.29	70
	B	60.7	.7834	.275		70
	C	67.0	.8064	.276	+.36	70
4	A	55.4	.6979	.300	+41.51	40
	B	61.0	.7883	.212		40
	C	68.8	.9217	.208	−1.89	70
5	A	57.5	.7313	.244	+5.18	70
	B	60.1	.7735	.232		70
	C	69.6	.9359	.234	+.85	70

III. RAW SUGARS (UNWASHED)

Sample No.	Designation of solution	Brix by refractometer	c in g/ml	−log t λ 560	Difference per cent on −log t B	Approximate temperature of solution
6	A	55.2	0.6948	1.224	+9.29	40
	B	61.4	.7949	1.120		70
	C	71.8	.9754	1.105	−1.34	70
7	A	55.1	.6932	1.201	+19.99	70
	B	61.4	.7949	1.001		70
	C	70.3	.9483	1.000	−.10	70

IV. MOLASSES

Sample No.	Designation of solution	Brix by refractometer	c in g/ml	−log t λ 560	Difference per cent on −log t B	Approximate temperature of solution
8	A	55.7	0.7027	33.10	+2.48	70
	B	60.5	.7801	32.30		70
	C	66.1	.8750	32.82	+1.55	70
9	A	56.2	.7106	53.00	+.57	70
	B	61.8	.8016	52.70		70
	C	66.2	.8763	53.10	+.76	70

VII. APPENDIX. TABLE 2.—DENSITIES OF PURE SUCROSE SOLUTIONS

This table is an expansion of Table 2, B. S. Tech. Paper No. 338, page 304, and gives values corresponding to degrees Brix to cover the higher densities recommended. It is to be used for finding values of *c* (g dry substance per ml) corresponding to degrees Brix, density, or apparent specific gravity of sugar solutions from analytical data. The tabulated values were derived in the manner already fully described in the publication referred to above.

TABLE 2.—*Densities of pure sucrose solutions*

Brix or true per cent d. s. by weight	True density (Plato) 20°	Apparent density 20°	Apparent specific gravity 20°/20°	g sucrose per 100 ml weight in vacuo	Brix or true per cent d. s. by weight	True density (Plato) 20°	Apparent density 20°	Apparent specific gravity 20°/20°	g sucrose per 100 ml weight in vacuo
1	2	3	4	5	1	2	3	4	5
59.0	1.28059	1.27958	1.28320	75.555	64.0	1.31028	1.30927	1.31297	83.858
59.1	118	1.28017	379	.718	64.1	089	988	359	84.028
59.2	176	075	437	.880	64.2	149	1.31048	418	.198
59.3	235	134	497	76.043	64.3	209	108	479	.367
59.4	294	193	556	.207	64.4	270	169	540	.538
59.5	352	251	614	.369	64.5	330	229	600	.708
59.6	411	309	672	.533	64.6	391	290	661	.879
59.7	469	367	731	.696	64.7	452	350	723	85.049
59.8	528	426	789	.860	64.8	512	412	784	.220
59.9	587	485	849	77.024	64.9	573	473	845	.391
60.0	1.28646	1.28544	1.28908	77.188	65.0	1.31633	1.31533	1.31905	85.561
60.1	704	602	966	.351	65.1	694	594	966	.733
60.2	763	661	1.29025	.515	65.2	755	655	1.32028	.904
60.3	822	720	084	.680	65.3	816	716	089	86.076
60.4	881	779	143	.844	65.4	877	777	150	.248
60.5	940	838	203	78.009	65.5	937	837	210	.419
60.6	999	897	262	.173	65.6	998	898	271	.591
60.7	1.29058	956	321	.338	65.7	1.32059	959	332	.763
60.8	117	1.29015	380	.503	65.8	120	1.32019	393	.935
60.9	176	074	439	.668	65.9	181	081	455	87.107
61.0	1.29235	1.29133	1.29498	78.833	66.0	1.32243	1.32142	1.32516	87.280
61.1	295	193	559	.999	66.1	304	203	577	.453
61.2	354	252	618	79.165	66.2	365	264	638	.626
61.3	413	311	677	.330	66.3	426	325	699	.798
61.4	472	370	736	.496	66.4	487	385	759	.971
61.5	532	430	796	.662	66.5	548	446	820	88.142
61.6	591	489	855	.828	66.6	610	509	884	.318
61.7	651	548	915	.995	66.7	671	570	945	.492
61.8	710	608	975	80.161	66.8	733	632	1.33007	.666
61.9	770	667	1.30034	.328	66.9	794	693	068	.839
62.0	1.29829	1.29726	1.30093	80.494	67.0	1.32855	1.32754	1.33129	89.012
62.1	889	786	153	.661	67.1	917	816	192	.187
62.2	948	845	212	.828	67.2	979	878	254	.361
62.3	1.30008	905	273	.995	67.3	1.33040	939	315	.536
62.4	068	966	234	81.162	67.4	102	1.33001	377	.711
62.5	127	1.30025	393	.329	67.5	163	062	438	.885
62.6	187	085	453	.497	67.6	225	124	500	90.060
62.7	247	145	513	.665	67.7	287	186	562	.235
62.8	307	205	573	.833	67.8	349	248	625	.411
62.9	367	265	633	82.001	67.9	410	309	686	.585
63.0	1.30427	1.30325	1.30694	82.169	68.0	1.33472	1.33371	1.33748	90.761
63.1	487	385	754	.337	68.1	534	433	810	.937
63.2	547	446	815	.506	68.2	596	495	872	91.112
63.3	607	506	875	.674	68.3	658	557	935	.288
63.4	667	566	936	.843	68.4	720	619	997	.464
63.5	727	626	994	83.012	68.5	782	681	1.34059	.641
63.6	787	686	1.31055	.180	68.6	844	743	121	.817
63.7	848	747	117	.350	68.7	906	805	183	.993
63.8	908	807	177	.519	68.8	968	867	245	92.169
63.9	968	867	237	.688	68.9	1.34031	930	309	.347

