

FIGURE 5

The spreading rate at 2 per cent contrast is very nearly twice the absolute hiding power at complete hiding as determined in this group of tests. This value, however, is probably closer to the practical value of the paint than is the complete hiding value, because under practical conditions paint is rarely required to cover up a background so easily seen through the film. Kraemer and Schupp (6) find that the least perceptible contrast increases considerably when the contrast line is not sharp and may reach a value of nearly 2 per cent under the conditions they studied. For comparing paints or pigments it should be desirable to approximate the least perceptible contrast under practical rather than extreme conditions.

Although the hiding powers reported have been determined at one-coat thickness by the new incomplete hiding method described, the method has also been employed for comparing paints at two or more coats and up to complete hiding over this background. It is easy to distinguish small differences in hiding power at contrasts between 1 and 2 per cent and even to make gradings at contrasts below 1 per cent and thus

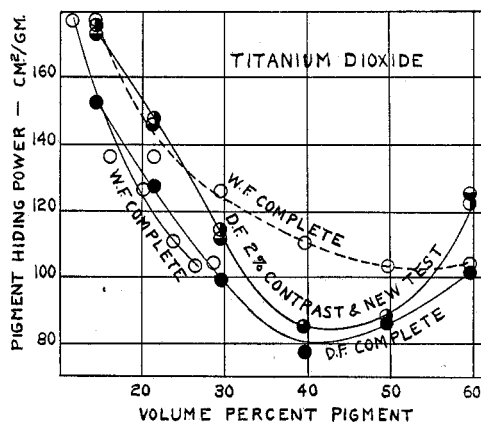


FIGURE 6

actually to see differences in paints over the design used at contrasts beyond complete hiding for less rigorous backgrounds. This is, in principle, similar to a method described by Haslam (5) except that visibility beyond "complete" hiding is secured by use of a more easily distinguished background rather than by alteration of the color temperature

characteristics of the source of illumination.

ACKNOWLEDGMENT

The writer acknowledges the criticisms and contributions of J. E. Booge, who suggested the study, and M. L. Hanahan, and the assistance of J. C. Knochel, R. S. Emslie, and J. W. Dunn in making the measurements for this paper.

LITERATURE CITED

- (1) Bruce, Bur. Standards, *Tech. Paper* 306 (1926).
- (2) Gardner, Sward, and Levy, *Am. Paint Varnish Mfrs.' Assoc., Sci. Sect., Circ.* 362 (1930).
- (3) Hallett, *Proc. Am. Soc. Testing Materials*, 30, 895 (1930).
- (4) Haslam, *IND. ENG. CHEM., Anal. Ed.*, 2, 69 (1930).
- (5) *Ibid.*, 2, 319 (1930).
- (6) Kraemer and Schupp, "Determination of Hiding Power of White Paints," presented before the 85th Meeting of the American Chemical Society, Washington, D. C., March 26 to 31, 1933.
- (7) Pfund, *J. Franklin Inst.*, 188, 675 (1919).
- (8) *Ibid.*, 196, 69 (1923).

RECEIVED June 21, 1933. Presented before the Division of Paint and Varnish Chemistry at the 85th Meeting of the American Chemical Society, Washington, D. C., March 26 to 31, 1933.

Comparative Clarification of Sugar Solutions

Copper Reduction and Iodine Titration Methods

L. G. SAYWELL AND E. P. PHILLIPS

Fruit Products Laboratory, College of Agriculture, University of California, Berkeley, Calif.

THE recent use of the iodine reduction method in the analysis of honey (8) and in plant materials (10, 12) raises the question of the effect of various clarification and clearing methods on the determination. The use of the iodine method for dextrose broadens the problem of clearing solutions for sugar analysis.

Many studies have been reported on the various methods of clarification and subsequent clearing. Englis and Tsang (4) reported that with clarification with basic lead acetate the de-leading with disodium phosphate appears to be most satisfactory. The work of Loomis (7) confirms that of Bryan (2) showing that the use of basic lead acetate results in the loss of some of the reducing sugars, probably through the formation of a less soluble lead oxide-sugar combination. This loss did not result with the use of neutral lead acetate. On the basis of the work of Sawyer (11), Eynon and Lane (5), and Mead and Harris (9), Loomis (7) used potassium oxalate as the deleading agent and found it convenient and satisfactory. Sodium oxalate instead of potassium oxalate may be preferable because of its lower solubility. Sodium

oxalate has been tentatively adopted by the Association of Official Agricultural Chemists (1, 15).

Inasmuch as Englis and Tsang (4) studied the effect of the various deleading agents with basic lead acetate only, and Loomis (7) in comparing basic and neutral lead acetates used potassium oxalate only, it appeared desirable to compare the use of disodium phosphate, potassium oxalate, and sodium oxalate with both the basic and neutral acetates.

The previous studies have employed only copper reduction methods of estimating the reducing sugars. Consequently a comparison was made of these several factors with both the copper reduction and iodine titration under the same laboratory conditions.

EXPERIMENTAL

All determinations were made on a standard invert sugar solution.

