PROCEEDINGS
OF THE
CHEMICAL SECTION
OF THE
FRANKLIN INSTITUTE.

[*Stated meeting held Tuesday, March 15, 1892.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, March 15, 1892.

Dr. W. H. WAHL, President, in the chair.

Dr. Wahl called attention to a number of bills for subscriptions to journals, the contraction of which had already been authorized. On motion, the Treasurer was instructed to pay them.

Dr. S. C. Hooker read a very interesting paper on derivatives of lapachic acid. Dr. Hooker included in his paper a *résumé* of some of the more important results obtained by him during the past two years and also contrasted the views entertained by E. Paterno and himself. The paper was received with marked attention and interest by the members present. Specimens of the substances discussed were exhibited. The complete publication of these results will be deferred by the author for some time.

The section then adjourned.

WM. C. DAY, *Secretary.*

NOTES ON IRON IN BONE-BLACK.

BY DR. BRUNO TERNE.

The freshly-prepared bone-black of the market yields on an average from 0.1 to 0.3 per cent. of iron in the form of metallic iron, originating principally from iron mixed with the bones gathered up by the junk dealers, another portion coming from the wear and tear of the bone crushers and mills, and a very little from the iron vessels used in burning the bones.

Having been in charge for the last fifteen years of one of the largest plants for manufacturing bone-black, I had never experienced any trouble with our product, on account of the iron, until several months ago, when one of our patrons complained of an excess of iron in our black, which, according to his investigation, had run up in one instance to one-half of one per cent.

This complaint was coupled with the assertion that an increase of 0.25 per cent. of iron above the average would materially impair the process of refining sugar.

This charge coming from a source commanding serious consideration, caused us to look into this matter thoroughly, but an examination of the literature of sugar refining, covering a period commencing with 1872 (*Wagner's Jahresberichte*) up to date, failed to disclose a single case in corroboration of the above-cited assertion.

The more I thought over the matter the more I became convinced that the complaint made against our black, that it impaired the work of refining sugar liquors, was merely a convenient pretext to shield some irregularities in the process of refining, which otherwise would have to be shouldered at home. We all know that organic acids will dissolve iron, but in refining sugars the liquors should be free from acids or at least nearly made free by previous neutralization; the traces of free organic acids must certainly all be absorbed by the six to seven per cent. of carbonate of lime contained in fresh bone-black. The fact that in discarded black the yield of carbonate of lime is reduced to three or four per cent., and the yield of iron considerably raised, demonstrates clearly that fresh black operates to free sugar liquors from iron as well as other impurities.

In order to ascertain what effect a solution acidified with organic acid would have on the iron in bone-black, I prepared two solutions of citric acid containing respectively 0.1 per cent. and 0.25 per cent. of free acid.

The acidity of these solutions is so great that no sugar liquor entering filters will ever approach it in acidity.

I selected a black which had given by analysis a yield of 0.5 per cent. of iron, and made the following experiments:

						Per Cent.
(a)	5	grammes	of	black	with	500 cc. citric acid solution of . . . 0.1
(b)	10	"	"	"	"	" . . . 0.1
(c)	5	"	"	"	"	" . . . 0.25
(d)	10	"	"	"	"	" . . . 0.25

I exposed the four flasks on the top of a steam heater for twenty-four hours to a temperature of 150° to 160° F., after

which I tested the still acid solution for iron with potassium sulphocyanide and potassium ferridcyanide, but no trace of iron could be found in the solution.

Not satisfied with this I kept the flask for eighteen hours on a steam-bath at a temperature of 200° to 212° F.; the results of the two experiments were absolutely the same.

To operate on a sample of black large enough to place the result of the experiment beyond any doubt, I took 250 grammes of the same black yielding one-half per cent. of iron and treated the same with two litres of citric acid solution containing 0.25 per cent. free citric acid, for twenty-four hours on the steam-bath at nearly 212° F.

At the end of this time the acidity of the solution had completely disappeared and the absolutely neutral solution showed not a trace of iron with the most sensitive reagents (potassium sulphocyanide and potassium ferridcyanide).

I went still a step further and prepared a solution of iron in citric acid, 200 cc. of which contained 1.01 grammes of iron. I took 100 cc. and diluted to 500 cc.; I mixed the dark-yellow solution in a flask with 500 grammes of fresh regular sugar-house black, boiled up for thirty minutes, filtered and obtained a perfectly limpid solution which contained not a trace of iron.

This experiment proved to my own satisfaction that an accidental excess of 0.25 per cent. of iron in fresh black could not be charged with creating irregularities in the process of refining sugar liquors. But not being an expert in sugar refining I submitted this problem with the above results of my own researches to my friend, Dr. Arno Behr, now Secretary and Treasurer of the Chicago Sugar Refining Company, an acknowledged expert in this branch of chemical industry at home and abroad. I submit herewith an abstract of his letter:

CHICAGO, January 4, 1892.

