

# DRY LEAD SUBACETATE

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Since the introduction of dry lead subacetate as a reagent for the clarification of sugar products for sucrose analysis this chemical has found wide application. This is due to the simplicity, accuracy and rapidity of the method employed. How dependent we in the sugar industry of this country have become on dry lead subacetate was seen when, at the beginning of 1943, it was realised that insufficient stock existed at a number of sugar factories for the year's work and that the chances of getting new stock from overseas were remote. Rather than to go back to the basic lead acetate solution method, it was decided to try and make the necessary dry lead here.

Before that position arose, however, samples of dry lead acetate obtained from different agents and manufacturers had been analysed at the Experiment Station. We also had occasion to examine samples which were rather old and sometimes exposed to air.

In our "Recommended Methods"<sup>8</sup> the following specification is made: "*Dry Subacetate of Lead.*—The well-known preparation, 'Horne's Dry Subacetate of Lead,' consists of four parts of the basic acetate  $3\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{PbO}$  and three parts of the basic acetate  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{PbO}$ . (C. A. Brown, Handbook of Sugar Analysis, 1912, 214-215.)

"There are on the market a number of other good proprietary brands of basic lead acetate which conform with the above formula."

It will be noticed that no stipulations are made as to the range of lead, basic lead, moisture content, etc., which can be allowed. It is stated, however, that a number of other brands conform with the formula. Spencer and Meade<sup>3</sup> state that the subacetate should be specially prepared for sugar analysis and should contain 72.8 per cent. of lead. According to Brown and Zerban<sup>1</sup> the finely powdered salt must be dry and should contain the requisite amount of basic lead. The chemist must be certain of his preparation, as some samples sold were found to be almost entirely normal acetate. A very pure sample of lead subacetate analysed at the New York Trade Laboratory gave the following results:—

	Total Pb.	Basic Pb.
Found ... ..	73.00	30.03
Theory for $3\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{PbO}$ ... ..	72.84	29.14

In the International Sugar Journal<sup>6</sup> attention is drawn to the fact that lead subacetate is sold as Horne's, although quite unauthorized by that chemist. Most of the material sold as Horne's has a lead content well below the specified 72.7 per cent. and is coarse and difficult to dissolve, giving poor clarification.

In Czechoslovakia, K. Sandera<sup>2</sup> found that the following specifications were required:—

Basic lead from 30.2 to 31.7 per cent.; moisture less than 2 per cent.; grams per c.c. between 1 and 1.2 and never above 1.4.

Von Stieglitz<sup>4</sup> examined samples of lead subacetate commercially sold in Australia as well as prepared at the mills. Most of the samples were well below the standard 72.8 per cent. total lead. The moisture was as high as 6.4 per cent. in one case. The composition of the samples varied substantially, but there was but little variation in polarization, especially when the minimum amounts of basic lead acetate were used. The clarification efficiency varied chiefly with the fineness of the powder. The author recommended that the chemical composition and physical quality of the reagent should be specified if the "dry method" were to be employed as the only standard. This has apparently been done by legislation.

To control the purity of basic lead acetate for use in the analysis of juice for cane payment purposes, the following regulations are now laid down in Queensland<sup>5</sup>:—

Moisture content not more than 3 per cent.

Total lead not less than 70 per cent.

Lead content as lead oxide (PbO) not less than 30 per cent.

The reagent must also pass a test for fineness.

**Analysis of Lead Acetate Samples on the Market.**—Samples of lead subacetate used here and obtained from a number of manufacturers were analysed. These showed considerable variation in composition. Some were from old stock and probably exposed to air, with the result that they were not a fine powder and, being rather insoluble, did not clarify solutions well. It is, of course, absolutely essential to keep this reagent in air-tight containers, but it is unfortunately often sold in paper packets.

The analyses of samples of dry lead subacetate:—

Manufacturer ...	A		B		C		D	
Moisture ... ..	0.9	1.0	1.1	2.0	2.0	1.9	4.2	
Total lead (Pb) on dry basis...	72.5	72.7	71.2	69.9	68.6	73.7	71.5	
Basic lead (Pb) on dry basis...	28.9	30.5	25.8	24.8	20.2	34.9	26.9	
Basic lead per cent. total lead	39.9	41.9	36.2	35.5	29.4	47.4	37.6	

## PREPARATION OF DRY LEAD SUBACETATE.

The Laboratory Manual for Queensland Sugar Mills<sup>7</sup> gives as a method of preparing "Basic Lead Acetate Dry (Horne's Dry Lead)" the evaporation to dryness of the concentrated decanted solution of basic lead acetate. The resulting mass is ground up in a mortar or grinding mill. The solution is made by boiling 430 grams of neutral lead acetate and 130 grams litharge for 30 minutes, allowing to cool and decanting. This is, of course, the normal stock solution of basic lead acetate, but theoretically the dry salt cannot correspond to the composition of Horne's dry lead acetate, the basic lead being too low.

