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LABORATORY NOTES.

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I. Alumina in Wheat.—The recent experiments of Yoshida (*Jour. Chem. Soc.*, li., 748) and Young (*ANALYST*, xiii. 5), showing that alumina is a natural constituent of the ash of wheat, have rendered it desirable to see how far their conclusions modify the views hitherto held on this subject.

In the discussion of a paper read by Mr. Wanklyn at the first meeting of this Society, I stated that "in my experience an allowance of 3 milligrammes per 100 grammes of bread, for phosphate of aluminium naturally present, is amply sufficient." This would correspond to about .005 per cent. of aluminium phosphate in the flour. Mr. Jones said his experience confirmed mine absolutely. Dr. Dupré had met with as much as .009 per cent., and Dr. Stevenson agreed with him. Dr. Muter mentioned a case where the bread was made with salt containing alumina had met with nearly .010 per cent. Mr. Wigner was in the habit of allowing .008 for phosphate of aluminium natural to the article.

More recently it has been shown—I think by Dr. Dupré—that the alumina natural to flour bears more or less relation to the proportion of silica present, from which it may be inferred that the alumina exists wholly or chiefly as silicate, and hence is probably of extraneous origin. On the results of these experiments I based the statement in my "Commercial Organic Analysis" (vol. i., page 373), that "it may be taken as a rule that from the amount of alum calculated from the total aluminium of the bread should be subtracted a weight equal to the silica found, when the difference will be approximately the true amount of alum added." Thus if the total aluminium corresponded to .040 per cent. of alum, and the silica was .008 per cent., the corrected proportion of alum would be .032 per cent.

Dr. James Bell considers that his experiments do not indicate any definite relation between the silica and alumina of flour, but his figures show that, broadly speaking, the alumina tends to follow the silica.

The experiments of Yoshida, which appear to have been very carefully made, were conducted on cereals and leguminous plants grown on a soil of volcanic origin, remarkable for containing a large proportion of alumina soluble in hydrochloric acid. Under these circumstances, Yoshida found 2.62 per cent. of mineral matter in the whole wheat, and this mineral matter contained 0.106 per cent. of alumina, equivalent to 0.2536 per cent. of aluminium phosphate. Calculated on the original wheat, this is 0.0066 per cent., or just about what was previously admitted to be normally present.

Mr. Young comes to an exactly similar conclusion, obtaining from Vienna flour of the best quality, containing 0.7 per cent. of ash, 0.0075 per cent. of aluminium phosphate.

All these amounts are so insignificant that they do not materially invalidate the dictum that "flowering plants do not contain aluminium as a normal constituent," though in strict accuracy, and in view of recent experiments, the words "except in extremely minute proportions," should be added. The practical interest attaching to the question exists in the fact that the proportion of alumina found to be naturally present in wheat confirms the justice of making a deduction of 7 or 8 grains of alum per 4 lb. loaf from the amount corresponding to the total aluminium found by analysis.

I may here remind the members that it has been raised as a defence for the presence of alum in flour that alum formed a leading constituent of the composition used for stopping the holes and cracks produced in millstones by wear.

I may call the attention of those interested in the mode of existence of aluminium in bread and flour to a process I devised some years since, by which I obtained very

encouraging results and rendered unnecessary the questionable correction for the aluminium existing as silicate. It consisted in effecting the solution of the starch by malt-extract, destruction of the resultant soluble carbohydrates by fermentation with yeast, acidulation of the liquid by nitric acid, followed by filtration, evaporation of the liquid, ignition of the residue, and precipitation of the aluminium as phosphate in the usual way.

Before leaving the subject, I may add that if the results of the analysis of samples of flour and bread may be regarded as indicating the general character of the articles, adulteration with alum is practically obsolete in the districts for which I act as analyst.

