silver selenite ammonia with hydrochloric acid, wash the paper free from chlorine and reduce the selenious acid in the filtrate by means of sodium bisulphite.

(*b*) In case zinc nitrate is used: Filtering after the decomposition with hydrochloric acid may be omitted.

INDIANA UNIVERSITY, BLOOMINGTON, IND.,
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[CONTRIBUTION FROM THE LABORATORY OF THE PENNSYLVANIA STATE COLLEGE EXPERIMENT STATION.]

THE DETERMINATION OF SULPHUR AND PHOSPHORUS IN PLANT SUBSTANCES.

BY C. P. BEISTLE.

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IT IS commonly known to chemists that plant materials, in their conversion to ash by burning, lose not only water, carbon dioxide, and nitrogen as the gaseous products of their ignition, but generally some portion of their sulphur and phosphorus as well.[1] Experience of other analysts has shown that such losses can not be avoided, like those of alkaline chlorides, by any simple precaution. The accurate determination of sulphur and phosphorus is of great importance in calculating the heat of combustion in plant substances from their elementary analysis, and the determination of phosphorus in estimating the soil-exhausting action of vegetable products. The ordinary ash analysis is insufficient for such purposes.

The following work was undertaken at the suggestion and under the direction of Dr. William Frear. The determination of sulphur and phosphorus in plant substances is carried on by a number of different methods and a comparison of results on a few of these methods is all that was attempted. The substances analyzed were cottonseed-meal and timothy hay. There were also a few determinations made on egg albumen. These substances were chosen on account of the wide difference in their sulphur and phosphorus content, the cottonseed-meal containing relatively large amounts, while the timothy hay is very poor in these elements. The methods used were as follows:

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[1] Wiley's "Principles and Practice of Agricultural Analysis." Vol. I, pp. 419-420; Vol. III, pp. 37, 430 and 446.

First. Determination of the sulphur and phosphoric acid in the ashes of the substances.—About 5 or 10 grams of the sample were incinerated in a platinum dish; the ash was digested with a little dilute hydrochloric acid and then washed on a filter with hot water. The filtrate and washings were made up to about 150 cc. and then, while hot, barium chloride solution was added. After standing twelve hours, the solution was filtered, and the barium sulphate was washed, ignited, and weighed; the amount of sulphur was calculated from the weight of barium sulphate. The filtrate and washings from the barium sulphate precipitation were evaporated to a small bulk, the hydrochloric acid neutralized with ammonia and the solution was acidified with nitric acid. Phosphoric acid was then determined in the usual way with ammonium molybdate and magnesia mixture.

Second. Destruction of organic matter by fusion with potassium hydroxide and nitrate and determination of sulphur and phosphoric acid in the fused mass.—Two grams of the sample were fused with a mixture of 20 grams of potassium hydroxide and 6 or 8 grams of potassium nitrate. The fusion was made in platinum crucibles heated by gasoline gas. Blank determinations were made, which gave no trace of sulphur or phosphorus, showing both the purity of the reagents used, and that no sulphur was absorbed from the gas. After complete fusion was obtained the mass was cooled, dissolved in hot water, and then carefully acidified with hydrochloric acid. Sulphur and phosphoric acid were determined in this solution as before. A blank determination was made on the potassium hydroxide and potassium nitrate but neither sulphur nor phosphoric acid was found.

Third. Destruction of organic matter by action of potassium hydroxide followed by chlorine, and determination of sulphur and phosphoric acid in residues.—Two grams of the sample were boiled with about 200 cc. of a strong potassium hydroxide solution for thirty minutes. Chlorine was then passed through the solution till it was decolorized. The solution was then acidified with hydrochloric acid and filtered. The sulphur and phosphoric acid in the solution were determined in the usual way.

