

It is evident that, by using a stronger standard solution (N/10) in the absorbers, and by treating the sample with an acid, the total fixed carbonic acid can easily be determined, after the free acid has been expelled.

I have been very much pleased with the performance of the simple apparatus described, as I am sure any one will be who gives it a trial. Its obvious advantages are its simplicity, its portability, its permitting work to be done on comparatively large volumes of water, and its doing away with the need of carrying any measuring apparatus, other than a pipette, into the field.

Among other tests to which I have subjected it, I may say that I have driven air for half an hour through an aqueous solution of sodium bicarbonate (1 gram in 500 cc.) without decolorizing 5 cc. N/10 barium hydroxide (diluted with 20 cc. water) in the absorber. This of course merely served to prove the absence of free carbonic acid in the water operated on. To the sample I added 20 cc. sulphuric acid, passing the air through three absorbers containing respectively 25 cc., 10 cc., and 5 cc. of barium hydroxide. In twenty minutes the first absorber was decolorized; in thirty minutes the second absorber, while the color had all but gone from the third. The air was passed at the rate of 3 to 5 bubbles per second.

---

## DRY DEFECTION IN OPTICAL SUGAR ANALYSIS.

BY W. D. HORNE.

Received December 7, 1905.

THE analysis of raw sugars, which is of so much importance both from the commercial and technical sides, naturally has received the closest attention by chemists, and the International Commission for Uniform Methods of Sugar Analysis has done much to perfect the methods employed. The errors involved in polariscopic determination of sucrose have been gradually eliminated and several battles royal have been waged by the advocates of different ideas in arriving at the truth. Probably the most important error that remains and which has defied many earnest attempts to overcome it, is that due to the volume of the precipitate formed when clarifying the raw sugar solution with subacetate of lead to prepare it for observation in the polariscope. A year ago the writer devised a method for obviating, in great part, this error

and succeeded in adapting it to the technical analysis of refinery samples. Last June Dr. Wiechmann presented an admirable paper to the Berlin Congress advocating the careful search for a method of analysis which would overcome this error due to the volume of precipitate. The writer has now developed his method so that it gives very good results with raw sugars.

Ordinarily, in preparing a sample of raw sugar for polarization, the normal weight of the sugar is dissolved in about 80 cc. of water in a 100 cc. flask, a little solution of lead subacetate is added, sufficient to precipitate coloring-matter and some other impurities, the whole made up with water to the 100 cc. mark, shaken, filtered and polarized. The precipitate formed occupies a definite volume within the 100 cc., thus forcing the sugar to be diffused through a volume of solution somewhat less than the 100 cc. for which the polariscope is designed. This concentration of the sugar solution of course raises the polarization in proportion and these incorrect polarizations are very objectionable both from the commercial and manufacturing standpoints. The writer's idea is to defecate the solution in such a way that after defecation the sugar shall remain dissolved in exactly 100 cc. of solution, and that whatever precipitate there is may occupy space exterior to that solution.

In order to accomplish this, the normal weight of sugar is dissolved in water in a 100 cc. flask and made up to the mark without defecation. The concentration is thus at exactly the proper degree. It now remains to defecate the solution properly by precipitating the impurities in such a way as to produce the minimum change in the concentration of the solution of sucrose. This is accomplished by adding to the 100 cc. of liquid small quantities of powdered anhydrous lead subacetate until the impurities are nearly all precipitated. This point is as easily determined as in the defecation by a solution of the same salt. The organic and mineral acid radicals in the solution combine with and precipitate the lead and lead oxide of the dry salt, while the acetic acid radical of the lead subacetate passes into solution to combine with the bases originally united to the other acid radicals. If the acetic acid occupies the same volume in solution as the acid radicals replaced by it, there should be no change in the volume of the solution and no change in concentration of sucrose. If the acetic acid is of less volume than the acids replaced, the volume of solu-

tion should be less after the addition of the lead subacetate, and this concentration of solution should increase the polarization. One would expect the acetic acid radical to be lighter and smaller in volume than the more complex acid radicals of the coloring-matters and other impurities present. And in fact this supposition appears to be borne out, for apparently there is a slight concentration of solution during the above described method. But a very long step has been taken in the right direction, because whereas in the usual procedure the error is proportional to the volume of the total precipitate, in this dry defecation the error is only proportional to the difference in volume of acetic acid and the precipitated radicals involved. Means of eliminating this small residual error are under investigation.

In order to test the correctness of this theory, various samples of typical raw sugars of different grades and from different countries have been subjected to comparative tests by the two methods and to the determination of their true polarizations corrected for the volume of the precipitate.

