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ON THE LOSSES OF SULPHUR IN CHARRING AND IN ASHING PLANT SUBSTANCES; AND ON THE ACCURATE DETERMINATION OF SULPHUR IN ORGANIC SUBSTANCES.

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It has been known for a long time that in ashing a plant-stuff in an open dish in the ordinary way there is always a danger, and in many cases a certainty, of the volatilization of part of the alkalies, phosphorus compounds, chlorine, and sulphur compounds. The extent of this loss depends on the temperature employed and on the nature of the substance ashed, and is many times greater for sulphur than for the other substances mentioned.[1]

The methods which have been devised, either to prevent the volatilization of sulphur compounds or to estimate the volatilized substances separately in special forms of apparatus, fall under three groups:

A. Methods in which alkaline substances (such as barium

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[1] Thus, Lechartier (*Compt Rend.*, 109 (1889) page 727), in working with wheat, buckwheat kernels and straw, the wheat plant, and artichokes, found the loss of sulphur to be from 12 to 60 times greater than that of phosphorus. Similarly Berthelot ("Chimie Vegetale et Agricole." Tome IV. Chap. VI, Paris, 1899), in an investigation of *Cynosurus cristatus*, found that the loss of sulphur, from the leaves and ears, was from 3 to 20 times as great as the loss of phosphorus.

hydroxide, calcium carbonate, calcium acetate, and sodium carbonate) are added to the substance before ashing, or in which fusion with alkalies is employed with or without previous oxidation in the wet way.

B. Methods of oxidation in the wet way, not accompanied by fusion with alkalies.

C. Methods involving the use of special forms of apparatus.

The writer has tested representative methods—twelve in all—from each group, using as material for analysis, first, mustard seeds, the leaves of the plane tree, peas, oats and maize; secondly, pure protein substances such as edestin, excelsin and casein; thirdly, soft coal and hard coal. As the result of numerous analyses it became obvious that the figures for sulphur obtained by existing methods could not be regarded as final—since the methods were, in every case, open to some objection or other. It seemed a useful task, therefore, to try to work out an accurate, convenient and inexpensive method for the determination of sulphur in plant-stuffs and organic substances generally. It is confidently believed that such a method has been developed.

In addition to the comparison of existing methods, and the working-out of the method to be described later, several points of more purely scientific interest were investigated. Among these may be mentioned the determination of the amounts of sulphur lost during ashing, both with and without the previous addition of alkalies, potassium nitrate or nitric acid; and the investigation of the proportion between the sulphur volatilized during the preliminary charring and that lost during the final burning of the charred mass to an ash.

The work—a much-abbreviated account of which follows—was carried out in the Agricultural Chemical Laboratory of the University of Göttingen, under the friendly guidance of the Geheimrath Professor B. Tollens.

DESCRIPTION OF THE METHOD AS FINALLY EMPLOYED.

It will be convenient to begin by describing, as completely and accurately as possible, the process as it was finally adopted. A detailed account of the many experiments made in the development of the method would take up too much space. Some of the more important points will, however, be mentioned briefly at the end of this description.

It should be said that the method is not difficult, and that one may be assured of obtaining good results, after the first trials, if close attention is paid to the following particulars and directions.

Arrangement of Apparatus.—A combustion tube of Jena glass, 60 or 70 cm. in length and 1.5 cm. in diameter, is drawn out at one end and bent down. At about 30 cm. from the bend a side tube of the same kind of glass, and of 6 to 7 mm. internal diameter, is fused on to the combustion tube. Such a joint is made without special difficulty by a skilled glass-worker. Mr. Mittelbach, in Göttingen, has made several for me, and I have been able to use one and the same tube in some fifteen or twenty combustions. The part A D of the main tube is from 30 to 40 cm., depending on the number of boats to be used and the amount of substance to be burnt. A convenient length for D B is 30 cm. This allows a little play at the end of the furnace, marked in the figure by the line H H. The lateral tube rises vertically about 3 or 4 cm. so as to clear the furnace, and is then bent approximately at right angles so as to rest on the side rail of the furnace. The tube is dressed in the following manner: At G is placed a perforated disk of platinum foil provided with a loop of platinum wire as a handle. This is pushed into place by means of a long glass tube. A plug of asbestos may be substituted, but the platinum is cleaner and more convenient to handle in the subsequent operations. If asbestos is used it must first be ignited in such a way that it does not come into contact with the naked Bunsen flame. The column of absorbing material F, from 12 to 20 cm. in length, depending on the amount and nature of the substance to be burned, is next filled in. In the first experiments pure granulated sodium carbonate was used for this purpose. It was found, however, that the resulting solution was inconveniently

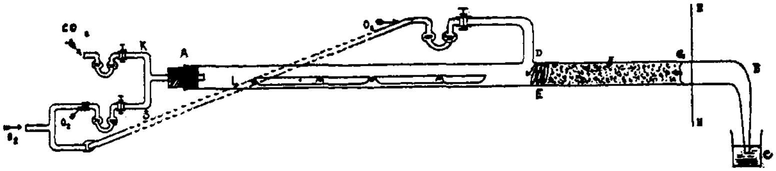

Fig. 1.

rich in salts, and in order to avoid this the following method was resorted to, for diminishing the quantity of soda used and yet obtaining a long absorption column. Clean sand was thoroughly extracted with pure acids, washed, and ignited. A portion of it was then transferred to a dish with 3 grams of sodium carbonate and enough water to dissolve the latter. The mixture was carefully evaporated to dryness, with gentle stirring, and the resulting coarse powder, consisting of sand grains coated with a thin layer of sodium carbonate, was sifted free from fine dust. Afterwards fragments of pure quartz, as uniform as possible in size and no larger than split peas, were substituted for the sand grains and found preferable. In this way it was possible to obtain a column 25 cm. long by using only 2 or 3 grams of salt—a sufficient amount for the absorption when it is distributed in this finely divided condition. The purity of the sodium carbonate used was established in two ways: First, by heating 25 grams to redness in a current of oxygen in the combustion tube, and secondly by mixing the same weight with several grams of potassium chlorate and projecting the mass into a red-hot platinum crucible. In both cases not a trace of sulphate was found.