Fourth. Destruction of organic matter by ignition with oxygen in a bomb-calorimeter and determination of the sulphur and phos-

phoric acid in the products of combustion.—A 2-gram sample was pressed into a small tablet and placed in a Hempel-Atwater bomb-calorimeter. The bomb was then filled with oxygen at a pressure of 18 atmospheres. The sample was ignited by an electric fuse. During combustion, the bomb was surrounded by cold water, as is usual in determining heats of combustion, and kept thus cooled for fifteen minutes, so that the condensation of the vapors formed in the bomb might be as complete as possible. Owing to the high pressure of the gases enclosed within the bomb and the nature of its vent, the regulation of their escape, in such manner as to ensure the complete absorption of any substances containing sulphur or phosphorus that might have escaped condensation, seemed impossible. The method is, therefore, valid only in so far as the sulphur and phosphoric acid are retained in the solid and liquid residues within the bomb. The liquid contained only traces of phosphoric acid, this constituent appearing chiefly in the solid residues. After the ignition, the bomb was opened, the liquid it contained was washed into a beaker and the small amount of ash, which was usually in the form of an insoluble glassy slag, was fused with sodium carbonate. This fusion was dissolved in hot water, and the solution added to the liquid washed from the inside of the bomb. The sulphur and phosphoric acid were then determined in the solution.

Fifth. Destruction of organic matter by a boiling mixture of nitric and hydrochloric acids, and determination of sulphur and phosphoric acid in the resulting solution.—The samples were treated according to the method of the Association of Official Agricultural Chemists for total phosphoric acid. Two grams of the sample were boiled for thirty minutes in a mixture of nitricand hydrochloric acids. The sulphur and phosphoric acid were determined in the solution. In some of the determinations on cottonseed-meal the boiling was carried on for a much longer time and the acid lost by evaporation was replaced by more acid.

Sixth. Destruction of organic matter by burning in oxygen in a combustion tube and determination of sulphur and phosphoric acid both in the residual and escaping gases.—The sample was burned in a combustion tube in a current of oxygen. The products of combustion were passed through a series of absorption tubes containing a hydrochloric acid solution of bromine. After the combustion was completed, the solution in the absorption tubes was emptied into a beaker. The combustion tube was washed out to remove the ash, and the washings were added to the solution from absorption tubes. The mixed solutions were boiled till all the bromine was expelled. and then filtered. The sulphuric acid was then determined in the clear solution as usual. The complete combustion of the organic matter was attained with difficulty; undecomposed vapors tended to form a tarry deposit at the exit end of the tube; this was finally overcome, first, by introducing the oxygen not only at the end of the combustion tube, but also, by means of a small tube inserted at a point about an inch beyond the boat containing the burning material; and, second, by taking pains to keep the tube at a bright red heat for a few inches beyond the entrance of the second stream of oxygen. With these precautions, no condensaton of tarry products occurred. To secure the most complete contact of the escaping gases with the bromine solution, the latter was held in four 6-inch, 3-bulb U-tubes set in a pan of cool water, and the gases were evolved slowly as in a carbon determination.

Seventh. Ignition after saturation with a solution of calcium acetate.—The sulphur was also determined according to a modification of the method proposed by A. E. Shuttleworth of Ontario Agricultural College. Ten grams of the sample were saturated with 20 cc. of a solution of calcium acetate containing 29.2 grams to the liter. The material was then incinerated and sulphur determined in the ash. These incinerations took place in a platinum crucible.

Eighth. Ignition after saturation with a solution of barium hydroxide.—Ten grams of the cottonseed-meal were saturated with a solution of barium hydroxide, dried, and ignited. The ash was fused with sodium carbonate, the fused mass extracted with hot water, the solution filtered and the sulphur determined in the filtrate as usual.

A partial analysis of the organic substances used, was made with the following results:

TABLE I.—FODDER ANALYSIS OF MATERIALS.

	Moisture.		Fat.		Protein.[1]	Ash.	
Cottonseed-meal ..	7.08	7.13	10.05	10.00	42.12	5.73	5.70
Timothy hay	4.55	4.50	2.02	2.02	4.75	3.81	3.84
Egg white (dry)..	...	...	...	...	83.37	6.02	...