The method of investigation is as follows: The sample of sugar is thoroughly well mixed and put into a glass jar closed by a glass cover and rubber gasket. The normal weight of this sample is introduced into a 100 cc. flask and dissolved in about 80 cc. of water. Then a solution of lead subacetate of 25° Brix is carefully added from a burette until the impurities are nearly completely precipitated. The volume of lead solution used is noted and the flask is filled to the 100 cc. mark with water, shaken, filtered and polarized. Now another normal weight of the same sample of sugar is dissolved in the same flask with water and the solution is made up to the 100 cc. mark with water. Then a weighed amount of anhydrous lead subacetate, equal to the salt contained in the solution first used, is added, the whole shaken, filtered and polarized. This polarization may then be compared with the ordinary and with the true polarization obtained by correcting the ordinary for the volume of precipitate. There are various methods for doing this, but the one involving the fewest observations and manipulations and so the most correct, is a modification of Sachsse's method. The lead precipitate obtained in the ordinary defecation is washed on the filter until free from sugar by the  $\alpha$ -naphthol test and then

washed into a pycnometer, which is filled up with distilled water and weighed at standard temperature. The excess of this weight over that of the pycnometer full of water alone is equal to the excessive weight of the precipitate over the weight of an equal volume of water. The precipitate is now filtered upon a weighed filter, dried and weighed. The weight of the precipitate minus its excessive weight over an equal volume of water is of course equal to the weight of its own volume of water. Changing grams in the weight of the equal volume of water into cubic centimeters, we have the volume of the precipitate. From this one calculates the true polarization from the ordinary polarization by Sachsse's formula, which is essentially 0.01 of the observed polarization multiplied by 100 minus the volume of the precipitate in cubic centimeters. This method is similar to that employed by Dr. Wiechmann except that he first dried the precipitate and afterward determined its specific gravity in benzine and calculated its volume from the weight and the specific gravity. The specific gravities obtained by the writer vary from 1.96 to 3.20. The cause of the variations of specific gravities of precipitates is to be further investigated.

As it is practicably impossible to read on the polariscopic scale more closely than to  $0.05^\circ$  or  $0.1^\circ$ , it follows that where the error in polarization due to the volume of precipitate amounts to only  $0.1^\circ$  it is very difficult to draw correct conclusions from any single set of observations, but inferences drawn from averages are better and where the variation is several tenths between the observed and the true polarizations one can feel a greater certainty in regard to results. The analytical results obtained on a dozen sugars of different grades and origins are given in the accompanying table, an examination of which will show that in high grade centrifugal sugars where the volume of the precipitate is equal to 0.1 cc. or less this method has overcome on the average more than half of the error and in low grade sugars where the volume of the precipitate is 0.3 cc. to 0.8 cc. the dry defecation has overcome on the average over 84 per cent. of the error. Probably the dry lead method will be found to give as good results on the high grades as on the low grades when large numbers of tests are averaged. No single test on a very high sugar can be conclusive, as the errors of reading the polariscope are about as great as the error we are striving to eliminate.

## RESULTS OBTAINED FROM DRY DEFECACTION OF RAW SUGARS.

Grade.	Country.	Polarization.	Volume of precipitate.	Corrected polarization.	Dry lead polarization.	Difference from ordinary polarization.	Difference from corrected polarization.	Sp. gr. of precipitate.
1 Cent.	....	95.0	0.10	94.9	94.9	- 0.1	0.0	2.98
2 Centr.	{ Mixed samples }	94.5	0.0765	94.43	94.4	-0.1	-0.03	...
3 "	Trinidad	96.95	0.0378	96.91	96.95	0.0	+ 0.04	2.91
4 "	Java	97.425	0.0884	97.33	97.375	-0.05	+ 0.045	2.30
5 Musco.	St. Croix	85.8	0.4118	85.45	85.5	-0.3	+ 0.05	1.91
6 Mol.	Cuba	89.4	0.39	89.05	89.0	-0.4	-0.05	3.20
7 "	....	89.225	0.4204	88.85	88.85	-0.375	0.0	2.85
8 "	....	86.45	0.7108	85.84	85.95	-0.5	+ 0.11	1.96
9 "	....	90.675	0.3204	90.39	90.45	-0.225	+ 0.06	3.20
10 "	....	89.35	0.8500	88.59	88.775	-0.575	+ 0.185	...
11 "	....	89.4	0.4554	88.99	89.0	-0.4	+ 0.01	3.01
12 "	Cuba	88.4	0.4924	87.97	88.0	-0.4	+ 0.03	2.64

In the technical analyses of sugar factories and refineries the dry defecation offers marked advantages. By the commonly employed Cassamajor method of determining the quotient of purity of a sugar solution, it is necessary to take account of the amount of dilution caused by the addition of lead solution in clarifying. This is done by filling a flask graduated at 100 and at 110 cc. to the 100 mark with the sugar solution, adding enough lead solution to decolorize, making up to 110 cc. with water, filtering and polarizing. The polarization is increased to 110 per cent. of itself to compensate for the dilution and multiplied by a factor corresponding to the density of the solution, whereby the purity is obtained. The error due to the volume of precipitate still remains. In the dry defecation no such precaution need be taken as the concentration is unaffected by the defecating agent. After taking the density of the solution with a hydrometer in a tall cylinder, one adds dry lead subacetate directly to the solution, shakes, filters and polarizes. This polarization multiplied by the factor for density gives the purity.

