course, a blast-lamp is necessary. Direct combustions of difficultly soluble alloys may be made very readily in this crucible by mixing the finely divided alloy with lead chromate in a small porcelain crucible and placing the latter in the platinum crucible for combustion, as practised by Mr. C. A. Buck, of the Bethlehem Steel Co.

The construction of the crucible and stopper will be readily understood by reference to Figs. 1 and 2. The air or oxygen inlet is at *a*. The cold water enters the stopper at *c*, and leaves it at *d*, from which point it is led by means of a rubber tube to *e*, where it enters the platinum chamber surrounding the top of the crucible. The water runs to waste at *f*; or, the direction of the flow of water may be reversed, the water entering at *f* and escaping at *c*. The band of pure, black rubber, such as can be had at most stationers, is shown at *g*. It is essential that these bands be of the best quality of rubber obtainable, for such a band will make an absolutely tight joint with the crucible, and one band may be used for many combustions. Before inserting the stopper into the crucible, the band should be wetted with a little water, to lessen friction and secure a tight joint.

For the determination of combined water in ores, minerals, and cements, it may be mentioned here, the circulating water must be preheated to prevent condensation of the water driven out by the ignition of the sample on the cool stopper and upper part of the crucible.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE AGRICULTURAL EXPERIMENT STATION.]

THE COMPLETE ANALYSIS OF FEEDING MATERIALS.

BY C. A. BROWNE, JR., AND C. P. BEISTLE.

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IN the ordinary analysis of feeding-stuffs it has been the general custom to determine only a few of the many constituents present; for the computation of rations or for the determination of feeding values an estimation of the moisture, fat, protein, ash, and fiber is all that is usually required, the percentage of undetermined matter being simply designated "nitrogen-free extract."

This method of procedure, while sufficient for many purposes, is by no means scientifically accurate, and chemists have for a

long time felt that not only should a closer study be made of the various substances, or rather groups of substances, such as ether extract, protein, and fiber, but also that more attention should be given to that large group of undetermined bodies which make up the nitrogen-free extract.

Considerable work has been accomplished along these lines during the past few years, both in this country and abroad. Good workable methods have been adopted for the determination of sugars, starch, and pentosans, and some attempts have been made towards effecting a separation of the various lignin and cellulose bodies, which make up the greater part of what is termed crude fiber. In many cases, more particularly in the analysis of grains, the percentages of the various constituents will approximate very closely 100 per cent., but in other cases, as with feeds rich in fiber, such as hay and straw or even certain cereal products, a considerable discrepancy still exists.

In the spring of 1899 a sample of distillery waste or mash was received at the Penna. Experiment Station from the Heinz Pickle Co., of Pittsburg, Pa. A portion of the sample, which was very moist and had slightly fermented, was examined for alcohol, and fixed and volatile acids; the rest of the material was dried as quickly as possible, then ground, and subjected to the customary fodder analysis with the following results:

	Per cent.
Moisture	3.85
Crude fat	10.25
Crude fiber	17.73
Ash	1.82
Protein	23.44
Total	57.07
Nitrogen-free extract	42.93

A determination of starch in the material by the diastase method gave less than 3 per cent., showing that the malting process had been quite complete. A determination of the furfural-yielding compounds or pentosans gave about 25 per cent., showing the material to be very rich in these bodies as was to be expected from the concentration which other constituents of the mash would undergo, with the elimination of the starch. There still remained, however, some 15 per cent. of material unaccounted for. This appeared to us such an unusually large

amount for a cereal product, that we were led to make a more complete study of the undetermined residuum.

In the choice of a method applicable to a case of this kind, the writers were guided, to a great extent, by a scheme of analysis devised by H. C. Sherman.[1] The scheme adopted by us in the present instance is given herewith and differs from that of Sherman in but few respects. We have divided the lignin bodies into two classes,—the lignic acids which are removable directly by NaOH, and the lignin which is removable only after chlorination. While, as Sherman says, "there may be no established chemical difference on which to rest such a distinction," we believe that there is a physiological difference, in that the lignin which is removable only after chlorination is of a more condensed variety than that removed by direct treatment with NaOH. We have also introduced the step, since an opportunity was given of studying the solvent action exercised by the alkaline solution employed in ordinary crude-fiber analysis.

SCHEME FOR THE ANALYSIS OF DISTILLERY WASTE.

(Four samples of 5 grams each were taken for analysis.)

