[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

# THE CLARIFICATION OF SOLUTIONS CONTAINING REDUCING SUGARS BY BASIC LEAD ACETATE. THE EFFECT OF DIFFERENT DELEADING AGENTS

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The use of basic lead acetate as a clearing agent for solutions in which reducing sugars are to be determined is contrary to general practice in sugar analysis.

The work of Bryan,[1] Prinsen Geerligs[2] and others has clearly shown that loss of some reducing sugars, particularly fructose, accompanies its use. Several explanations have been advanced to account for this loss. W. A. Davis[3] contends that in dilute solutions there is no precipitation of fructose by the basic lead acetate even in the presence of chlorides, sulfates or carbonates if only a slight excess of the reagent is used and this excess removed immediately. The change in polarization he concludes is due to a conversion of fructose to glucose. Although this transformation probably does take place on long standing of the fructose in contact with the basic lead solution, nevertheless the work of Doerr[4] and of Pellet[5] demonstrates that the loss is due chiefly to the entrainment of the reducing sugars by the insoluble lead salts, since on decomposing the lead precipitate with sulfuric acid, practically the entire quantity of sugar lost is recovered. Such an entrainment may take place not only in the original clarification process but also in the subsequent deleading procedure when an excess of the reagent has been employed.

Pellet[6] has pointed out that the quantity and nature of the impurities, the amount of lead acetate used, and the concentration of the sugar solution, affect the quantity of sugar carried down. The nature of the impurity has usually received only passing notice. Still, its importance has been indicated.

In a study of the carbohydrates of the Snowdrop (*galanthus nivalis*) Parkin[7] investigated the effect of addition of tannin to a dilute sugar solution containing a mixture of sucrose, glucose and fructose and its removal by basic lead acetate. A very close agreement in rotation and copper reducing power was observed for the treated solution and a blank. In the analysis of molasses Meade and Harris[8] have found that even with the use of neutral lead acetate for clarification purposes, quite varied results are obtained when different deleading agents are used.

In view of these facts it appears that the nature of the lead precipitant is a very important consideration. It seems desirable then to determine the specific effect of different deleading agents in order that it may be ascertained whether the reported loss of sugars is due chiefly

[1] Bryan, *Bur. Chem. Bull.*, **116**, 73 (1908).
[2] Geerligs, *Z. ver. deut. Zucker-Ind.*, **59**, 761 (1908). *Intern. Sugar J.*, **11**, 276 (1909).
[3] Davis, *J. Agr. Sci.*, **8**, 1 (1916).
[4] Doerr, *Intern. Sugar J.*, **18**, 402 (1916).
[5] Pellet, *Ann. chim. anal.*, **21**, 217 (1916).
[6] Pellet, *Bull. assoc. chim. sucr. dist.*, **35**, 186 (1917).
[7] Parkin, *Biochem. J.*, **6**, 12 (1911).
[8] Meade and Harris, *J. Ind. Eng. Chem.*, **8**, 504 (1916).

to entrainment by precipitation of impurities naturally present in a plant extract or, perhaps, in some cases at least due in a large measure to the insoluble salts formed by the deleading agent.

## Experimental Part

About 5 g. of glucose was dissolved in water and made up to 500 cc. A solution of lead acetate was prepared according to the official method[9] From the dextrose solution 50cc. portions were measured into each of six 100cc. volumetric flasks. One was set aside as a blank and to each of the others 10 cc. of basic lead acetate was added. Solutions of the various salts indicated below, which were selected as representative deleading agents, were then added to the various flasks in a quantity which had been previously determined as just sufficient to precipitate 10 cc. of the basic lead acetate solution. All were made up to 100 cc., mixed thoroughly and filtered. Reducing sugar in 25cc. portions of the filtrates was determined by the method of Brown-Morris-Millar.[10]

The experiment was then repeated, using instead of glucose a fructose solution of about the same concentration.

The results are indicated in Table I below.