II. Precipitation of Hop-Bitter by Lead Acetate.—At a recent meeting of the Society Dr. Johnstone read a paper which was published in the last number of the ANALYST, describing experiments from which he concluded that neither neutral or basic acetate of lead effectually removed the bitter principle from an infusion of hops. As this view was opposed to my own experience, and that of all previous observers, except in a solitary instance mentioned by Dr. Muter, I suggested to Dr. Johnstone that we should both subject to the method the same sample of hops with a view of seeing whether the non-precipitation of the bitter by lead was in any way a consequence of his method of manipulating. In pursuance of this I examined a sample of hops which had been used by Dr. Johnstone in his experiments, and found that the treatment with lead in the manner prescribed by me did not remove the whole of the bitter. On the other hand, I sent a portion of a sample of hops which I had already submitted to the process with satisfactory results to Dr. Johnstone, when curiously enough he failed to precipitate the bitter principle although I had succeeded perfectly. With a second portion of hops from the same source, though not strictly the same sample, he also found the process to fail. In the case of this sample, therefore, there is a direct conflict of evidence, Dr. Johnstone failing to make the process to answer, whereas I had succeeded. But the fact that such an apparently simple operation could fail in the hands of another chemist seemed to me very serious, and I have consequently submitted to the process some eight or ten additional samples of hops. In most instances the process has succeeded fairly well, though when operating on a considerable quantity of hops the residue has usually retained a slight but distinct bitter taste. In one or two instances, however, the bitterness has been more strongly marked, as, indeed, it was in the sample sent me by Dr. Johnstone.

The experiments prove to my mind that precipitation with lead acetate cannot be relied on to remove all the bitter principle of the hop from all infusions containing it, especially when the delicacy of the method is increased by extracting the remaining traces of bitter with chloroform, instead of simply tasting the concentrated filtrate.

III. Note on the Determination of Sulphur in Oils.—I had occasion recently to analyse a sample of blast-furnace creosote oil, in which I was desired to determine the proportion of sulphur. The quantity likely to be present was, of course, much smaller than is usually met with in organic substances containing sulphur as an essential constituent, and hence the ordinary processes of determining sulphur, employed in ultimate organic analysis, seemed scarcely applicable, as a considerable quantity of the substance, at least 5 grammes, would be required for the experiment. Oxidation with nitric acid

was for obvious reasons an unsuitable process, and the same remark applied to treatment with dry oxidising agents. Under these circumstances it appeared to me that the best plan would be to burn the oil in a suitable lamp, and estimate the sulphur in the products of combustion, just as sulphur is estimated in coal-gas. I was here met, however, with the difficulty that when burned from a wick the creosote oil produced intolerable quantities of smoke, which could not be controlled and rapidly clogged the wick, whether of asbestos or cotton, thus bringing the experiment to an end. Various experiments in this direction were made until I decided to dilute the creosote oil with alcohol, hoping thus to obtain a better regulation of the combustion. With certain precautions this plan was found to answer, and ultimately the arrangement shown in the sketch was adopted.

A purified methylated spirit was made by distilling the ordinary spirit of commerce from caustic alkali, and this was saturated with solid ammonium carbonate. 5 grammes of creosote oil was then dissolved in 45 grammes of the spirit, and the whole placed in the lamp A, to the top of which the adapter C is fitted air-tight by means of a large bung. The upper end of the adapter is connected with a bent glass-tube passing nearly to the bottom of a vertical Liebig's condenser filled with wet glass marbles and broken glass. The lower end of the condenser is fitted with a glass tap, and the higher tubulure

is connected with a water-pump, or other aspirating arrangement by which a continuous steady current of air can be drawn through the apparatus. By preference a second Liebig's condenser, filled with glass beads, is introduced between the first condenser and the pump, but this is not really necessary. The apparatus being arranged, the spirit is ignited, when the combustion proceeds quietly, but the operation has to be conducted very slowly to prevent smoking, and it is desirable to cool the metal part of the lamp by wrapping round it copper gauze, as otherwise the alcohol vapour is liable to kindle with slight explosion, and the lamp is extinguished. The water condensed in D, and which is tapped off at intervals into the flask F, of course contains all the sulphur of the creosote oil in the form of sulphate or sulphite of ammonium. It is treated with bromine water, acidulated, and the sulphur precipitated as barium sulphate in the usual way. In this manner the particular sample of creosote oil for which the process was devised was found to contain 0.087 per cent. of sulphur, and on repetition by the same process 0.088 was found.