A spiral of platinum wire, E, one end of which is formed into a hook, is now pressed on top of the quartz-soda column. It should fit the tube, so as to act as a light support for the column. The front of the spiral should be directly opposite the opening of the side-tube D. The tube is now placed in the cold furnace, the weighed substance introduced, and the cork A, with the T-tube K S, inserted. The substance for analysis is conveniently contained in long porcelain boats. Such boats, 14 cm. long, of finest Meissener porcelain, are easily to be had. In the rare cases in which it is necessary to take larger amounts of substance for analysis, the substance may be filled into a cylinder of pure filter-paper a little smaller in diameter than the combustion tube, the ends of the cylinder twisted together, and the whole pushed into position. The paper burns off and does not interfere with the combustion. The use of boats—usually two are enough—offers, however, the considerable advantage that ash determinations may be made simultaneously with the sulphur determinations.[1] A space must be left, about 5 or 6 cm. long, between the front of the substance and the platinum spiral at E. This is indispensable, as will be seen later. A "safety-beaker" containing a little water is placed at C, in order to furnish a test as to the completeness of the absorption. It may be remarked that in no case was the slightest trace of sulphuric acid found here in using the method now described. The side-tube D is connected with an oxygen supply, and the tubes K and S with sources of carbon dioxide and oxygen respectively. All these gas-streams pass through small wash-bottles or bulbs to render the speed of the stream ascertainable, and are controlled by screw-clamps on short pieces of rubber tubing. The part of the tube near the cork is not to be heated, and is best kept free from any support in order to avoid the danger of charring the cork.

The Combustion.—Everything being arranged as above described, the clamps at S and D, controlling the oxygen, are closed. A slow current of carbon dioxide is passed in through K, and the part of the tube from E to H is heated to a low red heat. It is advisable to have the temperature a little higher at E than at H, and gradually diminishing along the tube from E towards H, where a temperature below dull red heat is to be maintained.[2] When the part E H is hot a very slow stream of oxygen is admitted through D, the carbon dioxide stream being left unaltered, and the heating is now carried very gradually from E towards the boat M.[3] One burner, sufficient to prevent any back distillation, is lighted near A. The instant the substance in the front part of the boat M' begins to char, the oxygen stream through D is increased, and after a short time—usually only a few seconds—the platinum spiral at E begins to glow, and the gases from M' catch fire in the excess of oxygen and burn with a small flame at or near the spiral. It is best in beginning to have a

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[1] In order to ascertain how closely duplicate or triplicate ash determinations made in this way might agree, the following experiment was made. A row of three boats was used in a combustion of oat-seeds, and the three ashes were weighed separately with the following results :

	Weight of substance.	Weight of ash.	Per cent. ash.
1st boat	1.9040	0.0686	3.60
2nd "	1.1820	0.0422	3.57
3rd "	0.8376	0.0286	3.42

[2] In this way one is sure that, if by accident the temperature rises even considerably too high at E during the combustion, the gases will, nevertheless, meet with a sufficiently long layer of absorbing material at the proper temperature before leaving the tube.

[3] The reason for leaving the empty space will now be clear. If no space were left, the substance would begin to char (owing to the conduction of heat by the body of the furnace) before the absorption column was ready, and a loss of gases would ensue.

fairly strong oxygen stream going through D. Once the gases have caught fire, the adjustment of the stream at D is an easy matter, the position and shape of the disk of flame itself indicating the state of affairs. In the accompanying figure (Fig. 2), the line *a b* shows in section the position assumed by the disk of flame when the oxygen supply is properly adjusted. When the flame becomes vertical and travels off towards the substance, assuming the position E F for example, a needless excess of oxygen is being used. On the other hand, if the oxygen be insufficient, the gases from the char tilt the disk of flame into some such position as that represented by *c d*. In this case the lower edge *d* begins to flutter, the flame turns smoky, and carbon is deposited on the first portions of the sodium carbonate. The soot, however, almost instantly disappears if the oxygen supply is momentarily increased. A supply of oxygen which just prevents the deposition of soot is sufficient.

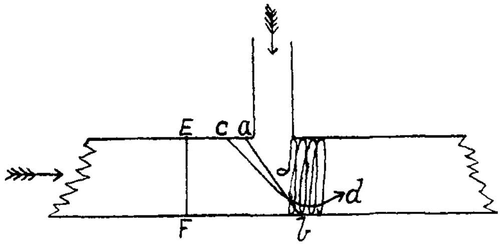

Fig. 2.

