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.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 71.]

THE DETERMINATION OF SULPHUR AND PHOSPHORUS IN ORGANIC MATERIALS.

BY H. C. SHERMAN.

Received September 17, 1902.

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.

(1) oxidation by means of nitric acid in a sealed tube; (2) heating in a combustion tube in a current of air, oxygen or some oxidizing vapor—the oxidation being sometimes completed by means of platinized asbestos; (3) fusion with an alkali (sometimes with previous treatment with nitric acid), the oxidation being completed either by the addition of an oxidizing agent to the fusion or by treating the alkaline solution with chlorine or bromine. The first method is quite inconvenient for samples low in sulphur because only small amounts of material can be decomposed at a time and determinations are frequently lost through breaking of the tubes. The second method requires the fitting up of special apparatus and is not apt to be used unless many determinations are required. Hence some modification of the third general method is apt to be preferred and the most common is perhaps the fusion of the substance with sodium hydroxide with the addition of nitrate or peroxide to complete the oxidation. This method, if carefully carried out, can be made to yield very accurate results, at least with ordinary materials, but it appears that equally accurate results can be more conveniently obtained by direct combustion in oxygen.

Berthelot in 1892[1] proposed the use of the calorimetric bomb for the elementary analysis of organic substances and stated that on combustion with 25 atmospheres of oxygen the sulphur, as well as the carbon and hydrogen, was completely oxidized, and in the presence of moisture remained entirely in the form of sulphuric acid. This method has been used to some extent, especially for the determination of sulphur in coals, and Hempel has described[2] a modification in which the combustion is accomplished in a large glass vessel with oxygen at ordinary pressure.

As an additional precaution the gases from the bomb after the combustion may be made to pass through bromine water to which the rinsings of the combustion chamber may afterwards be added and the whole boiled to insure the oxidation of any sulphurous acid which may have been formed. This is considered unnecessary by Hempel and the following experiments show that the bromine was not needed with the samples here used: Dried meat, dried curd and white of egg were burned and the sulphur deter-

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[1] *Compt. rend.*, **114**, 317, 318.

[2] *Ztschr. angew. Chem.* (1892), pp. 393-394.

mined as described below with the additional precaution of the use of bromine as just mentioned. The same samples were then treated in exactly the same way except that the wash-bottle through which the escaping gases passed contained only water, which was subsequently used for rinsing out the combustion chamber. After passing through the water the escaping gases were led through a second wash-bottle containing bromine water. The same portion of bromine water was used for these three combustions and was then examined and found to have absorbed no sulphur. The results with and without the use of bromine were as follows:

	Percentage of sulphur found.	
	Using bromine water.	Using water only.
Dried lean meat	0.814	0.816
Dried curd	0.611	0.609
Dried white of egg	1.406	1.410

These tests seemed to show conclusively that for these samples the use of bromine was entirely unnecessary and in the subsequent use of this method we have carried it out as follows:

Compressed Oxygen Method.—A suitable amount of sample is pressed into a pellet and burned in the bomb-calorimeter[1] in the same manner as in the determination of heat of combustion, using from 25 to 30 atmospheres of oxygen. By means of a coupling with small bore the bomb is then connected with a wash-bottle containing water, and the gas is allowed to bubble through the water until the contents of the bomb reaches atmospheric pressure, when it is opened and thoroughly rinsed with water. In order to keep down the volume, the water from the wash-bottle is used for the first rinsing. Any ash found in the combustion capsule is dissolved by means of hydrochloric acid and this solution added to the main solution. The whole is then boiled down to the desired volume, filtered if necessary, and the sulphuric acid determined by precipitation with barium chloride.

This method has been applied to a few sulphur compounds prepared by students in the organic laboratory, selecting such as contained sulphur in an "unoxidized" condition in order to make the test as decisive as possible. The following results were obtained:

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[1] In these experiments a platinum-lined Atwater-Blakeslee bomb was used.

	Percentage of sulphur.	
	Theoretical.	Found.
Benzyl sulphocyanide	21.49	21.52
Benzyl sulphide	14.96	14.77
Diphenyl thiourea	14.04	13.85
Benzyl sulphoxide	13.92	13.72

The oxygen method was then compared with the alkali method, using sodium peroxide as the oxidizing agent and with the "nitric acid method" as provisionally adopted for the determination of sulphur in plants at the last (1901) meeting of the Association of Official Agricultural Chemists.