I have also used the same process for determining the sulphur in rape oil. In this case the sample was mixed with an equal weight of ordinary kerosene, but instead of dissolving the carbonate of ammonium in the liquid it is preferable to suspend it over the flame in a small porcelain crucible. In this way a sample of rape oil was found to contain 0.017 per cent. of sulphur after making a correction for the sulphur in the kerosene oil with which it was mixed, which amounted to 0.000014. A convenient plan of ascertaining how much of the oil has been consumed is to weigh the lamp before and after the experiment.

DISCUSSION.

Dr. VIETH said they had heard a very interesting communication from their President. In a laboratory where there was a variety of work there must always be curious results cropping up, and that was just the place to bring those results forward. If that were always done, their meetings would become yet more interesting, and perhaps more members would be induced to contribute papers.

Mr. HEHNER said that with regard to the hop question he had intended to say a few words. He had also taken up the matter, and thought perhaps that a possible explanation of the difference in the results obtained by Dr. Johnstone and Mr. Allen was this—as there was no doubt that those two observers did get different results, and there should be some explanation—perhaps the quantity of acetate of lead used might be the cause, or the precipitate might possibly be more or less soluble in excess of lead solution.

He made an extract from pure hops himself, and added various quantities of lead acetate, removing the excess of lead with sulphuretted hydrogen, and evaporating to dryness, and in all cases he got a residue which was distinctly bitter; also on precipitation with basic acetate one could taste the bitter, but if the liquid was not evaporated to complete dryness, a bitter taste could not be perceived. In no case had he shaken out with chloroform and ether. He thought that the difference greatly arose from the fact that the test had been made rather too delicate, and that it was advisable to avoid evaporation to dryness, or to a very small bulk.

Dr. JOHNSTONE said that he got the bitter out of the beer—not out of the hops. With regard to alumina in flour, a discussion took place in the *Chemical News* some time ago upon the supposed finding of copper in bread. Dr. Edmonds wrote to that journal drawing attention to the blue colour which occurs very often. Other writers made some reply, and then the matter dropped. He had obtained the same results, and

examining the blue colour found it was due to phosphate of iron—vivianite, in fact.

Mr. HEHNER said that whenever he had tested flour for copper he had always found copper.

Mr. ADAMS said that he had made a number of experiments in the hop question, and had never failed to get rid of the bitter when it was due to hops, but perhaps that arose from his not having carried his experiments so far as Mr. Allen had done. He (Mr. Adams) made a decoction, and treated it with basic acetate of lead, threw down the lead finally by sulphuric acid, which was quicker than sulphuretted hydrogen, and then reduced the bulk from half a pint to about half an ounce, and in every case with that quantity he could always taste foreign bitter, while that of the hop had entirely disappeared. He did not know whether that explained Mr. Hehner's results, where he only carried his evaporations to a fluid state, and not dryness. With regard to the detection of bitters, there was only one that failed him, and that was camomile, the bitter of which, like hops, was precipitated by acetate of lead.

Mr. ALLEN said that the direct tasting of the concentrated aqueous liquid was doubtless a less delicate method of recognising a bitter principle than agitating the liquid with ether or chloroform, and tasting the evaporated chloroformic or ethereal solution. It appeared probable that the evaporation of a solution containing more or less free sulphuric acid would tend to decompose any trace of hop-bitter which had remained unprecipitated by lead.*