From this moment on, the combustion goes forward almost automatically. The heating is gradually extended towards the front end of the tube—the cork end. A high temperature should be avoided. All that is aimed at in this stage is the complete charring of the substance, and this takes place below red heat. The gases from the charring mass are carried by the stream of carbon dioxide (which may now be made very slow) to the flame. It will be seen at once that it is impossible for an explosive mixture to be formed between D and A, since the gases are prevented by the carbon dioxide stream from mixing with oxygen until they reach the surface of the flame, beyond which sharply defined surface there is a large excess of oxygen. As a matter of fact, the writer has never had such an explosive mixture when operating in this way. An attempt to substitute air for the carbon dioxide was, however, unsuccessful.

When the whole substance is charred, the flame assumes a vertical position and travels slowly towards the boat. If an attempt is now made to bring it back to *a b* by diminishing the supply of oxygen the flame grows smaller, flickers, and goes out. At this point the burners along the length from D to A are turned up, the carbon dioxide supply is shut off, and a stream of oxygen is passed through S, the oxygen stream at D being diminished but not entirely shut off. When the char has gained a proper temperature, the end nearest A takes fire in the oxygen and the mass glows steadily from A towards D. When the carbon is all consumed, the oxygen supply at D is stopped, that at S diminished, and the temperature is gradually lowered during ten minutes, when the burners are shut off, the oxygen stopped, and the tube allowed to cool somewhat in a slow stream of carbon dioxide.

Subsequent operations.—If boats have been used, they are now transferred to thin weighing tubes and placed in the desiccator while still warm. The ash is weighed, and then treated according to the well-known analytical methods for the determination of sulphuric acid in plant-ash. This sulphuric acid, expressed in per cent. of the dry substance employed, I have called throughout "the non-volatile SO_3." The sulphuric acid obtained from the absorption-column after treatment as described below I have called "the volatile SO_3." It is practically certain that the volatile sulphur is not entirely present in the plant as sulphuric acid, but both portions of sulphur are expressed as SO_3 because of the resulting convenience in comparing the results. If the object is merely to determine the total sulphur of the substance, the solution of the ash, ready for precipitation with barium chloride, is simply added to the solution obtained, as below, from the absorption-column, and the two precipitated together.

The tube is now removed from the furnace and the outside is cleaned. The spiral of platinum wire E is removed by means of a glass rod with a hooked end and the quartz fragments are shaken out into a dish standing on a sheet of glazed paper, any portions which stick being easily loosened by the rod. The disk G is removed, and E and G are rinsed into the dish with hot water. The combustion tube is also rinsed with hot water. Two courses are now open for the treatment of the quartz-soda, as follows:

(*a*) The whole mass is treated with dilute hydrochloric acid, carefully added in small portions, the dish being covered with a watch-glass or funnel as usual, until the solution is acid. The solution is then evaporated to dryness over an alcohol lamp-flame, the residue treated with a little concentrated hydrochloric acid, again evaporated, moistened with hydrochloric acid, allowed to stand for a few minutes and dried at 110°-115° for thirty minutes. The mass is then repeatedly extracted with successive small quantities of hot water, which are filtered through pure paper into a beaker where the precipitation with barium chloride is carried out as usual. In order to make sure that the sulphate is completely extracted, a few drops of hydrochloric acid are added before the first extraction with water, and the washing is continued until no trace of acid is left. The amount of silica left on the filter-paper is always small, but some is always present. The quartz fragments are now clean and ready for coating with sodium carbonate again.

(*b*) The other method of treating the quartz-soda, preferred by the writer, is as follows: The mass is treated with hot water, stirred well, allowed to settle, and the solution filtered into a 4-inch evaporating dish. This extraction is repeated. Enough dilute hydrochloric acid is now added to the quartz fragments to give an acid reaction—usually only a few drops are necessary. The extraction with successive small portions of hot water is now continued until the solution, tested as it runs from the end of the funnel, is no longer acid. The combined solution and washings do not need to exceed the contents of a 4-inch dish. The liquid is now concentrated to a small bulk over the alcohol flame, acidified with hydrochloric acid, evaporated to dryness and treated as before described.

Notes on the Method.—The time necessary for the actual combustion of a sufficient amount of a plant-stuff does not exceed, after a little practice, thirty minutes. Samples of coal take longer than plant-stuffs, and albuminous substances may need one hour.

Two points must be kept in mind: The operation of charring must be conducted slowly, and an excess of oxygen must be used.

Two other methods of absorbing the products of combustion were experimented upon. In the first of these the back part of the combustion tube, where the sodium carbonate was placed in the method just described, was filled with small fragments of well-cleaned and ignited porcelain. This part of the tube was kept at a good red heat during the combustion. The gases passed from the tube through two bulb U-tubes charged with a solution of bromine in hydrochloric acid. This solution, together with the washings of the combustion tube, was afterwards evaporated to dryness with a little potassium nitrate, and the sulphuric acid determined as usual. This method was abandoned because the large volume of absorption-liquid necessitated a tedious evaporation, and because the absorption of the sulphur compounds was not always complete. (The first experiment in Section 3 of this paper was made with the apparatus just described.)

Recourse was therefore had to the absorption apparatus of Classen and Bauer, slightly modified to fit the drawn-out end of the combustion tube. The apparatus, as used, consisted of a vertical tube filled with glass beads. The tube ended below in a narrower part provided with a glass stop-cock. This narrow part carried a side arm bent up so as to fit the drawn-out end of the combustion tube. At the top, the absorption tube was fitted with a cork carrying a stoppered separating funnel by means of which the absorption liquid could be allowed to drip slowly over the glass beads. The gases entered at the bottom, ascended through the wet beads, and were then conducted through a small "safety-beaker" containing water. This form of absorption apparatus was found to give very satisfactory results. It could not, however, be made entirely automatic, but always demanded some share of the operator's attention, thereby increasing the difficulty of controlling the combustion as a whole. The use of the quartz-soda column is easier, and all cork connections are avoided.

