

carry out. The ether, however, may be largely recovered by distillation. An investigation is now being made in this laboratory with the hope of so modifying the method as to overcome the above objection.

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REPLY TO CRITICISMS OF DRY LEAD DEFECACTION IN RAW SUGAR ANALYSIS¹.

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About the only objections which have been raised to the method² of defecating raw sugar solutions with anhydrous subacetate of lead, after making up the solution of the normal weight of sugar to 100 cc. and prior to polarizing, are those which Messrs. H. & L. Pellet have advanced. Of the seven objections originally raised³ I answered all, but in the past few months Mr. H. Pellet has readvanced one of these in a new form and has presented a new objection⁴. His new claim is that the lead precipitate absorbs sufficient sugar from solution to slightly more than counterbalance the concentration of solution which one would expect to find due to the occupancy of space within the 100 cc. by the lead precipitate formed.

In the other objection it is urged that anhydrous subacetate of lead added to a sugar solution dilutes such solution to the extent of 0.37 cc. for each gram of reagent, causing through this dilution a corresponding lowering of polarization, and this also, he claims, just counterbalances the error due to the volume of precipitate. Experiments are cited to illustrate the first of these points in which a normal weight of raw sugar or syrup was dissolved in a small amount of water, defecated with lead subacetate solution and thrown upon the filter and then carefully washed free from sugar; filtrate and washings being made up to 100 cc. and polarized. These polarizations are said to be the same as or a little higher than those obtained in the usual way, from which he concludes that the precipitate occludes or adsorbs sugar. Obviously, this is only one of several explanations that might be given and if it can be shown that the precipitate does not adsorb sugar I am sure it must be admitted that Mr. Pellet's explanation is at fault and his deductions without weight.

To controvert this I dissolved 26.048 grams of a Cuban molasses sugar in a 100 cc. flask, added 12 cc. of a solution of basic acetate of lead at 24° Brix. to obtain a satisfactory clarification, made the whole up to 100 cc. and filtered on a dry paper. The loss on evaporation was found to

¹ Read before the N. Y. Section of the American Chemical Society, April 5, 1907.

² J. Am. Chem. Soc., 26, 186.

³ Bull. assoc. chim. suc. dist., 23, 285-291.

⁴ Internat. Sugar J., 8, 455.

⁵ Bull. assoc. chim. suc. dist., 24, 473.

be 77.02 per cent. The sucrose was determined gravimetrically by obtaining the invert sugar with Fehling solution before and after inversion, calculated by Munson and Walker's table¹, and found to be 20.28 per cent. Thus the sucrose in the filtered portion amounts to 26.331 per cent. of the water present. The lead precipitate drained on the paper down to about 17 cc. Upon analyzing this precipitate portion the water was found to be 69.96 per cent. The sucrose was 17.70 per cent. which is only 25.300 per cent. of the amount of water present. Thus the sugar solution around the precipitate is a little less concentrated than is the portion which filters off, instead of more concentrated as suggested by Mr. Pellet. It was found that the precipitate portion contained a little more invert sugar than the filtrate portion, which might be due to a slight inversion of sugar in the precipitate portion, or it might be due to a different selective effect of the precipitate for invert sugar from its attraction for sucrose. The latter would not materially affect the matter under discussion, but as the former would tend to give an unjust advantage to the argument for my contention I believe it is better to consider all the sucrose and invert sugar collectively as invert sugar and to use in the calculations only the weights of total invert sugar found in the different portions after inversion. Thus in the filtrate portion we have 22.36 per cent. of total carbohydrates expressed as invert sugar, and 77.02 per cent. of water. The invert sugar thus is equal to 29.03 per cent. of the water. Similarly, in the precipitate portion I find the total invert sugar is only 28.69 per cent. of the water. This relative increase in water over sugar in the precipitate portion certainly refutes absolutely the claim that the precipitate adsorbs sugar.

The precipitate portion occupied about 17 cc., the actual precipitate having a volume of a mere trifle over 0.5 cc., and the specific gravity of the filtrate was 1.0995. From data thus in hand I calculated the ratios of sugar to water in the two portions according to the adsorption theory.

	Filtrate	Precipitate
1° Theory of no adsorption.....	29.03	29.03
2° Results actually found	29.03	28.69
3° Theory of adsorption.....	28.52	30.98

Thus it will be seen that the theory of adsorption will give us a difference between these sugars to water ratios more than seven times as great as that actually found, and in the *opposite* direction. I think no further comment is needed.

One of the reasons for the difficulty in determining whether the volume of the precipitate error is in any way counterbalanced by other errors is the inherent difficulty of knowing just what the correct theoretical polarization of a sugar solution is. With ordinary raw sugar or products containing matters precipitable by subacetate of lead it is

¹ This Journal, 28, 663, (1906).

greatly complicated by the presence of invert sugar and possibly other optically active bodies, by mineral salts and so on. By isolating the precipitable matter from some low raw sugar, by lead salt, decomposing with hydrogen sulphide, and filtering off I was later able to prepare solutions of pure sucrose containing organic matter which would give precipitates of known volume.