Inversion was obtained by mixing 100 grams of sugar with 30 ml. of distilled water, heating to boiling, adding 0.10 gram of crystalline tartaric acid previously dissolved in 3 ml. of distilled water, covering and boiling very slowly for 10 minutes, and cooling. Dilutions were made containing approximately 0.380 gram of invert sugar per 100 ml. of solution; 50-ml. aliquots were used for each determination, the lead compound being added to the aliquot (followed by filtration if cloudy). The lead was then precipitated by the desired deleading agent and the solution filtered. A saturated solution of neutral lead acetate was employed, 2.0 or 2.5 ml. being used for a determination. Varying quantities of the basic lead acetate (Horne's) were employed. Quantities of solid disodium phosphate, potassium oxalate, and sodium oxalate just sufficient to effect complete precipitation of the dissolved lead were added. The copper reduction method was that of Shaffer and Hartman (13), and the iodine oxidation method was that of Lothrop and Holmes (8).

RESULTS AND DISCUSSION

The data are given in Table I. In general neutral lead acetate and sodium oxalate constitute the most satisfactory combination of clarifying agents for both the iodine oxidation and copper reduction methods. Complete recovery of the dextrose was obtained with the iodine method and 99.7 per cent recovery with the copper method.

TABLE I. COMPARISON OF COPPER REDUCTION AND IODINE OXIDATION ESTIMATIONS OF CLARIFIED REDUCING SUGAR SOLUTIONS

IODINE OXIDATION				COPPER REDUCTION			
Blank dextrose	Re-covered dextrose	Recovery	Loss	Blank re-ducting sugars	Re-covered re-ducting sugars	Recovery	Loss
Mg.	Mg.	%	%	Mg.	Mg.	%	%
2.5 ML. OF SATURATED NEUTRAL LEAD ACETATE + POTASSIUM OXALATE							
94.4	93.9	99.5	0.5	188.8	186.4	98.7	1.3
94.4	93.7	99.3	0.7	188.8	186.5	98.8	1.2
2.0 ML. OF SATURATED NEUTRAL LEAD ACETATE + POTASSIUM OXALATE							
99.6	98.9	99.3	0.7	99.6 ^a	98.2 ^a	98.6	1.4
99.6	98.6	99.0	1.0	99.6 ^a	98.0 ^a	98.4	1.6
2.5 ML. OF SATURATED NEUTRAL LEAD ACETATE + SODIUM OXALATE							
94.4	94.4	100.0	0.0	188.8	188.4	99.7	0.3
94.4	94.4	100.0	0.0	188.8	188.0	99.5	0.5
94.4	94.4	100.0	0.0	188.8	188.4	99.7	0.3
94.4	94.4	100.0	0.0	188.8	188.4	99.7	0.3
2.5 ML. OF SATURATED NEUTRAL LEAD ACETATE + DISODIUM PHOSPHATE							
94.4	83.3	88.3	11.7	188.8	187.3	99.2	0.8
94.4	83.5	88.5	11.5	188.8	187.1	99.1	0.9
94.4	82.9	87.8	12.2	188.8	186.8	98.9	1.1
94.4	83.1	88.0	12.0	188.8	187.1	99.1	0.9
2.0 ML. OF SATURATED NEUTRAL LEAD ACETATE + DISODIUM PHOSPHATE							
99.6	90.7	91.1	8.9	99.6 ^a	98.2 ^a	98.6	1.4
99.6	91.1	91.5	8.5	99.6 ^a	98.3 ^a	98.7	1.3
0.17 GRAM OF BASIC LEAD ACETATE + POTASSIUM OXALATE							
95.5	95.3	99.8	0.2	191.0	183.4	95.1	4.9
95.5	95.1	99.5	0.5	191.0	183.6	95.2	4.8
0.34 GRAM OF BASIC LEAD ACETATE + POTASSIUM OXALATE							
95.5	94.9	99.4	0.6	191.0	180.5	94.5	5.5
95.5	94.7	99.2	0.8	191.0	180.3	94.3	5.7
0.50 GRAM OF BASIC LEAD ACETATE + POTASSIUM OXALATE							
95.5	94.5	99.0	1.0	191.0	177.1	92.7	7.3
95.5	94.7	99.2	0.8	191.0	177.0	92.7	7.3
1.0 GRAM OF BASIC LEAD ACETATE + POTASSIUM OXALATE							
99.6	92.3	92.7	7.3	99.6 ^a	91.8 ^a	92.2	7.8
0.17 GRAM OF BASIC LEAD ACETATE + SODIUM OXALATE							
95.5	95.5	100.0	0.0	191.0	185.0	96.9	3.1
95.5	95.3	99.8	0.2	191.0	184.5	96.6	3.4
0.34 GRAM OF BASIC LEAD ACETATE + SODIUM OXALATE							
95.5	94.9	99.4	0.6	191.0	181.0	94.7	5.3
99.5	95.1	99.5	0.5	191.0	181.1	94.7	5.3
0.50 GRAM OF BASIC LEAD ACETATE + SODIUM OXALATE							
95.5	95.3	99.8	0.2	191.0	179.2	93.7	6.3
95.5	95.3	99.8	0.2	191.0	179.2	93.8	6.2
LESS THAN 0.1 GRAM OF BASIC LEAD ACETATE + DISODIUM PHOSPHATE							
94.4	93.9	99.5	0.5	188.8	187.3	99.1	0.9
94.4	93.8	99.4	0.6	188.8	187.1	99.0	1.0
0.15 GRAM OF BASIC LEAD ACETATE + DISODIUM PHOSPHATE							
94.4	93.1	98.6	1.4	188.8	187.1	99.0	1.0
94.4	92.9	98.4	1.6	188.8	186.8	98.9	1.1
0.5 GRAM OF BASIC LEAD ACETATE + DISODIUM PHOSPHATE							
95.5	93.0	97.4	2.6	191.0	184.0	96.3	3.7
95.5	93.2	97.6	2.4	191.0	184.0	96.3	3.7