In order to avoid any possibility of error from the introduction of sulphur compounds from the coal-gas flame, all evaporations were made over the flame of an alcohol lamp.

Blank tests were made several times. The combustion tube, charged ready for use, was heated to redness for one hour, while slow streams of carbon dioxide and of oxygen (from the same sources as those used in actual analyses) were led through. The sodium carbonate was afterwards dissolved in hydrochloric acid, a little bromine was added, and the solution was evaporated to a small bulk and then tested with barium chloride. In no case was the slightest trace of precipitate observed.

OTHER METHODS FOR THE DETERMINATION OF SULPHUR.

In all, twelve methods were tested. The more important of these are considered below, together with the various sources of error noted and the conclusions to be drawn as to the values of the different methods.

Sauer's Method.[1]—The principle of the method is combustion in a stream of oxygen, and absorption of the gaseous products of combustion in acidified bromine water in bulbed U-tubes. The gases from the charring substance are burnt at a *constriction* in the tube by the help of an oxygen stream coming in the opposite direction through a narrow tube passing through the cork in the back end of the combustion tube. The method proved difficult of manipulation. It was hard to prevent the fusing together of the tube at the constriction, and the oxidation of the gases was not complete.

Berthelot's Method was more carefully tested. The method is described in Chap. IV, Tome 4 of Berthelot's "Chimie Végétale et Agricole." The substance, contained in boats in an ordinary straight combustion tube, is burnt in an oxygen stream coming from the front end of the tube, and the gases are absorbed in heated sodium carbonate in the rear of the tube. Berthelot's directions were carefully followed, but the results obtained were exceedingly unsatisfactory. It was not possible to get a complete combustion, for the evolution of great quantities of grayish brown vapors and tarry products could not be avoided. These products passed through the layer of sodium carbonate without being absorbed, and entered the "safety-beaker." In every case this "safety-beaker" contained sulphurous and sulphuric acid after the combustion. The tarry substances rapidly coated the sodium carbonate with a black layer which interfered with the absorption of the sulphuric acid. It was evident that there was a constant lack of oxygen, and this is very natural, since the oxygen enters at the front of the tube and the substance begins to burn at this end. The heat evolved by this combustion causes a kind of dry distillation of the part of the substance nearer the absorption column. The products of this distillation are partly decomposed by the hot sodium carbonate with the resulting deposition of

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[1] Fresenius: *Ztschr. anal. Chem.*, **12**, 32 and 178; see also Mixter: *Am. Chem. J.*, **2**, No. 6.

carbon, but this decomposition is never complete, and tarry products containing sulphur compounds pass through and escape. It seemed possible by using a *very rapid* stream of oxygen to keep the sodium carbonate clear, but for this purpose the stream had to be so rapid that complete absorption of the products of combustion was out of the question. The writer's method is based on that of Berthelot, but the modifications are all-important and essential for the success of the process. Some of the results obtained by the original Berthelot method are given in the tables at the end of this section. It will be seen that enormous losses of sulphur took place in almost every case.

Method V. Simple Ashing.—For the sake of comparison several determinations of sulphur were made in the ashes of the plant substances obtained in the ordinary way by ashing over the Bunsen flame, or over an alcohol lamp, in a platinum dish. The results are given in the tables.

Method VI. Ashing with Calcium Acetate in the Tucker Crucible.—Tucker's directions[1] for the preparation of calcium acetate and the use of the crucible were closely followed. The method was, briefly, as follows: The substance was weighed into the crucible and mixed with calcium acetate solution until wet throughout. The crucible was placed, without lid, in the special iron oven, and the mixture first dried and then charred until no more gases were evolved. The crucible was then transferred to a support of asbestos board, the lid was fitted on and made gas-tight, the connections with the small wash-bottle and the aspirator were made, and the final ashing was made over a small flame, the contents of the crucible being stirred from time to time by means of the special stirring apparatus and a slow current of air being drawn through. The contents of the wash-flask were then poured into the crucible, the liquid was evaporated and the crucible brought to low redness, cooled and weighed. The added calcium oxide was deducted from the weight of the ash found. The sulphuric acid was then determined in the ash, after the separation of the silica, in the usual way. The results are given in the tables. The following losses of sulphur, expressed as per cent. of SO_3 in the dry substance, were observed:

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[1] See *Journal f. Landwirtschaft.*, 48, 64. (1900).

TABLE I.

Substance.	True per cent. SO_3.	Found by Tucker method.	Loss by Tucker method.
Mustard seeds	2.869	1.281	1.588 or 55.2 % of the whole SO_3.
Plane-tree leaves	2.585	(*a*)[1] 1.860	(*a*) 0.725 " 28.0 " " "
		(*b*) 2.025	(*b*) 0.560 " 21.6 " " "
Peas	0.411	(*a*) 0.094	(*a*) 0.317 " 77.1 " " "
		(*b*) 0.249	(*b*) 0.162 " 39.4 " " "
Oats	0.475	(*b*) 0.130	0.345 " 72.0 " " "

There can be no doubt that the use of calcium acetate is valuable in preventing errors due to the fusion of the ash and to the formation of difficultly fusible silicates. Without calcium acetate the results by the Tucker process coincide roughly with the "non-volatile SO_3," as found by my method. It must be said that the process as described CAN NOT give exact results for sulphur. The loss of sulphur compounds *during charring* (when the crucible is still open) is the source of error. As will be shown later, the loss during this stage is much greater than in the burning of the charred mass to an ash.