This method of preparing dry lead subacetate was used at the Experiment Station, but the percentage of basic and total lead and the ratio of basic lead to total lead were found to be even lower than expected. This is, of course, due to the precipitate being almost entirely lead carbonate and an appreciable proportion of the original basic lead is thus lost. It was, therefore, found necessary to increase the proportion of litharge to about 19 or 20 grams to every 43 grams neutral lead acetate. The proportions will, of course, depend on the purity of ingredients and the subsequent formation of carbonate. Small quantities of dry lead subacetate prepared at the Experiment Station in this way were found to be of good quality. The following is the analysis of some preparations, using varying proportions of litharge to neutral lead acetate.

Quantity litharge taken...	43 gms.	43 gms.	43 gms.	43 gms.
Quantity neutral lead acetate taken ... ..	18 gms.	19 gms.	20 gms.	22.8 gms.
Total lead (Pb) ... ..	71.9	72.5	72.5	73.8
Basic lead (Pb) ... ..	28.0	28.5	29.5	32.3
Basic lead per cent. total lead ... ..	38.9	39.3	40.7	43.8

Another method of preparing lead subacetate was also used.

This is described in detail in another paper. Although, this being a dry method, no basic lead is thrown out of solution, the proportions of litharge used in our stock basic lead acetate solution was found to be low. Small quantities of litharge which have not been acted upon were on some occasions found in the preparation. The solution in water was rather cloudy, but good results were reported from factories where this preparation was used extensively for clarification.

The analyses of some of the samples are as follows:—

Quantity of litharge taken to 43 grams neutral lead acetate	13	13	13	13	17	17	17	17	17
Moisture per cent. ... ..	1.2	1.0	2.9	1.2	2.6	2.6	2.4	3.1	2.2
Total lead (Pb) per cent., dry basis... ..	68.5	68.5	69.8	69.1	71.8	71.8	71.8	71.6	72.0
Basic lead (Pb) per cent. on dry basis ... ..	23.3	23.1	23.7	23.3	28.3	28.9	28.6	28.9	29.1
Basic lead per cent. total lead ... ..	34.0	33.7	34.0	33.7	39.4	40.3	39.8	40.4	40.4

It will be observed that the percentage basic lead and total lead are slightly lower than would be expected from a compound consisting only of lead acetate and lead oxide. The basic lead per cent. total lead in those preparations where 17 grams litharge were used to 43 grams neutral lead are, however, within the analytical error.

The following table gives the theoretical relation between basic lead, total lead and basic lead per cent. total lead for a compound consisting only of lead acetate and lead oxide (PbO).

Basic lead (Pb) per cent.	Total lead (Pb) per cent.	Basic lead (Pb) per cent. total lead.	Basic lead (Pb) per cent.	Total lead (Pb) per cent.	Basic lead (Pb) per cent. total lead.
20	69.99	28.6	28	72.50	38.6
21	70.30	29.9	29	72.81	39.8
22	70.61	31.2	30	73.11	41.0
23	70.92	32.4	31	73.44	42.2
24	71.24	33.7	32	73.75	43.4
25	71.55	34.9	33	74.06	44.6
26	71.86	36.2	34	74.38	45.7
27	72.18	37.4	35	74.69	46.9

#### METHODS OF ANALYSIS.

**Moisture.**—About 5 grams are dried at 105°C.

**Total Lead.**—Total lead can be determined gravimetrically by dissolving the sample in weak acetic acid and precipitating as lead chromate or sulphate with potassium dichromate (5 per cent.) or sulphuric acid. The method mostly used by the author is, however, the volumetric permanganate method.

About 0.5 grams of basic lead acetate is weighed accurately and dissolved in 50 ml. water acidified with acetic acid in a 250 ml. beaker. Heat to near boiling point and add 10 ml. 10 per cent. oxalic acid. Cool well. The precipitate of lead oxalate is filtered and washed. Transfer the precipitate with about 30 ml. water into a clean beaker. Wash the filter paper further with 20 ml. 10 per cent. sulphuric acid and another 50 ml. water. Bring the acid mixture nearly to boil and titrate with N/10 potassium permanganate. Finally add the torn-up filter paper to the solution and complete the titration.

