

## I. POTASSIUM OXALATE AS A LEAD PRECIPITANT IN SUGAR ANALYSIS.

BY HARRIS E. SAWYER.

Received September 29, 1904.

THE official methods of analysis of the Association of Official Agricultural Chemists direct that a solution which is to be tested gravimetrically for reducing sugars shall first be freed of soluble impurities by means of lead subacetate, and that the excess of lead shall then be removed by sodium carbonate previous to the examination with Fehling's solution.<sup>1</sup> Unfortunately, the use of carbonate for this purpose is attended with disadvantages. It was shown some years ago<sup>2</sup> that when lead is removed as carbonate from solutions containing invert sugar or levulose, the use of an excess of alkaline precipitant tends to carry a portion of the precipitate back into solution so that the purpose of the separation is in part defeated. It was proposed, as a remedy for this evil, that the solution be saturated with carbon dioxide after the addition of sodium carbonate; and it was claimed that by this means the lead might be precipitated completely in a granular form well suited to filtration.<sup>3</sup>

The same end may be attained, according to the writer's experience, by substituting sodium bicarbonate for the carbonate. Lead is precipitated quickly and completely, even in the presence of invert sugar, and the precipitate filters well without seeming to redissolve in an excess of the reagent. Unfortunately, however, the use of the bicarbonate has the undesirable effect of converting into carbonate a portion of the sodium hydroxide of the Fehling's solution.

So far as the writer is aware, no exact data have ever been published to show that the addition of a *little* sodium carbonate to a mixture of reducing sugar and Fehling's solution has any effect upon the sugar-copper ratio, so long as the amount of sodium hydroxide in the solution remains constant.<sup>4</sup> Indeed, experiments

<sup>1</sup> Bull. 46; Bureau of Chemistry, U. S. Dept. Agr., p. 33.

<sup>2</sup> Stern and Fränkel: *Ztschr. angew. Chem.*, 1893, p. 579; Borntträger: *Ibid.*, 1894, p. 521.

<sup>3</sup> Stern and Hirsch: *Ibid.*, 1894, p. 116.

<sup>4</sup> Borntträger (*Ztschr. anal. Chem.*, 37, 160 (1898)) and Bruhns (*Ibid.*, 37, 244) claim that sugar solutions suffer changes of reducing power when an excess of sodium carbonate is used for the removal of lead, but they refer, presumably, to the use of a *large* excess.

conducted in this laboratory seem to contradict such a view. Thus, to each of four 50 cc. portions of freshly prepared Fehling's solution, 30 cc. of a certain sugar solution were added. To two of these, 20 cc. portions of water were added, bringing the total volumes to 100 cc. To the other two, 20 cc. portions of decinormal sodium carbonate were similarly added. The first two portions gave respectively 0.5155 and 0.5150 gram of cupric oxide; the second two, 0.5151 and 0.5144 gram. The differences between the two sets of results are too slight to be attributed to the influence of the added carbonate.

On the other hand, it is well established that if the amount of sodium hydroxide present in Fehling's solution is varied, the sugar-copper ratio may be affected.<sup>1</sup> It is true that the reducing powers of dextrose and levulose are less influenced by such a variation than those of certain other sugars, and it may be that a reduction in the amount of hydroxide present, through its partial conversion into carbonate, would have less effect upon the sugar-copper ratio than an actual diminution of total alkalinity. But it seems none the less desirable to maintain the proportion of hydroxide as nearly constant as possible, and to avoid the introduction of a bicarbonate or of carbon dioxide in a sugar solution which subsequently is to be tested with Fehling's solution.<sup>2</sup>

On this account it has been attempted to remove the lead in other forms than carbonate. Thus, Gill has recommended its precipitation as sulphite, claiming that an excess of sulphurous acid is without effect on Fehling's solution;<sup>3</sup> and Pellet has employed both sodium sulphite and sulphurous acid, obtaining, however, precipitates which passed readily through filter-paper.<sup>4</sup> Bornträger has studied the use of sodium phosphate as a precipitant, finding that its action is rapid and complete, but that it leaves the filtrate acid and increases the reducing power of the invert sugar contained therein.<sup>5</sup> Many analysts have used sodium sulphate; and Bornträger considers it more generally satisfactory than either the carbonate or phosphate, since the reaction and reducing power of the filtrate remain unchanged.<sup>6</sup>

<sup>1</sup> Kjeldahl: "Meddelelser fra Carlsberg Laboratoriet," 4, pp. 6 and 22 (1895).

<sup>2</sup> Bruhns: *Ztschr. anal. Chem.*, 38, 82 (1899).

<sup>3</sup> *J. Chem. Soc.*, April, 1871, p. 91.

<sup>4</sup> *Bull. de l'Ass'n des Chimistes*, 15, 524 (1987-1891).

<sup>5</sup> *Ztschr. angew. Chem.*, 1894, p. 521.

<sup>6</sup> *Ibid.*, 1894, pp. 528, 555.

In other respects, however, the sulphate has proved unsatisfactory. The precipitate comes down so slowly as to retard filtration materially, and frequently separates from the filtrate upon the inside of burettes and flasks, making much extra labor in the cleansing of apparatus. These facts have led the writer to the study of another neutral precipitant.