^a Dextrose.

Neutral lead acetate and potassium oxalate are only fairly satisfactory in the iodine method, 99.3 to 99.5 per cent re-

covery of dextrose being observed. Basic lead acetate and sodium oxalate are apparently quite satisfactory in the iodine method, 99.8 per cent of the dextrose being recovered. The use of basic lead acetate and either potassium oxalate or disodium phosphate resulted in losses of 0.5 to 7.3 per cent of dextrose, varying with the increase in basic lead acetate from 0.1 to 1.0 gram (per 50 ml. of test solution). The use of neutral lead acetate and disodium phosphate resulted in losses ranging from 11.5 to 12.2 per cent.

As above, the use of neutral lead acetate and sodium oxalate with the copper reduction method is satisfactory, an average of 99.7 per cent of the dextrose being recovered. All other methods resulted in losses of 0.8 to 7.8 per cent. These results confirm in general and extend those of the many previous studies and also provide a source of comparison. The difference in effectiveness of potassium and sodium oxalate with neutral lead acetate is marked, losses ranging from 0.5 to 1.0 per cent with the potassium salt to slightly over 0.3 per cent with sodium oxalate.

The marked buffering effect of the phosphate on the iodine reaction is evident in the two series with neutral lead acetate and disodium phosphate. In both cases there is a distinctly high loss of recovered dextrose (8.5 to 12.2 per cent) in the iodine titration. This loss would be expected on the basis of the lower hydroxyl-ion concentration in the phosphate solutions, incomplete oxidation occurring in such solutions (3, 6, 14) under the conditions of the determination.

SUMMARY

Solutions of invert sugar analyzed by the copper reduction and iodine oxidation methods are most satisfactorily clarified by neutral lead acetate and sodium oxalate, complete recovery of dextrose being observed with the iodine method and 99.7 per cent recovery with the copper method.

Other methods were less satisfactory, though with the iodine method, using neutral lead acetate and potassium oxalate or basic lead acetate and sodium or potassium oxalate, recoveries of 99.5 to 99.8 per cent of dextrose were observed.

All methods except that with neutral lead acetate and sodium oxalate resulted in losses of 0.8 to 7.8 per cent of dextrose or reducing sugars determined by the copper reduction method.

LITERATURE CITED

- (1) Assocn. Official Agr. Chem., Official and Tentative Methods, p. 112 (1930).
- (2) Bryan, A. H., U. S. Bur. Chem., *Bull.* 116, 73 (1907).
- (3) Englis, D. T., and Dykins, F. H., *IND. ENG. CHEM., Anal. Ed.*, 3, 21 (1931).
- (4) Englis, D. T., and Tsang, C. Y., *J. Am. Chem. Soc.*, 44, 865-7 (1922).
- (5) Eynon, L., and Lane, J. H., *J. Soc. Chem. Ind.*, 42, 143-6T (1923).
- (6) Hinton, C. L., and Macara, T., *Analyst*, 49, 2-24 (1924).
- (7) Loomis, W. E., *Plant Physiol.*, 1, 179-89, 403-7 (1926); 2, 195-204 (1927).
- (8) Lothrop, R. E., and Holmes, R. R., *IND. ENG. CHEM., Anal. Ed.*, 3, 334 (1931).
- (9) Mead, G. P., and Harris, J. B., *J. IND. ENG. CHEM.*, 8, 504-9 (1916).
- (10) Morris, V. H., and Wesp, E. F., *Plant Physiol.*, 7, 47-62 (1932).
- (11) Sawyer, H. E., *J. Am. Chem. Soc.*, 26, 1631-5 (1904).
- (12) Saywell, L. G., and Robertson, P., *Plant Physiol.*, 7, 705-10 (1932).
- (13) Shaffer, P. H., and Hartman, A. F., *J. Biol. Chem.*, 45, 349-90 (1921).
- (14) Slater, C. S., and Acree, S. F., *IND. ENG. CHEM., Anal. Ed.*, 2, 274 (1930).
- (15) Sullivan, J. T., *J. Assoc. Official Agr. Chem.*, 14, 225-8 (1931); 15, 509-16 (1932).

RECEIVED September 20, 1933. Presented before the Division of Agricultural and Food Chemistry at the 86th Meeting of the American Chemical Society, Chicago, Ill., September 10 to 15, 1933.