Method VII. Ashing with Addition of Sodium Carbonate.—The substance was mixed in a porcelain crucible with an amount of sodium carbonate varying in the different experiments from half the weight of the analyzed substance to three or four times its weight. The mixture was charred, with gentle stirring, at the lowest possible temperature, and the carbon remaining was burnt by adding small successive portions of the finely powdered potassium nitrate or chlorate. (The former is to be preferred, since less is needed and the resulting mixture fuses more readily.) The heat was now increased and the mass fused. After cooling, the crucible was cleaned on the outside and the sulphur trioxide (SO_3) determined in the melt as usual. In the tables the amounts of sodium carbonate used and the nature of the flame over which the ashing and subsequent evaporations were made are indicated. The results are exceedingly interesting, and are discussed in full in the conclusions.[2]

Method VIII. The Eschka-Heath Method.[3]—The method was tested with three samples of coal, with mustard seeds, and with

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[1] (*a*) without addition of calcium acetate ; (*b*) with addition of calcium acetate.

[2] See p. 363.

[3] *Oester. Ztschr.*, **22**, 111, and *Chem. Centrbl.* (3 Folge) **5**, 301 ; also, This Journal, **21**, 1127.

casein. The results are given in the tables. The method is, briefly, as follows: "One gram of the substance is mixed with 1 gram of light and porous magnesium oxide and 0.5 gram of pure, dry sodium carbonate in a 75 cc. or 100 cc. platinum dish. The dish is then gradually heated over an alcohol lamp with frequent stirring. Towards the end the bottom should be at a low red heat. When the carbon is all burnt, the mixture is transferred to a beaker, and the dish rinsed, about 50 cc. of water being used. Fifteen cc. of saturated bromine water are then added and the whole boiled for five minutes and then allowed to settle. The liquid is decanted through a filter, and the residue again extracted with 30 cc. boiling water, filtered and washed. The volume of the filtrate should be about 200 cc. One and a half cc. of concentrated hydrochloric acid are added, and the now liberated bromine is boiled out. Ten cc. of 10 per cent. barium chloride solution are used for the precipitation, which is carried out as usual." The method does not give exact results for the total sulphur. In the case of the samples of coal investigated, the loss by this method was from 3.5 to 18.2 per cent. of the whole sulphur. Further, duplicate determinations on the same sample of coal did not give concordant results. With plant-stuffs the results were even worse. Mustard seeds lost over 23 per cent. of the total sulphur.

With substances like casein the method fails utterly (see table of results).

The best that can be said for the Eschka-Heath method is, therefore, that it is easy to carry out, but gives only a rough approximation to the total sulphur of a coal, and quite unreliable results with plant-stuffs and albuminous substances.

The Effect of the Magnesium Oxide and of the Sodium Carbonate in the Eschka Method.—It was deemed of interest to compare the effect of the two alkalies. The substance used for analysis was mustard seed containing 1.148 per cent. sulphur.

First, two determinations of sulphur were made exactly according to Eschka-Heath; that is, with the addition of an equal weight of magnesium oxide and half the weight of sodium carbonate. Secondly, the substance was ashed with half its weight of sodium carbonate, no magnesium oxide being added, but the treatment otherwise being exactly as before. Thirdly, the substance was ashed with an equal weight of magnesium oxide and no sodium carbonate.

The mean of three determinations in which the substance was ashed with an equal weight of sodium carbonate is also adduced in the following table. The results show clearly that the retention of the sulphur is due almost entirely to the magnesium oxide added, since the figure obtained without sodium carbonate is practically the same as the average of the results by the unaltered Eschka-Heath process.

TABLE II.

True per cent of sulphur		1.148
By Eschka-Heath	(a) 0.828 (b) 0.929 Mean	0.878
With equal weight magnesium oxide		0.868
With equal weight sodium carbonate		0.613
With half the weight of sodium carbonate		0.488

Method IX. Treatment with Potassium Hydroxide and Nitrate.—The substance was weighed into a nickel dish and an equal weight of solid potassium hydroxide added. Enough water was added to wet the mixture, and the whole was then evaporated to dryness four or five times. The blackish residue (in the case of plant-stuffs) was charred at a low temperature and the carbon burnt off with the help of finely powdered potassium nitrate. The mass was then fused, treated with water, transferred to a porcelain dish, evaporated with hydrochloric acid, etc. The figures obtained were higher than those obtained by the Tucker method, the Eschka method, or by ashing with sodium carbonate. There was, nevertheless, a considerable loss of sulphur.

Method X. Fraps' Process.[1]—The method is, briefly, as follows: The plant substance is treated with concentrated nitric acid and warmed until the danger of overflowing is past. The solution is then partly evaporated, a solution of potassium nitrate added, and the whole is evaporated to dryness, and ignited, at first gently, finally over the blast-lamp until white. The resulting ash is treated as usual for the determination of sulphuric acid. For a full description of the method the original paper should be consulted.

Fraps found that the addition of calcium acetate gave better

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[1] This Journal, 24, 346.

results than simple ashing, but that his method gave from 1.3 to 2.7 times as much sulphur as the calcium acetate method. He concludes, justly, that "it is evident that the calcium acetate method does not give correct values for the total sulphur."