It is found that some refinery solutions, notably such as have been subjected to the influence of bone-black, have a tendency to coat the grains of lead salt with insoluble adherent crusts, preventing the solution of the interior portions. This is probably due to a preponderance of mineral matter, but is readily overcome by ad-

ding coarse dry sand with the lead salt before shaking. The attrition grinds off the crusts instantly, allowing the lead to be completely acted upon and so defecating the solution.

Following are a few polarizations of typical samples from a refinery, showing the very close agreement between the two methods, an agreement as close as would obtain between duplicate tests by the same method:

Sample.	Observer.	Wet method.	Dry method.	Difference from wet.
Washed sugar solution.....	A	60.4	60.3	--0.1
	B	60.1	60.05	--0.05
Bag filtered washings.....	A	27.0	27.0	0.0
	B	26.9	26.9	0.0
Char filtered washings.....	A	48.4	48.3	--0.1
	B	48.3	48.2	--0.1
Medium massequite .....	A	30.7	30.6	--0.1
	B	30.6	30.6	0.0
Medium syrup .....	A	23.2	23.2	0.0
	B	23.2	23.2	0.0
Low sweet water .....	A	3.2	3.1	--0.1
	B	3.1	3.0	--0.1
Residual syrup.....	A	28.16	28.15	-0.01
	B	28.16	28.20	+0.04

A set of about 35 tests on refinery samples by different observers showed as close an agreement as between duplicate tests by the ordinary method, *viz.*: differences from  $0^\circ$  to  $0.2^\circ$  and the average of the polarizations by the dry defecation was about  $0.02$  of a degree lower than by the wet defecation. Strangely enough the error due to the volume of precipitate seems to be smaller in partially refined solutions than in raw sugars, although the volume of the precipitate may be as large or larger. This is probably due to other errors, which tend to compensate the former.

The dry defecation method has been employed for several months in two sugar refineries with perfectly satisfactory results and with the added advantages of greater speed of work, the elimination of volume measurements and the simplification of calculations.

The first anhydrous subacetate the writer prepared for himself, but later it has been very satisfactorily prepared by E. R. Squibb and Sons. The sample tested contained 72.76 per cent. of lead as against 8.88 per cent. of lead in the solution usually employed, whose specific gravity was  $1.1049 = 24.61^\circ$  Brix. Thus 1 cc.\* of

the solution is equal to 0.1346 gram of the dry salt, and this equivalent has been used in the experiments cited.

The writer trusts that these results may help to solve the difficult question of errors due to the volume of precipitate and offers the above method as one which at least will go a long way toward arriving at correct results in optical sugar analysis.

---

## REVIEWS.

### Some Abstracts from the Recent Literature of Industrial Chemistry.

BY FRANK H. THORP.

PROGRESS in the various chemical manufacturing lines is more or less correctly indicated by the number and character of the investigations published, and future changes are often foreshadowed thus. The abstracts in the *Review of American Chemical Research* contain a summary of recent chemical work in this country. In the following article it has been desired to bring together certain of the more important contributions to the literature of industrial chemistry, with especial reference to those appearing in foreign journals.

To give exhaustive reviews, or even to enumerate all the material bearing upon the technical applications of chemistry, published within the last year or two, would far exceed the limits of this article, and if anything of value has been omitted, the limits of time and space and the liability to overlook something in so hasty a survey, must be the reasons given. Articles of a purely theoretical character, where immediate practical applications are not obvious, and those relating to analytical and organic processes, having but a remote connection with industrial requirements, have generally been passed over, but some attempt has been made to select material from a few of what appear to be the most important of the many patents recently issued.

**Technical Education.**—The subject of education in technical branches, including chemistry and chemical engineering, continues to receive much attention both in this country and abroad. The English Parliament last year passed an Educational Bill, which, however, does not appear to meet the ideas of those who are working for a higher grade of secondary education. Defects in the bill are pointed out by Mr. Levinstein in his presidential address to the Society of Chemical Industry, at Bradford. He shows that the efforts now being made in England to increase the number of technical schools, are in a large measure, misdirected energy, and he says very truly, that what the country needs is