RESEARCH PAPER RP723

*Part of Journal of Research of the National Bureau of Standards, Volume 13,
October 1934*

A NOTE ON THE PURIFICATION OF α -D-XYLOSE AND ITS
MUTAROTATION

By Horace S. Isbell

ABSTRACT

The method of purifying sugar solutions by treatment with basic lead acetate has been applied with excellent results to the purification of dark-colored xylose residues from cottonseed hulls. The sirup obtained after such treatment crystallizes during the evaporation and yields a practically colorless product of good keeping quality and high purity.

Mutarotation measurements on the purified product show that the reaction rate decreases during the first few minutes after solution.

In the preparation of xylose and other sugars from natural products the crude sugar is frequently contaminated with various gums and other substances which interfere with the crystallization. Although lead acetate has been widely used¹ in the clarification of raw sugars, its use has not been heretofore reported for the preparation of xylose from cottonseed hulls. As is well known, basic lead acetate forms difficultly soluble salts with nearly all the alpha hydroxy acids and with many complex substances. Unless these acids and complex substances are removed they are instrumental in inhibiting crystallization of the sugar, and frequently cause excessive foaming. When xylose is prepared from cottonseed hulls, dark-colored sirups are sometimes obtained from which it is difficult to separate a high-purity sugar. If the sugar solution is treated with basic lead acetate a nearly colorless sirup results, from which a pure product can be obtained in good yield. Crude xylose prepared from cottonseed hulls without the lead treatment frequently turns dark in a short time; the product obtained after the lead treatment usually remains colorless for a much longer time. The lead treatment removes impurities to such an extent that the sugar crystallizes readily during the evaporation so that it may be "grained" in the evaporation pan. It is thus possible to eliminate a large part of the time and expense that would otherwise be incurred in the growing of crystals in a crystallizer.

The amount of lead acetate used should be sufficient to precipitate the impurities without an unduly large loss of sugar; that is, the minimum amount required to give a light-colored sirup which can be evaporated without foaming. If desired, the excess lead can be removed from the sirups in one step with hydrogen sulphide. Removing the lead with phosphoric acid as described in this paper usually gives a slightly better clarification, but probably there is a larger loss

¹ Browne, Handbook of Sugar Analysis, p. 207. John Wiley & Sons, New York, 1912.

of sugar, as the phosphate precipitate is fine and difficult to wash free from sugar. Equally satisfactory results may be obtained by using either a solution of lead subacetate or dry lead subacetate. In some cases normal lead acetate will effect sufficient purification and it has the advantage that an excess does not cause a loss of sugar.

Ten kilos of crude xylose² containing considerable calcium sulphate, gums, and other impurities was dissolved in water and treated with 1 kg of decolorizing carbon and filtered. The volume of the filtrate was 16 liters and its density corresponded to 46.5 Brix. The dark-colored filtrate foamed badly because of the large amount of impurities present. After adding 1 kg of dry lead subacetate and 500 g of kieselguhr the sugar solution was filtered. The major part of the excess lead in the filtrate was precipitated by adding phosphoric acid (115 ml of 85 percent acid) until a faint purple reaction was obtained with Congo red paper. The lead phosphate was separated by filtration, using 500 g of kieselguhr. The lead remaining in the filtrate was removed by treatment with hydrogen sulphide, followed by another filtration using 100 g of decolorizing carbon. The lead-free filtrate which was nearly colorless was concentrated in vacuo. At about 60 Brix crystalline xylose began to separate; evaporation was continued until the solution contained about 73 percent of dry substance. The sirup containing considerable crystalline xylose was placed in a flask arranged so that it could be slowly rotated. After rotating overnight 3.3 kg of nearly pure xylose was separated by centrifuging. The mother liquor after evaporation gave an additional 3.4 kg of white crystalline sugar.

The same process was applied by the writer in cooperation with M. J. Proffitt, N. L. Bowman, P. E. Golden, and W. Pigman to the purification of a 139 kg batch of crude xylose. The sugar was dissolved in 259 kg of water and then treated with decolorizing carbon, lead subacetate, phosphoric acid, and hydrogen sulphide as described before. All operations were conducted with factory equipment. In this operation the crude xylose sirup after treatment with decolorizing carbon had a color index³ of $-\log t = 8.68$; after treatment with lead the color index dropped to $-\log t = 0.02$. The sugar was crystallized in a copper evaporating pan, the temperature of which was held at about 40° C and the crystals grown in the manner used in refining sucrose.

The product was purified in glass containers by recrystallization from water according to the following procedure: 14 kg of the sugar was dissolved in boiling water (6 kg) containing about 200 g of decolorizing carbon, filtered, and placed in a flask which was rotated slowly for 2 days at room temperature. Large crystals formed which were separated on a centrifuge, washed with a small quantity of water, and dried in air. The first crop of crystals weighed 7 kg. The sirups were concentrated in vacuo to about 75 Brix and crystallized as before. By continuing the process nearly all the sugar was recovered.

² The crude xylose was furnished by W. E. Emley, Chief of the Organic and Fibrous Materials Division of the National Bureau of Standards. It was part of the residues obtained from the xylose plant at the Anniston, Ala., plant of the Swann Corporation (Schreiber, Geib, Wingfield, and Acree, *Ind. Eng. Chem.* 22,497(1930)). The purification of these residues by other methods has also been investigated by G. M. Kline and S. F. Acree of this Bureau.

³ Peters and Phelps, *Techn. Pap.* BS 21,261(1927);T338.

A 1.1000-g sample of α -*d*-xylose dissolved in water to make 25 ml, gave $[\alpha]_D^{20} = +89.2^\circ$, 1.6 minutes after solution; $+83.9^\circ$, 3.1 minutes; $+78.7^\circ$, 4.9 minutes; $+73.2^\circ$, 7 minutes; $+65.0^\circ$, 10.4 minutes; $+55.7^\circ$, 15 minutes; $+48.0^\circ$, 20 minutes; $+36.8^\circ$, 30 minutes; $+27.1^\circ$, 45 minutes; $+22.8^\circ$, 60 minutes; $+20.0^\circ$, 90 minutes; $+18.3^\circ$, 24 hours. The extrapolated initial rotation (graphically) is $+94.8^\circ$. The mutarotation coefficients ($k_1 + k_2$) calculated for these rotations are: 0.0225, 0.0211, 0.0206, 0.0206, 0.0207, 0.0205, 0.0205, 0.0209, 0.0205, and 0.0183. Although these results are in excellent agreement with the value ⁴ 0.0207, usually accepted for xylose at 20° C, attention is directed to the fact that the coefficient decreases slightly during the first few minutes. ⁵ This indicates that the mutarotation reaction which gives the constant 0.0207 is preceded by a more rapid reaction. This rapid reaction occurs whenever crystalline xylose is dissolved in water and will be discussed in a further publication relating to the products formed by the oxidation of the sugar with bromine water.

WASHINGTON, August 16, 1934.

⁴ Int. Crit. Table, vol. 2 352.

⁵ The importance of small deviations in the mutarotation coefficients has been emphasized by the results of Riiber, Lowry, and others who have shown the mutarotation reaction for many sugars is complex. See Kgl. Norske Videnskab. Selskabs Forh. 3, no. 17, 66(1930); and J. Phys. Chem. 33,9(1929).