Alkali Method.—This was carried out essentially as described by Osborne.[1] Fifteen grams of sodium peroxide were weighed and most of it introduced at once into a large silver crucible and converted into hydroxide by adding a little water and boiling over an alcohol lamp until the excess of water was expelled. The hydroxide was allowed to cool until pasty when the sample was added and stirred into the alkali as quickly as possible. The heat was then gradually raised and the remainder of the peroxide added in small portions to complete the oxidation. The fused mass was then allowed to cool, was dissolved and washed into a beaker with water,[2] acidulated with hydrochloric acid and boiled. Finally the solution was filtered, neutralized with ammonia, brought to the desired volume and acidity and the sulphuric acid determined as usual.

With the vegetable materials the acidulated solution was evaporated to dryness and heated to dehydrate any silica which might have been present.

Nitric Acid Method.—Except that only 2 grams of the sample were taken, the method was carried out as described by Fraps.[3] The material was placed in a 4-inch porcelain evaporating dish, 20 cc. of concentrated nitric acid added and the mixture heated on the water-bath, cautiously at first and then at the temperature of boiling-water. When frothing had ceased and the solution was partly evaporated, 10 cc. of a 5 per cent. solution of potassium nitrate were added and the mixture evaporated to dryness and ignited, at first very cautiously over a Bunsen burner and finally

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[1] This Journal, **24**, 142.

[2] In one case it was necessary to filter at this point as the crucible had been attacked by the peroxide.

[3] This Journal, **24**, 347.

over the blast-lamp until the residue was white. The residue was dissolved in hydrochloric acid, evaporated to dryness and heated for some time at 110° to 120° to render silica insoluble. Finally the residue was taken up with water and a little hydrochloric acid, filtered, the filtrate brought to the desired bulk and acidity and the sulphuric acid determined as usual.

With each method about 2 grams of the sample were used in each case and the final precipitation of barium sulphate was made in a solution of about 150 cc. containing about 2 cc. of concentrated hydrochloric acid. The amount of sulphur introduced by the reagents was determined for each method by making a "blank" test with sugar or benzoic acid.

Six samples were used in comparing the three methods. These were: (1) dried lean beef; (2) curd precipitated from cows' milk by acetic acid and reduced to a fine, dry, neutral powder; (3) coagulated yolk of egg, dried, ground and partially extracted with ether; (4) coagulated white of egg, dried and ground; (5) wheat bran; (6) dried beans, outer coating and germ removed before grinding. All of these samples were analyzed in the air-dried state. The results obtained are shown in the following table:

	Percentage of sulphur found.		
Substance.	Compressed oxygen method.	Hydroxide-peroxide method.	Nitric acid method.
Dried lean beef	0.815	0.811	0.679
Dried curd	0.610	0.608	0.495
Yolk of egg	0.822	0.819	0.810
White of egg	1.408	1.421	1.146
Wheat bran	0.264	0.259	0.182
Beans	0.217	0.229	0.165
Average	0.689	0.691	0.580

While the results by the first two methods are practically identical, those obtained by the nitric acid method are lower, the average amount of sulphur found being about five-sixths of that present. A part of this discrepancy is probably due to mechanical loss. Carrying out the method as described it was found in most cases that on heating the residue left on evaporation after the addition of the nitrate, no matter how slowly the heat was applied, there was a short period of vigorous oxidation at about the time the material had become thoroughly charred. At this point there may easily have occurred a very slight mechanical loss of substance. It seems probable, however, that the greater part of the discrepancy was due to volatilization of sulphur in some form of combination not sufficiently oxidized to stand the heat generated at this point. Such a loss could doubtless be avoided by repeated evaporation with nitric acid or by the addition of alkali along with the nitrate but the method would then become practically that of Salkowski. It is possible also that by sufficient experimentation one might find the proportions of substance, acid, and nitrate which would give good results with a single evaporation, but the proportions would probably differ according to the material to be analyzed and in the writer's hands the method did not promise sufficient advantage to justify such a study. If all loss of sulphur could be avoided, it would become necessary to guard against an absorption of sulphur from the gas flame when the residue is heated over the blast-lamp.