MY DEAR DR. TERNE: * * * "Iron is a very objectionable substance to have in filtered sugar solutions, because the refined soft sugars which are produced from such solutions take on a more or less gray appearance, which reduces

their value considerably compared with others, which are free from iron and of a bright yellow color.

"Colonial raw sugars contain sometimes a considerable amount of iron, and in the absence of good chemical methods for the removal of this iron from the unfiltered liquor, the refiner relies on the bone-black to absorb it.

"In some refineries the sugar solutions enter the black practically neutral, in others they are left a little acid, but this is of no consequence, for you have found yourself that new black will absorb the iron even from a strongly acid solution. Even old working bone-black contains enough carbonate of lime (three to four per cent.) to neutralize any considerable excess of acid. There is, however, a considerable difference in the behavior of new and old black. Say you want to filter 100 pounds of dry sugar over 100 pounds of bone-black. Say this sugar contains two to three-hundredths of one per cent. of Fe_2O_3 . The solution will come from the new black absolutely free from iron, while from the old black half of it perhaps will be free, and the other half will contain it in increasing quantities.

"This will happen with properly neutralized liquor and without any fermentation having occurred. Even if the sugar solution enters the black free from iron, towards the end it will come from the old black containing iron.

"It works this way without any attempt having been made to wash the liquor out of the black. As soon as that is done matters become worse. Even from very good black the diluted sugar solution carries away a certain amount of iron.

"Now in working it is found that the amount of iron increases in the black with its age, and that in the same proportion the amount of iron increases in the liquor. There is no way of removing the iron once absorbed by the black.

"There are three sources of iron in the black:

- (1) "The iron originally contained in the black.
- (2) "The iron in the raw sugar.
- (3) "The iron taken up by the liquors and the bone-black in the sugar refining.

"The liquor has very little chance to dissolve iron, but

the bone-black gets more or less of it by its passages through the kilns. The iron in the raw sugar the refiner has to take and make the best of, but in the case of the iron in the new black he will naturally fall back on the bone-black manufacturer and I do not blame him.

"It is reasonable to expect that a black with 0.1 per cent. Fe will furnish iron-free liquors for a longer time than one with 0.3 per cent. Fe. Most of the iron in new bone-black is in the metallic state and can be removed by running the crushed black over a magnetic separator.

"With best regards,

Yours very truly,

"ARNO BEHR."

Certainly every one will agree with my friend, Dr. Behr, that 0.1 per cent. impurity of anything is to be preferred to 0.3 per cent.; the self-interest of the manufacturer will command the adoption of such means as to keep the percentage of iron as low as possible.

In the interest of manufacturers of bone-black everywhere, I thought it, however, of sufficient importance to refute the theory that an accidental excess of a fraction of a per cent. over the acknowledged unavoidable proportion of iron in new black, could be held accountable for any disturbance in the process of sugar refining, and to have my protest recorded with the section against such a claim.

This point has been fairly covered by my own experiments, and is clearly corroborated by the opinion of one of the most competent sugar chemists of this country.

Regarding the chemical methods of iron determination which are far too laborious to perform every day, I have been trying to find a method which could be carried on with sufficient accuracy without requiring previous chemical training.

I found that a boy, with the help of a magnet, could, by exercising the necessary care, make a determination, sufficiently accurate for the daily control of a bone-black mill.

Take 100 grammes of the black and spread it in a thin layer over a sheet of white paper, then plow through it with a good magnet (I am using a six-inch horseshoe) and it will be

found that most of the iron will be picked up at the first few passes.

After repeating the passes of the magnet in every direction, carefully observing that no part of the mass is missed, in a very few minutes all the iron will have been gathered on the watch glass ready for weighing. The results thus obtained come sufficiently close to those obtained by chemical test to serve as a control upon the process of manufacture, as the following examples will show :

The following tests have all been made within the last four months :

	<i>By Chemical Analysis. Per Cent. Iron.</i>	<i>By Magnetic Test. Per Cent. Iron.</i>
October, 1891,	0'360	0'410
1891,	0'160	0'219
December, 1891,	0'387	0'501
January, 1892,	0'100	0'130
1892,	0'169	0'213
1892,	0'080	0'107
1892,	0'199	0'224

While the magnetic test is invariably too high, it is sufficiently close to control the work of the black mills. The adherence of particles of carbon to the iron fully explains this result.

Regarding the chemical determination of iron, I consider a previous incineration of the black necessary, because there is a possibility that traces of organic matter left in the fresh black may be mistaken for iron by the reduction of the potassium permanganate.