As previous statements indicate, the results are somewhat differently expressed for the two elements under consideration, those for sulphur being given in terms of the element itself, those for phosphorus in terms of the pentoxide, P_2O_5, commonly spoken of, in agricultural chemical literature, as "phosphoric acid". The reason for the distinction is that evidence points to the existence of phosphorus in plants principally in the form of phosphoric acid, except in the seeds where it exists largely in the organic form in lecithins and other similar compounds; and to the fact that sulphur is present principally in some other state of combination than sulphuric acid.

The following experiment clearly shows this fact. Any sulphates present in a plant substance can be removed by careful extraction with hydrochloric acid of moderate strength and can be precipitated from the solution directly. The cottonseed-meal was thus extracted with acid of 1.06 sp. gr.; the solution contained sulphuric acid (SO_3) equivalent to 0.159 per cent. of the meal (as the result of duplicate, exactly concordant determinations); this corresponds to 0.064 per cent. of sulphur, about one-ninth of all the sulphur present.

The results of the several determinations of sulphur and phosphoric acid in cottonseed-meal and timothy hay by the foregoing eight methods are presented in Tables II-IV.

TABLE II.—SULPHUR.

	Cottonseed-meal.			Timothy hay.	
Methods.	I. Per cent.	II. Per cent.		I. Per cent.	II. Per cent.
1. In ash	0.046	0.040	....	0.048	0.042
2. Fusion with potassium hydroxide and nitrate	0.570	0.550	....	0.145	0.135
3. Destruction by potassium hydroxide and chlorine	0.280	0.280	....	....	....
4. In bomb-calorimeter products ..	0.440	0.410	....	0.075	0.068
5. In solution with hydrochloric and nitric acids	0.230 0.220[2]	0.240 0.230[2]	....	....	....

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[1] Nitrogen × 6.25.

[2] After extraction with ether.

Methods.	Cottonseed-meal. I. Per cent.	Cottonseed-meal. II. Per cent.		Timothy hay. I. Per cent.	Timothy hay. II. Per cent.
6. In products of ignition in combustion tube	0.470	0.440	0.450	....	....
7. Ignition after saturation with calcium acetate	0.120	0.120	....	0.044	0.044
8. Ignition after saturation with barium hydroxide	0.065	0.070	....	....	....

TABLE III.—PHOSPHORIC ACID.

Methods.	Cottonseed-meal. I. Per cent.	Cottonseed-meal. II. Per cent.	Timothy hay. I. Per cent.	Timothy hay. II. Per cent.	Timothy hay. III. Per cent.
1. In ash	2.41	2.31	0.355	0.345	...
2. Fusion with potassium hydroxide and nitrate	2.51	2.45	0.34	0.32	...
3. Destruction by potassium hydroxide and chlorine	0.42	0.46	...	...	...
4. In bomb-calorimeter products	2.21	2.34	0.29	0.29	...
5. In solution with hydrochloric and nitric acids	1.35	1.33	0.35	0.36	0.32
6. In products of ignition in combustion tube	0.78[1]	0.73[1]	...	...	...

[1] After extraction with ether.

TABLE IV.—ANALYSIS OF EGG ALBUMEN.

Method.	Calculated to dry substance. Sulphur.	Calculated to dry substance. Phosphoric acid.
1. In ash	0.196	0.21
2. Fusion with potassium hydroxide and nitrate	1.60	0.22

Sulphur.—It will be seen from these results that the fusion with potassium hydroxide and potassium nitrate gave the highest results for sulphur in all three of the substances examined, and that this method gave results on sulphur in egg albumen closely coinciding with those found by Hoppe-Seyler in the same substance; *viz.*, 1.57 per cent. The amount of sulphur in the ash of the various samples is so low that it gives no indication of the total amount of sulphur present, showing that the greater portion is driven off by ignition. The sulphur obtained by boiling with potassium hydroxide solution, with subsequent oxidation with chlorine, gave only half the sulphur found by the fusion method. The sulphur found by ignition in the bomb-calorimeter is about the same in amount as that found by combustion in a stream of oxygen and absorption of the products of combustion in a hydrochloric acid solution of bromine, but is still considerably less than is obtained by fusion.[1] It seemed to be impossible to completely oxidize and fix all the sulphur by any other method than by fusion with alkaline nitrate. The methods of saturating the substance with barium hydroxide solution and calcium acetate solution, respectively, before ignition, give results considerably higher than simple incineration without previous saturation; still, they are so far below those given by other methods that they are of slight value.