TABLE I

EFFECT OF DELEADING AGENTS ON ENTRAINMENT OF GLUCOSE AND FRUCTOSE

Precipitates not washed

| Deleading agent | Glucose | Per cent. after deleading | Fructose | Per cent. after deleading | Deleading agent | Glucose | Per cent. after deleading | Fructose | Per cent. after deleading |
|---|---|---|---|---|---|---|---|---|---|
| | G. of CuO | | G. of CuO | | | G. of CuO | | G. of CuO | |
| Blank | 0.3045 | | 0.2737 | | $K_2SO_4$ | 0.2680 | 87 | 0.1675 | 60 |
| | 0.3040 | | 0.2765 | | | 0.2630 | | 0.1670 | |
| $K_2C_2O_4$ | 0.2895 | 96 | 0.1790 | 65 | $KNaC_4H_4O_6$ | 0.2700 | 90 | 0.2295 | 81 |
| | 0.2910 | | 0.1800 | | | 0.2720 | | 0.2300 | |
| $Na_2HPO_4$ | 0.2930 | 92 | 0.2725 | 98 | $Na_2CO_3$ | 0.2810 | 93 | 0.2528 | 91 |
| | 0.2940 | | 0.2730 | | | 0.2785 | | 0.2549 | |

Since the presence of the precipitate would tend to counterbalance some loss of sugar carried down by the lead precipitate another experiment was performed with this variation: the solutions were filtered and precipitates washed until the volume of the filtrate was 200 cc. In addition to the salts tannic acid was introduced as a lead precipitant. The results are recorded in Table II.

[9] "Methods of Analysis A. O. A. C." p. 74, **1920.**

[10] Brown, Morris and Millar, *J. Chem. Soc.*, **71,** 281 (1897).

TABLE II

EFFECT OF DELEADING AGENTS ON ENTRAINMENT OF GLUCOSE AND FRUCTOSE

Precipitates washed

| Deleading agent | Glucose | Per cent. after deleading | Fructose | Per cent. after deleading | Deleading agent | Glucose | Per cent. after deleading | Fructose | Per cent. after deleading |
|---|---|---|---|---|---|---|---|---|---|
| | G. of CuO | | G. of CuO | | | G. of CuO | | G. of CuO | |
| I Blank | 0.1565 | | 0.1425 | | V $KNaC_4H_4O_6$ | 0.1486 | 93 | 0.1320 | 95 |
| | 0.1580 | | 0.1430 | | | 0.1480 | | 0.1350 | |
| II $K_2C_2O_4$ | 0.1530 | 98 | 0.1185 | 85 | VI $Na_2CO_3$ | 0.1514 | 95 | 0.1250 | 90 |
| | 0.1540 | | 0.1160 | | | 0.1510 | | 0.1255 | |
| III $Na_2HPO_4$ | 0.1570 | 99 | 0.1402 | 99.5 | VII Tannic acid | 0.1570 | 99 | 0.1410 | 99.6 |
| | 0.1565 | | 0.1400 | | | 0.1560 | | 0.1400 | |
| IV $K_2SO_4$ | 0.1410 | 91 | 0.1132 | 82 | | | | | |
| | 0.1405 | | 0.1100 | | | | | | |

## Discussion and Conclusions

It is shown from these experiments that the loss of reducing sugars varies greatly when different insoluble lead salts are thrown out of solution by basic lead acetate. The loss of fructose is in general much greater than that of glucose, which result is in accord with those of previous workers. It is quite interesting that carbonates, sulfates and oxalates, which have been perhaps most extensively employed as deleading agents cause most marked losses while with disodium phosphate the loss is nearly negligible. The use of disodium phosphate seems to have an added advantage, in that a clear filtrate is nearly always obtained, while with some of the other deleading agents there is a great tendency to give turbid filtrates. With tannic acid a very slight loss is to be noted. If tannin may be taken as a representative of natural impurities in plant extracts it would seem that loss of sugar, due to the deleading agents, may be as great as that of the natural impurity in case a large excess of basic lead acetate was used in the original clarification procedure.

The loss of sugar appears to be caused primarily by occlusion in the lead precipitate, since on washing the precipitate a much smaller loss is observed.

## Summary

A comparative study has been made of the effect of removal of basic lead acetate from solutions of glucose and fructose by means of potassium oxalate, disodium phosphate, potassium sulfate, potassium sodium tartrate and sodium carbonate. With glucose the quantity of sugar carried down by the lead precipitates, as indicated by loss in reducing power, varies from less than 1% to as much as 10%; with fructose, from less than 1% to as much as 35%. Disodium phosphate seems to be the most satisfactory deleading agent.

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