Then the following experiments were made :

- (a) 26.048 gms. dry granulated sugar + H₂O to 100 cc. was polarized. Pol. = 99.6
 (b) " " " " ± 10 cc. organic sol. — 1.5 cc. lead solution (being just about sufficient to precipitate the organic matter), the whole made up to 100 cc. and polarized = 99.7
 (c) Same sugar ± 50 cc. organic sol. + 7.5 cc. lead sol. to 100..... = 99.9
 (d) " " ± 50 cc. " " ± water up to the 100 cc. mark, and 1.011 grams dry lead subacetate, Pol..... = 99.7

A portion of (c) was used for determining the weight of the lead precipitate, its specific gravity by Watt's and Tempany's method and from these figures, the volume of the precipitate. Its weight was 0.7965 gram, its specific gravity was 2.497 and its volume 0.319. As the precipitate occupies 0.319 cc. it follows that the sugar must all be included in the remaining volume of the 100 cc. flask or 99.681 cc. and consequently we must multiply the obtained polarization, 99.9, by 99.681 per cent. to give us the polarization as it would be, corrected for the volume of the precipitate; and we obtain as our result 99.58 as compared with our known 99.60 that we started with.

The results on (b) are no less satisfactory, for the 99.6 polarizing sugar would be raised by the volume of precipitate present up to 99.656 and my reading was 99.7 which is less than half a tenth away—a difference which is perfectly admissible. In (d) I obtained with 50 cc. of organic solution, using my dry lead defecation a polarization of 99.7 as against a theoretical polarization of 99.6. As the volume of the solution was made up to 100 full cc. before the lead was added there would be no factor present tending to increase the polarization, for we have the normal weight of sugar in the normal volume of solution. On adding the dry reagent a precipitate is formed having an ascertained volume of 0.3 cc. but this cannot have the effect of concentrating the sugar solution unless it absorbs water, which is not claimed. According to the sugar adsorption theory, however, it would have the effect in this case of reducing the polarization 0.3°, giving us 99.3 instead of 99.6 theoretical and 99.7 determined.

Answering the second criticism of Messrs. Pellet that dry subacetate of lead dilutes the solution by 0.37 cc. for each gram used and so accounts for the differences between polarizations by the two methods, experiments show that one gram only occupies 0.22 cc. when in solution; and determinations of lead as chromate in filtrates from muscovado and molasses

sugars showed that the amount of lead was so slight as to account for only 0.044 and 0.042 cc. respectively, amounts too small to affect appreciably the polariscopic reading, even in these samples of the lowest grades. In high grade sugars, which constitute by far the greater portion of the world's supply, the dilution is correspondingly small and insignificant.

It will thus be seen that these authors are in the unfortunate position of having explained away twice as much difference as ever exists, and that by indirect methods; while the most direct possible methods thoroughly demonstrate the fallacies of their claims and the superiority of the dry defecation over the process heretofore in use.

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CHEMICAL METHOD FOR THE DETERMINATION OF THE AVAILABLE PHOSPHORIC ACID IN SOILS.

BY ALEXIUS DE SIGMOND.

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Though the first steps in Agricultural Sciences were based upon the chemical analysis of soils, there is still a need of methods, for the determination of available plant food in soils. The ingredient most needed in Hungarian soils is undoubtedly phosphoric acid. The author, as chemist of the *Hungarian State Experiment Station of Plant Industry in Magyar Övár: Hungary*, has studied this problem during more than seven years, and has devised a method, by which he has tested nearly 100 different soils of Hungary, having made control fertilizer experiments on the same soils. The work of the author was rewarded by the prize of the *Hungarian Academy of Sciences in Budapest, Hungary*, and published recently¹ by the same scientific institute. The author here gives a brief report of this work, and a complete description of his method for the determination of the available phosphoric acid in soils.

The starting point of his investigations was, to find *a natural limit* in the solubility of the phosphoric acid in soils.

In 1899 Th. Schlösing, *jun.* in France, published some of his experiments, which seemed to divide the phosphoric acid in the soil into two distinct parts, the slightly soluble and less soluble part of phosphoric acid². Schlösing tested but four different soils, and the author has repeated the experiments of Schlösing on eleven different Hungarian soils. The experiments of both authors agree in so far, that there is a distinct point which separates the phosphoric acid of soils in the above mentioned two parts. When we start with distilled water, and increase gradually

¹ *Mathematikai és Természettudományi Közlemények XXIX, No. 1. 1906.* A könnyen átsajátítható phosphorsav jelentősége és "meghatározása talajaink trágyaszükségletének megállapítása céljából."—Dr. Sigmond Elek.

² *Compt. rend., 128, 1004.* Action des liqueurs acides très éntendues sur le phösphates du sol.—Th. Schlösing fils. 1899. Paris.