	Original substance. Per cent.	Per cent.
I. Samples were dried for 8 hours at 100°C.....	Loss = Moisture,	3.83
II. Residues from I extracted with anhydrous ether 16 hours.....	Extract = Crude fat,	10.25
III. Residues from II boiled with 95 per cent. alcohol 30 minutes, cooled, made to 100 cc. with alcohol, filtered, and filtrates combined:		
a. Extract determined in aliquot	3.62	
b. Ash " " "	0.10	
c. Protein " " "	1.20	
d. Sugars " " " (by copper reduction)....	0.00	Sugar, 0.00
Undetermined matter [*a* — (*b* + *c* + *d*)].....	2.32	
IV. Residues from III treated with water at laboratory temperature over night; made to 100 cc. with water, filtered, and filtrates combined.		

[1] This Journal, **19**, 297.

e. Extract determined in aliquot	4.50	
f. Ash " " "	0.46	
g. Protein " " "	0.73	
h. Dextrin (?) " " " (by inversion and copper reduction).....	2.13	Dextrin (?), 2.13
Undetermined matter [*e* — (*f* + *g* + *h*)]	1.18	
V. Residues from IV dried and weighed, then reground and the starch determined by the diastase method; residues dried and reweighed.		
i. Residue determined before diastase treatment.....	78.29	
j. Starch determined in extract from diastase treatment..	2.66	Starch, 2.66 (?)
k. Residue determined after diastase treatment.....	73.87	
VI. Residues from V boiled 30 minutes with 200 cc. H_2SO_4 1.25 per cent., filtered, washed with hot H_2O and alcohol, dried, weighed, and then combined.		
l. Residues determined after H_2SO_4 treatment	45.42	
m. Protein determined in aliquot of combined residues	16.56	
n. Ash determined in aliquot of combined residues.....	0.95	
o. Carbohydrates in residue [*l* — (*m* + *n*)].....	27.91	
VII. Aliquots from combined residues of VI boiled 30 minutes with 200 cc. NaOH 1.25 per cent., filtered, washed with hot H_2O and alcohol, dried, and weighed.		
p. Residue determined after NaOH treatment.....	17.94	
q. Protein determined in aliquot of residue	0.63	
r. Ash determined in aliquot of residue	0.21	
s. Carbohydrates in residue [*p* — (*q* + *r*)]	17.10	
t. Carbohydrates removed by NaOH treatment (o — *s*)	10.81	Lignic acids, 10.81 (?)

VIII. Residues from VII chlorinated 1 hour, then boiled 5 minutes with 2 per cent. Na_2SO_3 and 0.2 per cent. NaOH solution (method of Cross and Bevan), filtered, washed, with hot H_2O and alcohol, dried, and weighed.		
u. Residue determined after chlorination process	16.26	
v. Protein determined in aliquot of residue	0.19	
w. Ash determined in aliquot of residue.....	0.11	
x. Carbohydrates in residue $[u - (v + w)]$	15.96	
y. Carbohydrates removed by chlorination process $(s - x)$	1.14	Lignin, 1.14
z. Pentosans in residue *u* 5.62 per cent., or of original substance	0.91	
Cellulose $[u - (v + w + z)]$	15.05	Cellulose, 15.05
Pentosans determined in original substance by phloroglucin method.....		Pentosans, 24.86
Nitrogen determined in original substance 3.75 per cent., $N \times 6.25 =$ protein		Protein, 23.44
Ash determined in original substance.....		Ash, 1.84
Total.....		96.01

The sum of the various ingredients in the above table amounts to 96.01 per cent., thus leaving an undetermined residuum of about 4 per cent. It was thought at first, that the undetermined matter in the alcoholic and aqueous extracts might explain this deficiency; the sum of this undetermined matter in the above scheme, it will be seen, amounts to 3.5 per cent., and if this be estimated as resin or gum, as is sometimes done, there would remain but about 0.5 per cent. of material unaccounted for.

Before working upon this assumption, however, it was thought best to make further studies as regards the actions of the various solutions employed in the above scheme. A second series of 4 samples were carried through exactly as the first with the additional determination of the pentosans in the residues after each stage of the process. The following results were secured:

	Per cent.
I. Pentosans in original material	24.86
II. Pentosans in residue after alcohol and water treatment	22.16
III. Pentosans in residue after malt digestion	20.98
IV. Pentosans in residue after H_2SO_4 treatment	3.32
V. Pentosans in residue after NaOH treatment	0.87

It appears from the above results that several per cent. of material of a pentose nature finds its way into either the alcoholic or aqueous extracts. Such substances, owing to their marked copper-reducing power, would naturally affect the sugar or dextrin determinations. Since no copper-reducing bodies were removed by the alcohol, the inference is, that the pentoses dissolved were removed entirely by the water. The writers believe that the copper-reducing power of the aqueous extract, as shown in the scheme, was due mostly or even entirely to bodies of a pentose nature, and that a serious error may thus exist in the process usually employed for determining dextrin in feeding materials.