While the results obtained by the first two methods are equally accurate, the combustion in oxygen has some distinct advantages. It requires much less attention, complete oxidation being instantaneously obtained with no danger of loss by volatilization. No reagents are used except the compressed oxygen and a little hydrochloric acid, both of which are apt to be free from sulphur, whereas it is difficult to obtain an alkali which does not contain an appreciable amount. Moreover, by doing away with the use of alkali any danger of absorption of sulphur compounds from the air of the laboratory is avoided and the solution in which the final precipitate is obtained is free from any large amount of foreign salts.

THE DETERMINATION OF PHOSPHORUS.

The following three methods for determination of phosphorus were compared.

Compressed Oxygen Method.—The combustion was carried out as described above. The ash in the platinum combustion capsule was dissolved by means of strong nitric acid and this solution added to the rinsings of the bomb and the whole boiled and then allowed to cool. Ammonia was then added in excess and the solution slightly acidulated with nitric acid and precipitated with molybdate solution, the ammonium phosphomolybdate being afterward dissolved and the phosphoric acid precipitated with magnesia mixture in the usual manner. The details of manipulation recommended by the Association of Official Agricultural Chemists[1] were here followed, especial care being given to the conditions of the final precipitation.

Sodium Carbonate Method.—The sample was mixed in a platinum dish with 6 or 7 grams of dry sodium carbonate and 3 or 4 grams of the latter spread over the mixture. The dish was then heated carefully over a Bunsen burner until all danger of vigorous reaction was past. The heat was then raised and pulverized potassium nitrate added in small portions, the mass being occasionally stirred with a platinum rod. This was continued until the mass was entirely white, the whole amount of nitrate added being usually about 1 gram. After cooling, the fusion was transferred to a beaker, dissolved in water and nitric acid, and the determination completed as described above.

Sulphuric Acid and Ammonium Nitrate Method.—This was carried out essentially as described by Neumann.[2] The sample is placed in a Kjedahl digestion flask, 20 cc. of concentrated sulphuric acid and 10 grams of ammonium nitrate added, and the mixture heated carefully until frothing ceases, then allowed to cool somewhat and 10 grams more of ammonium nitrate added and the digestion continued until organic matter is entirely destroyed and a colorless solution obtained. This is allowed to cool, washed out into a beaker, about 15 grams of ammonium nitrate added, and the phosphoric acid determined by the molybdate-magnesia method as already described. This method had already been found to yield the same results as the carbonate method when applied to feces and urine, and the ease and rapidity of manipulation recommended it for trial upon substances containing a larger proportion of phosphorus in organic combination.

In comparing the three methods care was taken to secure approximate uniformity in the amounts of samples taken and of reagents used. Of the beef and of the beans about 2 grams were

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[1] Bulletin 46, revised edition, Bureau of Chemistry, U. S. Dept. of Agriculture.

[2] Du Bois Reymond's Archiv., physiol. abth., (1897), pp. 552–553 through *Jahr. Thierchemie*, **27**, 643.

taken for each determination; of each of the other samples about 1 gram was used.

The table below shows the results obtained by these three methods upon five of the samples already described (the white of egg being omitted as it contained only 0.1 per cent. of phosphorus, all of which remained in the ash), and on a sample of caseïn prepared in the laboratory and containing less than 0.5 per cent. of ash.[1]

	Percentage of phosphorus found.		
Substance.	Oxygen method.	Carbonate method.	Neumann's method.
Dried lean beef	0.490	0.492	0.499
Dried curd	1.341	1.335	1.327
Caseïn (air-dried)	0.789	0.789	0.797
Yolk of egg	1.364	1.368	1.366
Wheat bran	1.382	1.402	1.393
Beans	0.481	0.470	0.452
Average	0.975	0.976	0.972

The three methods thus yield practically the same results. As shown below it was found that most of the samples lost extremely little phosphorus when burned to ash in the usual manner. It is believed that these samples are fairly representative of ordinary food materials, rich in proteid matter. If so, the determination of phosphorus in food materials is attended with very much less danger of loss than the determination of sulphur.

In the case of the prepared caseïn about seven-eighths of the phosphorus was lost when the material was burned to ash, but in the determination of total phosphorus practically identical results were obtained by the three methods studied, indicating that these three methods are equally applicable to practically ash-free organic compounds of this nature as well as to food materials and ordinary physiological products.

LOSS OF SULPHUR AND PHOSPHORUS IN PREPARING ASH.