The writer made determinations of sulphur exactly according to Fraps in a number of plant-stuffs. The final ignitions were, however, made over a Bunsen flame, since the use of a blast-lamp seemed certain to lead to error from the absorption of sulphur compounds from the flame. The following losses, expressed as per cent. of SO_3 in the dry substance, were noted:

TABLE III.

Substance.	True per cent. SO_3.	Found by Fraps' process.	Loss by Fraps' process.
Mustard seeds..........	2.869	2.495	0.374 or 12.7 % of the whole SO_3.
Plane-tree leaves July 15	1.388	1.326	0.062 " 4.8 " " "
Plane-tree leaves Aug. 22	1.681	1.605	0.076 " 4.5 " " "
Maize..................	0.350	0.30	0.050 " 13.0 " " "
Oats	0.475	0.40	0.075 " 14.2 " " "
Casein (*a*)	0.763	0.34	0.423 " 56.48 " " "
Casein (*b*)	0.785	0.357	0.428 " 56.70 " " "

The results given in the following tables show that the method is better than the Tucker process. In no case, however, was a perfect result obtained, and the investigation in Section 3 of this paper shows why this must be the case.

The method, as published, is open to serious objections. The plant substance swells enormously, even in the cold, on addition of the acid, and overflowing is hard to avoid. Charring takes place suddenly with a violent evolution of gas, the whole dish being filled with spongy carbon. This may well occasion a slight mechanical loss, in addition to the loss by volatilization during charring. The carbon is hard to burn, and the dish often breaks in the flame. The use of a blast-lamp flame, especially when, as in this method, potassium carbonate is present, seems certain to result in absorption of sulphur from the flame. It is probable that most of the figures obtained by this process are increased by this cause; yet, even so, they are lower than the correct values. The heat of an alcohol lamp would not, however, suffice. The method fails utterly with casein, giving less than half the total sulphur. Other albuminous substances would probably yield similar results.

Method XI. Treatment with Hydrochloric Acid and Potassium Chlorate.—The substance was digested in a large dish for three hours with concentrated hydrochloric acid and successive small portions of potassium chlorate. The solution was then repeatedly evaporated to dryness with fresh portions of hydrochloric acid. The dried mass was finally charred, and the carbon burnt off with the help of more potassium chlorate. The silica was separated, and the sulphur trioxide determined as usual in the filtrate. The method was long and inconvenient and gave no better results than ashing with an excess of sodium carbonate.

In the following table (Table IV) are given some of the analytical results obtained by the various methods tested. The results obtained by methods VIII, IX and XI are not included, but in every case the sulphur trioxide found by these methods was too low. The results obtained from coal and from pure albuminous substances are given separately later.

RESULTS WITH PROTEINS.

In order to demonstrate the applicability of the method to the determination of sulphur in pure protein substances, several analyses were made of carefully purified casein, fibrin from horse-blood, edestin and excelsin.

Casein.—Two specimens were investigated. Preparation *A* was taken from the collection of Professor Tollens. It contained 12.6 per cent. water and 1.13 per cent. ash. The ash contained no sulphur, and determinations of phosphoric acid and calcium led to the conclusion that it consisted entirely of calcium phosphate. The other specimen, preparation *B*, was made by the writer according to the method used by Chittenden and Painter. It contained 12.01 per cent. water and 0.37 per cent. ash. The ash was free from sulphur.

Fibrin.—Horse-blood fibrin was washed until quite clean and free from color, the last washings being made with distilled water in order to free the preparation from calcium salts. The product was treated with alcohol and with ether until it became brittle enough to be powdered. It was then dried at 98° and preserved in a stoppered bottle inside a desiccator. The preparation contained 0.745 per cent. moisture and 0.63 per cent. ash in the dry substance. The ash contained no sulphur.

TABLE IV.—ABSTRACT FROM RESULTS WITH PLANT-SUBSTANCES.

Per cent. sulphur trioxide in the dry substance.

Substance.	According to the Barlow-Tollens method, as described in this paper.			Method III. Berthelot's process.			Method V. Simple ashing.	Method VI. Tucker process.	Method VII. Ashing with sodium carbonate.	Method X. Fraps' process.
	Non-volatile.	Volatile.	Total.	Non-volatile.	Volatile.	Total.				
Black mustard seeds	0.345	2.54	2.885 (*a*)	0.354	1.492	1.846	Mean of 12 determinations 0.363	1.284 (*b*)	1.50	2.46
	0.445	2.38	2.825 (*a*)	0.395	2.240	2.635		1.279 (*b*)	1.44 } (*c*)	2.53
	0.36	2.472	2.832	0.361	1.410	1.771		....	1.66	..
	0.36	2.50	2.86	....	....	....		....	1.72 } (*d*)	
	0.32	2.53	2.85	....	....	....		....	1.79	..
	0.33	2.56	2.89	....	....	....		....	1.22 (*e*)	..
	0.365	2.49	2.855	....	....	....	....	....	1.93 (*f*)	..
	0.369	2.49	2.86	....	....	....	....	....	....	..
	0.354	2.52	2.874	....	....	....	....	....	....	..
Leaves of plane-tree collected Oct. 24th	Mean of 2 analyses :							1.59 (*g*)	Mean of 4 analyses :	
	1.995	0.593	2.585					1.86 (*g*)	2.29 (*f*)	
	....	....	....					1.95 (*b*)	....	
	....	....	....					2.10 (*b*)	....	
Plane-tree leaves collected July 15th	Mean of 3 analyses :								1.29 (*c*)	Mean of 3 analyses :
	0.758	0.64	1.388						1.33 (*d*)	1.326
Plane-tree leaves collected Aug. 22d	Mean of 3 analyses :									Mean of 3 analyses :
	1.048	0.597	1.681				1.037		1.272 (*e*)	1.605
Peas	Mean of 5 analyses :							0.094 (*g*)	0.306 (*e*)	
	0.075	0.336	0.411					0.249 (*b*)	0.372 (*c*)	
									0.398 (*d*)	
White American maize	Mean of 3 analyses :					0.0026			0.19 (*d*)	Mean of 2 analyses :
	0.002	0.352	0.354			0.004				0.30
Oat seeds	Mean of 5 analyses :			Mean of 2 analyses :				0.13 (*b*)	0.11 (*c*)	Mean of 2 analyses :
	0.012	0.467	0.475	....	....	0.192		0.13 (*b*)	0.16 (*d*)	0.40