Some years ago the use of ammonium oxalate was suggested by Zamaron;<sup>1</sup> and more recently, Wendeler<sup>2</sup> also recommended precipitating the lead as oxalate, though he insisted that an alkaline oxalate should be employed rather than the ammonium salt. Unfortunately, neither of these writers seems to have given any data regarding the rate or completeness of precipitation, the character of the precipitate, or the action of soluble oxalates on Fehling's solution; and accordingly, the present writer has been obliged to supply these details for himself. He believes that the results about to be reported are not anticipated by any previous publication.

It is desirable, as has already been indicated, that a lead precipitant for use in sugar analysis shall act promptly and completely; that the precipitate shall filter readily, and remain insoluble when an excess of the precipitant is employed; and that the reducing power of the filtrate shall not be altered, either by a change in its reaction or in consequence of the presence of the precipitant. It will be shown that the neutral oxalates of sodium and potassium meet all of these requirements.

#### EXPERIMENTAL.

Trials have been conducted with both of the above salts, and the two have been found to behave alike; but since the potassium salt is materially more soluble than the sodium compound, it has been given preference. It is now used in the writer's laboratory in the form of a dinormal solution, containing 184.3 grams of the crystallized salt in a liter.

The saccharine lead solution employed in the following experiments was prepared by dissolving 26 grams of cane-molasses in about 500 cc. of water, adding 8 cc. of a solution of basic lead acetate thereto, and filtering after a few moments' shaking. The clear yellow solution thus obtained, containing a considerable

<sup>1</sup> *Bull. de l'Ass'n des Chimistes*, 13, 346 (1895-'96); 14, 181 (1896-'97).

<sup>2</sup> *Deutsche Zuckerindustrie*, 1901, p. 1542; *Stammer's Jahresbericht*, 41, 108 (1901).

amount of lead, will be referred to subsequently as the "sugar-lead" solution.

#### RAPIDITY AND COMPLETENESS OF PRECIPITATION.

*Amount of Precipitant.*—To three 80 cc. portions of the sugar-lead solution, labeled A, B and C, were added respectively 1, 2 and 10 cc. of the dinormal potassium oxalate. Each portion was made up to 100 cc. with distilled water, and the mixtures were allowed to stand for about three hours.

In A the lead oxalate precipitate separated slowly, and showed a persistent tendency to pass the filter. Only by using doubled No. 602 S. & S. papers, was it possible to obtain a clear filtrate. Examined under the microscope, the precipitate was seen to consist of granules about  $1\mu$  in diameter, mostly isolated.

In B the precipitate settled more rapidly than in A, and filtered better. Microscopic examination showed that the ultimate particles of the precipitate, still  $1\mu$  in diameter, showed a tendency to form small aggregations.

In C the precipitate settled very rapidly and filtered perfectly. Under the microscope the granules were seen to be gathered into large aggregations.

Portions of all three filtrates were acidified with hydrochloric acid and saturated with hydrogen sulphide. No precipitate or discoloration was observed in any of them, and it was thereby established that the lead had been removed completely, even in A, and that it had not been redissolved by the large excess of precipitant used in C.

The greater ease of filtration displayed by C showed it to be advantageous to use a decided excess of precipitant in case the latter proved to have no effect upon the reducing power of the filtrate.

*Rate of Precipitation.*—Ten cc. of the potassium oxalate solution were added to about 80 cc. of the sugar-lead solution, and after shaking, three portions were filtered off—respectively, after ten, twenty-five and forty minutes' standing. The perfectly clear filtrates were treated with hydrochloric acid and hydrogen sulphide. In no case was any discoloration to be seen, and it therefore is obvious that precipitation was complete within ten minutes.

## EFFECT OF POTASSIUM OXALATE UPON THE SUGAR FILTRATE.

*Reaction.*—Two 50 cc. portions of the sugar-lead solution were rendered, respectively, very faintly acid and very faintly alkaline toward neutral litmus paper, and to each was added 6 cc. of neutral oxalate solution. When the precipitates had settled, the supernatant liquids were tested again with litmus and were found not to have suffered any change of reaction.

*Reducing Power.*—The filtrates A, B and C, previously mentioned, were tested for reducing sugars by the gravimetric method, according to Meissl and Hiller. In each case 31 cc. of the sugar filtrate were added to 50 cc. of the freshly mixed copper reagent, the volume was made up to 100 cc. with distilled water, and the mixture boiled for two minutes. Gooch crucibles, loaded with carefully washed asbestos, were used for the filtration, and the precipitate was ignited to constant weight in a muffle, and weighed as cupric oxide. The following weights of oxide were obtained: A, 0.5169 gram; B, 0.5177 gram; C, 0.5177 gram. The one discrepancy is no greater than may occur between duplicate determinations by this method, and the close agreement between the weights of oxide shows that the excess of oxalate was without effect upon the reducing power of the sugar solution.

Further test was made by boiling a mixture of potassium oxalate and freshly prepared Fehling's solution. No reduction was observed.

It may be concluded, therefore, that the neutral oxalate of potassium is a satisfactory precipitant for lead; and since it possesses none of the faults of the carbonate and sulphate, it may advantageously be substituted for them for use in sugar analysis. Did it possess any latent faults, these undoubtedly would have shown themselves in the eighteen months during which it has been employed in the writer's laboratory. So far, the only point noted to its disadvantage is that its solutions show slight growths of mold after long standing. However, no trace of decomposition has been detected as yet, and if such should ever appear, the trouble could, in future, be averted by the addition of an appropriate antiseptic.