The proportion of sulphur which remains in the ash of animal and vegetable substances may not be of much significance in itself, yet as most ash analyses include the determination of sulphates and as the relation of total sulphur to sulphur in ash is being determined in some cases[2] it was thought advisable to include it here.

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[1] For this sample the writer is indebted to Mr. P. B. Hawk, of the Department of Physiological Chemistry of this University.

[2] Fraps: This Journal, **23**, 199; **24**, 346.

In the case of phosphorus the loss in preparing the ash is in most cases much smaller and in view of the large number of recorded determinations of phosphorus in the ashes of animal and vegetable materials the relation of this to the total phosphorus becomes a matter of considerable importance.

The percentages of total ash in the air-dried samples, of total sulphur and phosphorus, and of sulphur and phosphorus which remained when the material was reduced to ash in the usual manner,[1] are shown in the following table:

SULPHUR AND PHOSPHORUS REMAINING IN ASH.

Substance.	Total ash. Per cent.	Percentage of sulphur.		Percentage of phosphorus.	
		Total.[2]	In ash.	Total.[3]	In ash.
Dried lean beef........	2.21	0.813	0.036	0.494	0.457
Dried curd............	8.10	0.609	0.072	1.334	1.332
Yolk of egg	4.92	0.821	0.013	1.366	1.307
White of egg..........	5.22	1.415	0.206	0.105[4]	0.105
Wheat bran	6.58	0.262	0.016	1.392	1.392
Beans.................	3.02	0.223	0.036	0.468	0.461

Thus while the loss of phosphorus was practically *nil* in four cases and very small in the other two, the loss of sulphur ranged from over four-fifths to practically all of that present.

It should be noted that the sample of curd contained, in addition of some of the salts originally present in the milk, a small amount of sodium acetate, formed by neutralization of the acetic acid used in precipitation, which doubtless aided in the retention of sulphur and phosphorus. As already stated, the sample of prepared caseïn used in the work on phosphorus lost about seven-eighths of its phosphorus on being burned to ash. In the case of the yolk of egg the reduction of the ash to whiteness required two or three hours at the moderate red heat which was used. When the burning was completed over a blast-lamp the ash was reduced to 4.19 per cent., and the phosphorus remaining in the ash to 1.143 per cent. of the original material.

CONCLUSIONS.

For the determination of sulphur the method of combustion in compressed oxygen is preferred. Equally good results were ob-

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[1] Bulletin 46, revised edition, Bureau of Chemistry, U. S. Department of Agriculture.

[2] Averages of results by the oxygen and alkali methods.

[3] Averages of results by the three methods used.

[4] Determined by the carbonate method.

tained by the hydroxide-peroxide method but the manipulation is less convenient. The nitric acid method as used gave low results.

In the determination of phosphorus practically identical results were obtained whether the material was oxidized by combustion in oxygen, by heating with carbonate and nitrate, or by boiling with sulphuric acid and ammonium nitrate. For the analysis of food materials and physiological products the last-mentioned method will probably be found most convenient, especially in laboratories where the Kjeldahl method for nitrogen is largely used.

In analyzing animal and vegetable materials there is very much greater danger of loss by volatilization of sulphur than of phosphorus.

The writer desires to express his indebtedness to Prof. W. O. Atwater of Wesleyan University, who encouraged this work in many ways and in whose laboratory a large part of it was done, and to Mr. Emil Osterberg who assisted with many of the determinations.

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FURTHER NOTES ON THE BROMINE ABSORPTION OF OILS.

BY PARKER C. MCILHINEY.

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IN TWO papers published in the Journal of this Society,[1] the writer submitted a method of examining fats and oils in which the substance to be examined was acted upon by bromine dissolved in carbon tetrachloride. The most important advantage claimed for the method was that if the oil or fat contains substances with which bromine reacts to form substitution products, the fact will be made known by the production of a certain amount of hydrobromic acid which is determined in one part of the process. The ordinary animal and vegetable oils and fats, such as olive oil, lard, cottonseed oil, linseed oil, etc., which are practically pure glycerides, absorb almost the whole of the bromine which disappears during its action upon them by direct addition, that is to say, the bromine unites with pairs of carbon atoms which had previously been connected by double or triple bonds, and consequently but

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[1] Vol. **16**, 275, and **21**, 1084.