*Example.*—Weight of sample taken 0.5487 grams.

Amount of N/10 KMnO<sub>4</sub> used 38.3 ml.

Therefore per cent. total lead Pb

$$= \frac{207.22 \times 38.3 \times 100}{20,000 \times 0.5487} = 72.3.$$

**Basic Lead.**—The principle of this determination depends on the precipitation of all the lead as lead sulphate. The sulphuric acid is used up quantitatively by the basic part of the lead, whereas acetic acid is set free equivalent to the sulphuric acid used in precipitating the lead from the lead acetate. By using a known quantity of sulphuric acid and back titrating with standard caustic soda, the quantity of sulphuric acid used to neutralise the basic lead is known and the basic lead can be calculated.

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South African Sugar Association,  
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About 2 grams of basic lead acetate is weighed out accurately and washed into a 250 ml. measuring flask. Add 10 ml. N acetic acid to dissolve the sample. Add 200 ml. N/10 sulphuric acid (or 20 ml. N) to precipitate all the lead as lead sulphate. Make up to mark and shake. Allow to stand overnight. Pipette out a portion of clear liquid (50 or 100 ml.) and titrate the excess acid with N/10 caustic soda, using phenolphthalein as indicator.

*Example.*—

Weight of sample ... .. 2.0008 grams

10 ml. N CH<sub>3</sub>COOH (f=1.032) added ... .. 103.2 ml. N/10

200 ml. N/10 H<sub>2</sub>SO<sub>4</sub> (f=1.000) added ... .. 200.0 ml. N/10

Therefore 250 ml. contains ... .. 303.2 ml. N/10

Therefore 50 ml. contains ... .. 60.6 ml. N/10

NaOH used in back titrating ... .. 48.8 ml. N/10

Therefore H<sub>2</sub>SO<sub>4</sub> used in 50 ml. solution ... .. 11.8 ml. N/10

Therefore 50 ml. contain  $\frac{11.8 \times 207.2}{10,000 \times 2}$  grams Pb.

Therefore basic lead as Pb per cent.

$$= \frac{11.8 \times 207.2 \times 250 \times 100}{10,000 \times 2 \times 50 \times 2.0008} = 30.5.$$

A correction for the precipitate of lead sulphate can be made if necessary by calculating the weight of lead sulphate precipitated (the per cent. total lead being known from the previous determination). The volume is then obtained by dividing the weight of lead sulphate by its specific gravity. This correction is negligible in our case, however.

#### SUMMARY.

Basic lead subacetate sold by firms for sugar work varies in composition. Analyses of some samples are given, as well as standards suggested in other countries. Methods of preparing a basic lead subacetate which compares favourably with products sold by many firms are discussed and the analyses of the preparations given. The methods of analysing samples for moisture, total lead and basic lead are given.

#### REFERENCES.

- <sup>1</sup> Browne, C. A., and Zerban, F. W. (1941): "Physical and Chemical Methods of Sugar Analysis." Third edn., John Wiley & Sons, 319.
- <sup>2</sup> Sandera, K. (1935): "Examination of Dry Basic Lead Acetate for Use in Sugar Analysis." I.S.J. 311. Abstract from Zeit. Zuckerind. Czechoslov., 1935, 59, 177.
- <sup>3</sup> Spencer, G. L., and Mead, G. P. (1929): "A Handbook for Cane-Sugar Manufacturers and their Chemists." Seventh edn., John Wiley & Sons, 225.
- <sup>4</sup> Von Stieglitz, C. R. (1939): "Basic Lead Acetate—its Composition and Clarifying Qualities." Dep. of Agric. Queensland Tech. Communications, No. 10.
- <sup>5</sup> Von Stieglitz, C. R. (1939): "Methods for Evaluating Certain Reagents used in Factory Control." Proc. of the Queensland Soc. of Sugarcane Tech., 12, 55.
- <sup>6</sup> (1932): I.S.J., 407.
- <sup>7</sup> (1939): Laboratory Manual for Queensland Sugar Mills, 73.
- <sup>8</sup> Recommended Methods of Chemical Control. S.A. Sugar Tech. Assoc., 14.