The undetermined matter of the alcoholic extract is no doubt made up of some unclassified constituents, such as resin, etc., and at this stage of the analysis there is probably to be found a part of the discrepancy which sometimes exists in the complete analysis of feeding materials.

Another fact in connection with the pentosan determinations is that 1.18 per cent. of pentosans disappears during the malt digestion. To test this in another way, the pentosans were determined in the extract from the malt digestion. The following results were secured:

	Per cent. of original substance.
Pentosans in extract from malt digestion	2.71
Pentosans in malt solution	1.29
Difference equals pentosans actually removed	1.42

This figure coincides very closely with the value previously given, and proves unquestionably that the malt solution does exert some solvent action upon the pentosans. In order to determine how much the removal of pentosans was due to the solvent action of water alone, a blank experiment was run, using the same amount of water as malt solution, and conducting the digestion for the same length of time; the aqueous extract was then concentrated, and a determination of pentosans made in the

usual way ; the amount thus obtained amounted to 0.85 per cent. of the original material, thus showing that a considerable amount, but not all, of the pentosans removed during the malt digestion, was due simply to the solvent action of water.

A removal of pentosans during the diastase digestion introduces somewhat of an error into the starch determination. Starch was present in the material analyzed, as was shown by the slight iodine reaction, but the percentage indicated in the scheme is undoubtedly too high. The error thus introduced into the starch determination by the solubility of pentosans, would probably never be much greater than the above case, owing to the large amount of pentosans present and the long period of digestion, which, in the present instance, was twelve hours.

From the table of pentosan determinations, it is seen that 17.66 per cent. of pentosans disappears during the treatment with sulphuric acid. The extract from this treatment was saved in order to make a comparative determination of the pentosans removed, by the copper reduction process.

The extract was diluted to 300 cc., after adding sufficient H_2SO_4 to make the total amount 2 per cent. of the solution after diluting, and the whole boiled for six hours in a 500 cc. flask connected with a condensing tube. After cooling, the solution was neutralized with dilute NaOH, using phenolphthalein, and the volume completed to 500 cc. 25 cc of this solution gave a weight of reduced copper[1] equivalent to 21.65 per cent. dextrose, which would be equivalent to 21.00[2] per cent. pentoses, or 18.48[3] per cent. pentosans.

Another point which must not be overlooked in the complete analysis of feeding materials, is the presence of furfural-yielding constituents in the material left after the chlorination process. In the scheme, the writers have estimated these bodies as pentosans, and subtracted their percentage from the percentage of fiber after chlorination, in calculating the percentage of cellulose. It may be, however, that these furfural-yielding constituents of the fiber, after chlorination, are of an oxycellulose nature, as appears from the work of Cross and Bevan, in which case the total percentage of pentosans would need to be corrected.

[1] Allihn's method of copper reduction was followed in this and all other instances.

[2] Dextrose × 0.97. Stone : *Am. Chem. J.*, **13**, 73.

[3] Pentoses × 0.88.

In conclusion, it may be said that, while the sum of the percentages of the different constituents in many feeding stuffs does not equal exactly 100 per cent., the results are as close as could be expected with the present methods of analysis. In addition to the uncertainties of some of the analytical steps just pointed out, it should also be noted that the factors used for the calculation of protein and pentosans are more or less of an arbitrary nature, and cannot be considered absolute in the case of any particular feeding material. In view of this, and our present incomplete knowledge of many of the various proximate constituents of feeding materials, the exactness attainable in some other departments of analytical chemistry is not at present to be hoped for.

CATALYSIS IN CONCENTRATED SOLUTIONS.

BY J. M. CRAFTS.

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THE study of the catalytic action of acids in very dilute solutions has led to the discovery of a number of simple relations between ionic dissociation, chemical affinity, and electrical conductivity, and the conclusion is universally accepted that the active agent is the hydrogen ion. The ratio of the velocity of the reaction to the concentration of the catalysor is nearly constant in dilute solutions of strong acids, but when ionic dissociation is diminished by increasing concentration, or in the case of weak acids by the presence of bodies which reduce the concentration of hydrogen ions, the ratio of velocity to concentration diminishes ; a small acceleration has, however, been observed when certain salts are added to the solutions of strong acids. Most of the subjects for experiments, such as the decomposition of esters, the inversion of sugar, etc., do not admit of the employment of very concentrated acid solutions, because the catalysor would then enter into the reaction, forming by-products.

It seemed interesting to study the hydrolysis of the sulphonic acids by means of chlorhydric acid and other strong acids, because here the reaction is catalytic in the sense that it is induced by the presence of a strong acid which does not enter into the final products, nor does it even form intermediate products in the same evident way as in esterification by sulphuric acid, or in the oxidation of sulphurous acid through the medium of nitrous fumes, nor does the degree of concentration of the catalysing