Notes.—(*a*) Using bulbed U-tubes charged with bromine in hydrochloric acid for the absorption; (*b*) with addition of calcium acetate; (*c*) with an equal weight of sodium carbonate; (*d*) with twice the substance's weight of sodium carbonate; (*e*) with one-half the substance's weight of sodium carbonate; (*f*) with a large excess of sodium carbonate; (*g*) without addition of calcium acetate. In the first determination (Plane-tree leaves of Oct. 24th) the ash was not completely oxidized. Some sulphur was left as sulphide, and, on dissolving the ash, was lost as hydrogen sulphide. The result is included because such an error is easily made in carrying out the Tucker process.

The results obtained by the methods VIII, IX, and XI are not included, but in every case the sulphur trioxide found was much too low by these methods.

Edestin.—The crystalline globulin of hemp seed was prepared according to the method of Osborne.[1] See also Leipziger,[2] and Chittenden and Mendel.[3] The product was entirely crystalline. The crystals were octahedra and combinations of the octahedron and hexahedron. They varied in size from $^1/_{100}$ mm. to $^1/_{30}$ mm. in diameter. The reactions corresponded exactly with those of Osborne's preparation 5. The dry substance gave 0.299 per cent. ash, which was quite free from sulphur.

Excelsin.—The globulin of the Brazil-nut was prepared essentially according to Osborne. The specimen used for analysis was snow-white in color, and consisted wholly of the hexagonal plates with rounded outlines, as described by Osborne. Another preparation, made in a slightly different manner, consisted of extremely minute crystalline particles. Some of these resembled the hexagonal plates mentioned above, but the large majority were triangular plates with curved outlines and an inner nucleus. The substance analyzed contained 1.24 per cent. ash in the dry substance. The ash contained no sulphur.

The results obtained with proteins are given in Table V. All evaporations were made over an alcohol flame.

TABLE V.—RESULTS WITH PURE PROTEINS.

	Barlow-Tollens method.						
Substance.	Per cent. sulphur in dry substance.	Per cent. ash.	Per cent. sulphur in ash-free substance.	Eschka-Heath method. Per cent. sulphur.	Fraps' method. Per cent. sulphur.	Ashing with equal weight of sodium carbonate. Per cent. sulphur.	Sodium peroxide method. Per cent. sulphur.
Casein *A*	0.76	1.11	0.768	0.441	0.344	0.127	....
	0.75	1.15	0.758	....	0.283	0.180	....
	..	..	....	....	0.371	....	....
Casein *B*	0.79	0.23	0.792	....	0.39	....	0.635
	0.782	0.42	0.785	....	0.29	....	0.730
	0.777	0.47	0.780	....	....	....	....
Fibrin	1.208	0.655	1.216	....	....	....	....
	1.206	0.608	1.213	....	....	....	....
Edestin	0.845	0.240	0.847	....	....	....	....
	0.842	0.359	0.845	....	....	....	....
Excelsin	1.241	1.46	1.259	....	....	....	....
	1.250	1.03	1.263	....	....	....	....

Results of Other Authors.—*Casein.* Hammarsten (*Ztschr. physiol Chem.*, 7, 269) found 0.78 per cent. sulphur ash-free. Chittenden (Studies from *physiological laboratory* of Yale Univ., Vol. II, p. 156) found 0.82 per cent. slu-

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[1] *Am. Chem. J.*, 14, No. 8; also Griessmayer: "Die Proteide," p. 271.

[2] Pflueger's Archiv., 78, 402.

[3] *J. Physiol.*, 17, 48.

ash-free. *Fibrin*. Hammarsten (Pflueger's Archiv, **22**, 489) found 1.10 per cent. sulphur ash-free. *Edestin*. Ritthausen (*J. prakt. Chem.*, **23**, 481) found 0.82 per cent. sulphur ash-free. Osborne (*Am. Chem. J.*, **14**, No. 8) found 0.86 per cent., 0.94 per cent. sulphur ash-free. *Excelsin*. Osborne (*Am. Chem. J.*, **14**, 662) found 1.05 per cent., 1.12 per cent. sulphur ash-free. Weyl found 0.55 per cent. sulphur ash-free. Sachsse found 1.37 per cent. sulphur ash-free. Ritthausen, in a crystalline product, found 1.32 per cent. sulphur ash-free.

SULPHUR IN COAL.