TABLE 2.—*Densities of pure sucrose solutions*—Continued

Brix or true per cent d. s. by weight	True density (Plato) 20°	Apparent density 20°	Apparent specific gravity 20°/20°	g sucrose per 100 ml weight in vacuo	Brix or true per cent d. s. by weight	True density (Plato) 20°	Apparent density 20°	Apparent specific gravity 20°/20°	g sucrose per 100 ml weight in vacuo
1	2	3	4	5	1	2	3	4	5
69.0	1.34093	1.33992	1.34371	92.524	75.5	1.38220	1.38119	1.38510	104.356
69.1	155	1.34054	433	.701	75.6	285	184	575	.543
69.2	217	116	495	.878	75.7	350	249	640	.731
69.3	280	179	558	93.056	75.8	415	314	705	.919
69.4	342	241	621	.233	75.9	480	379	770	105.106
69.5	405	304	684	.411	76.0	1.38545	1.38444	1.38835	105.294
69.6	467	366	746	.589	76.1	610	510	902	.482
69.7	530	429	809	.767	76.2	675	575	967	.670
69.8	592	491	871	.945	76.3	740	640	1.39032	.859
69.9	655	554	934	94.123	76.4	805	705	097	106.047
70.0	1.34717	1.34616	1.34997	94.302	76.5	870	770	162	.236
70.1	780	679	1.35060	.481	76.6	935	835	228	.424
70.2	843	742	123	.660	76.7	1.39000	900	293	.613
70.3	906	805	186	.839	76.8	065	965	358	.802
70.4	968	867	248	95.017	76.9	130	1.39030	423	.991
70.5	1.35031	930	311	.197	77.0	1.39196	1.39096	1.39489	107.181
70.6	094	993	375	.376	77.1	261	161	554	.370
70.7	157	1.35056	438	.556	77.2	326	225	619	.560
70.8	220	119	501	.736	77.3	392	291	685	.750
70.9	283	182	564	.916	77.4	457	356	750	.940
71.0	1.35346	1.35245	1.35627	96.096	77.5	523	422	816	108.130
71.1	409	308	691	.276	77.6	588	488	882	.320
71.2	472	371	754	.456	77.7	654	554	949	.511
71.3	535	434	817	.636	77.8	719	619	1.40014	.701
71.4	598	498	881	.817	77.9	785	685	080	.892
71.5	661	561	944	.998	78.0	1.39851	1.39751	1.40146	109.084
71.6	725	625	1.36008	97.179	78.1	916	816	211	.274
71.7	788	688	072	.360	78.2	982	882	277	.466
71.8	851	751	135	.541	78.3	1.40048	948	344	.657
71.9	914	814	198	.722	78.4	113	1.40013	409	.848
72.0	1.35978	1.35877	1.36261	97.904	78.5	179	079	475	110.041
72.1	1.36041	940	324	98.085	78.6	245	145	541	.232
72.2	105	1.36004	389	.268	78.7	311	211	607	.425
72.3	168	067	452	.449	78.8	377	277	674	.617
72.4	232	131	516	.632	78.9	443	343	740	.809
72.5	295	194	579	.814	79.0	1.40509	1.40409	1.40806	111.002
72.6	359	258	643	.997	79.1	575	475	872	.195
72.7	423	322	707	99.179	79.2	641	541	938	.388