The great difficulty in the determination of sulphur in organic substances is to get all the sulphur completely oxidized. This was shown by the fact that when cottonseed-meal was fused with potassium hydroxide without enough nitrate being added to completely burn up the organic matter, the results were too low; also, the fusion thus obtained gave off hydrogen sulphide gas when treated with hydrochloric acid, showing that part of the sulphur had been fixed by the alkali but not oxidized.

Phosphoric Acid.—The fusion method gave slightly more phosphoric acid than the ash in the case of the cottonseed-meal, but practically the same for the timothy hay and egg albumen. This would indicate that in the substances examined, the phosphoric acid was volatile to a very slight extent if it all. Boiling with potassium hydroxide solution and treating with chlorine gave results so low, that this method may be discarded for the analysis of this class of bodies. The phosphoric acid found by ignition in the bomb-calorimeter was slightly less than by fusion, and this difference was probably due to mechanical loss of the smaller particles of the glassy slag which contained almost all the phosphoric acid.

The amount of phosphoric acid obtained from the hay by boiling with nitrohydrochloric acid was practically the same as found by fusion or incineration. When the cottonseed-meal was treated in this way only about half of the phosphoric acid present was obtained. It was thought at first that the phosphoric acid had not been taken into solution. When a sample of the cottonseed-meal was placed on a paper filter and extracted with nitric acid (sp. gr. 1.15), the phosphoric acid determined in the filtrate by direct precipitation amounted to 0.16 per cent. Other samples were treated as above, except that the filtrate was evaporated to dryness, the residue ignited, cooled, and then dissolved in nitrohydrochloric

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[1] [See, however, the following article. EDITOR.]

acid. The phosphoric acid was determined in the resultant solution, and in three determinations the results were respectively 2.18, 2.22, and 2.31 per cent. This shows that the phosphoric acid was readily taken into solution by the action of nitrohydrochloric acid on the seed meal, but in such form that it could not be entirely precipitated by ammonium molybdate till after ignition and subsequent solution in nitric acid. Work done by Hardin[1] indicates the presence of meta- and pyrophosphoric acid in cottonseed-meal; but these forms of phosphoric acid should be converted into orthophosphoric acid by boiling with strong nitric acid.

Possibly the phosphoric acid in cottonseed-meal is in organic combination that is not broken up by boiling with strong nitrohydrochloric acid and can only be set free by ignition or fusion.

The cottonseed-meal was extracted with anhydrous ether, and the ether extract was fused with potassium hydrodixe and potassium nitrate and the sulphur and phosphorus determined. The extract contained 0.47 per cent. phosphorus pentoxide, probably contained in ether-soluble lecithins; most of the phosphorus in these compounds is driven off by ignition and this would account for some of the difference in results between the methods of fusion with alkali and simple ignition.

The sulphur obtained from the ether extract by the fusion method amounted to 0.30 per cent. of the extract, or calculated to original substance, 0.03 per cent.

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THE DETERMINATION OF SULPHUR AND PHOSPHORUS IN ORGANIC MATERIALS.

BY H. C. SHERMAN.

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THE DETERMINATION OF SULPHUR.

IN order to secure complete oxidation of the sulphur of organic materials without loss through the formation of volatile compounds a great many modes of procedure have been described. Without attempting an enumeration of these it may be said that nearly all of them fall under one of three general heads:

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[1] Bulletin 35 U. S. Dept. of Agriculture, Division of Chemistry, p. 50.