72.8	486	385	771	.362	79.3	707	607	1.41005	.581
72.9	550	450	836	.545	79.4	774	674	072	.775
73.0	1.36614	1.36514	1.36900	99.728	79.5	840	740	138	.968
73.1	678	578	964	.912	79.6	906	806	204	112.161
73.2	742	642	1.37028	100.095	79.7	972	872	270	.354
73.3	805	705	092	.278	79.8	1.41039	939	337	.549
73.4	869	769	156	.462	79.9	105	1.41005	404	.743
73.5	933	833	220	.646	80.0	1.41172	1.41072	1.41471	112.938
73.6	997	896	283	.827	80.1	238	138	537	113.131
73.7	1.37061	960	347	101.014	80.2	304	204	603	.326
73.8	125	1.37024	411	.198	80.3	371	271	670	.521
73.9	189	088	476	.383	80.4	437	337	737	.715
74.0	1.37254	1.37153	1.37541	101.568	80.5	504	404	804	.911
74.1	318	217	605	.753	80.6	571	472	872	114.106
74.2	382	281	669	.937	80.7	637	537	937	.301
74.3	446	345	733	102.122	80.8	704	604	1.42004	.497
74.4	511	410	798	.308	80.9	771	671	072	.692
74.5	575	475	864	.493	81.0	1.41837	1.41737	1.42138	114.888
74.6	639	539	928	.679	81.1	904	804	205	115.084
74.7	704	604	993	.865	81.2	971	871	272	.280
74.8	768	668	1.38057	103.050	81.3	1.42038	938	339	.477
74.9	833	733	122	.237	81.4	105	1.42005	906	.673
75.0	1.37897	1.37797	1.38187	103.423	81.5	172	072	474	.870
75.1	962	862	252	.609	81.6	239	139	541	116.067
75.2	1.38026	926	316	.796	81.7	306	206	608	.264
75.3	091	991	381	.983	81.8	373	273	675	.461
75.4	156	1.38055	445	104.170	81.9	440	340	742	.658

TABLE 2.—*Densities of pure sucrose solutions*—Continued

Brix or true per cent d. s. by weight	True density (Plato) 20°	Apparent density 20°	Apparent specific gravity 20°/20°	g sucrose per 100 ml weight in vacuo	Brix or true per cent d. s. by weight	True density (Plato) 20°	Apparent density 20°	Apparent specific gravity 20°/20°	g sucrose per 100 ml weight in vacuo
1	2	3	4	5	1	2	3	4	5
82.0	1.42507	1.42407	1.42810	116.856	83.0	1.43181	1.43081	1.43486	118.840
82.1	574	475	878	117.053	83.1	248	148	553	119.039
82.2	642	543	946	.252	83.2	316	216	621	.239
82.3	709	610	1.43013	.449	83.3	383	283	688	.438
82.4	776	677	080	.647	83.4	451	351	756	.638
82.5	843	744	148	.845	83.5	519	419	824	.838
82.6	911	811	214	118.044	83.6	587	488	894	120.039
82.7	978	878	282	.243	83.7	654	555	961	.238
82.8	1.43046	946	350	.442	83.8	722	623	1.44029	.439
82.9	113	1.43013	417	.641	83.9	790	691	097	.640

WASHINGTON, December 19, 1932.