With the object of demonstrating the applicability of the method to coal, and at the same time of ascertaining the degree of accuracy of the Eschka method as modified by Heath, the following analyses were made: The samples of coal were a brown coal from Vollpriehausen in Sollingen; a "brikette" coal made from brown coal; and an anthracite. The results given in Table VI speak for themselves. The inaccuracy of the Eschka method has already been pointed out. As a side issue the two methods in common use for the determination of sulphur existing as gypsum in coal were compared. It was found that extraction with dilute hydrochloric acid is to be preferred to boiling with sodium carbonate, since the residue settles quickly and may be quickly and thoroughly washed, and the whole operation is cleaner and more pleasant. In the case of brown coal boiled with sodium carbonate, it was necessary to warm the acidified solution for two or three hours and allow to stand for twenty-four hours before a clean filtration from the earthy residue could be made.

SULPHUR PRESENT AS CALCIUM SULPHATE IN COAL

(Per cent. sulphur in dry substance.)

Method.	Brown coal.	Brikette coal.	Non-Baking anthracite.
Extraction with hydrochloric acid	0.046	0.039	0.023
Extraction with sodium carbonate	0.033	0.04	0.027

LOSS OF SULPHUR DURING CHARRING.

1. *Investigation of the Amount of Sulphur Lost during Charring, and during the Final Burning of the Charred Mass to an Ash, Respectively, without Addition of Alkali or Nitric Acid.*—The combustion tube charged with fragments of porcelain (without sodium carbonate), and the Classen and Bauer absorption tube, with a solution of bromine in dilute hydrochloric acid, were used.[1] Mustard seeds were charred in a stream of

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[1] (See *notes* on Barlow-Tollens method, at end of Section 1.)

TABLE VI.—SULPHUR IN COAL.

	Brown coal.		Brikette coal.		Non-caking anthracite coal.	
	Water .... 8.04 per cent. Ash............ 5.81 per cent.		Water .... 8.58 per cent. Ash............ 10.01 per cent.		Water .... 1.47 per cent. Ash............ 6.20 per cent.	
Method.	Weight of substance employed.	Per cent. sulphur in dry substance.	Weight of substance employed.	Per cent. sulphur in dry substance.	Weight of substance employed.	Per cent. sulphur in dry substance.
Eschka-Heath ..	(1) 0.5020	3.70	1.5617	2.74	2.1778	1.09
	(2) 0.7354	3.55	1.9116	2.62	1.1739	1.04
	(3) 1.1497	3.20	1.2073	2.66	....	..
	(4) 2.0954	3.46	....	..	....	..
Mean...........	....	3.477	....	2.67	....	1.065
Barlow-Tollens..	(1) 0.9157	volatile 3.04	2.4508	vol. 2.246	2.1605	vol. 1.256
		non-volatile 0.75	....	non-vol. 0.743	....	non-vol. 0.039
		total 3.79		total 2.99		total 1.295
	(2) 1.0545	total 3.72	....	..	1.2556	total 1.310

Average loss by Eschka-Heath method, 7.4 per cent. of the whole.

Average loss by Eschka-Heath method, 10.7 per cent. of the whole.

Average loss by Eschka-Heath method, 18.2 per cent. of the whole.

carbon dioxide until no more inflammable gas was evolved. The heating of the boat was then stopped. The porcelain column was, however, heated ten minutes longer in a stream of carbon dioxide, in order to sweep all the products of combustion over into the absorption tube. The combustion tube was cooled and the boat with the charred mass removed; the combustion tube was carefully rinsed into the absorption liquid, and then dried and replaced in the furnace. The bead tube was now charged with a *fresh absorbing solution.* The boat was now replaced and the charred mass was burnt in an oxygen stream. In this way the two portions of sulphur trioxide were collected separately and estimated separately. The results were as follows:

EXPERIMENT 1.

		Per cent. sulphur trioxide in substance.
Non-volatile		0.32
Volatile (*a*) during the charring in carbon dioxide	2.01	
Volatile (*b*) during the burning of the charred mass to an ash	0.52	2.53
Total		2.85

EXPERIMENT 2.

Non-volatile		0.33
Volatile (*a*)	2.14	
Volatile (*b*)	0.42	2.56
Total		2.89

It follows that about 80 per cent. of the total loss occurs *during the charring.*

2. *Amounts of Sulphur Lost (a) during Charring, (b) during the Burning of the Charred Mass to an Ash, when the Substance Had Been Evaporated with Nitric Acid and Potassium Nitrate—as in Fraps' Method—Previous to the Combustion.*—The neck of a Jena glass retort was bent down, and fitted by means of a thick piece of rubber tubing (from which the sulphur had been extracted by boiling with sodium hydroxide) into one limb of a bulbed U-tube charged with concentrated nitric acid. The retort neck entered about 4 inches, fitting closely. In the retort were placed 22.7376 grams of mustard seeds, with 80 cc. concentrated nitric acid and 40 cc. of 5 per cent. potassium nitrate solution. After the liquid in the retort had been evaporated to a syrup, a cork carrying a piece of glass tubing, open at both ends

and long enough to reach nearly to the surface of the liquid, was inserted in the tubule, and the farther end of the U-tube was connected with an aspirator. The heating was now continued over a small flame, while a slow current of air was drawn through, until charring commenced. The heat was then increased and the air stream quickened. When practically no more gases were evolved, *care being taken to avoid the actual burning of the charred mass to an ash,* the apparatus was cooled and taken apart.

On the top of the absorption solution (A) was a layer of red oil (B). The main portion (A) was evaporated almost to dryness, diluted, filtered from a little oil, and precipitated with barium chloride. The barium sulphate weighed 0.09 gram, corresponding to 0.136 per cent. sulphur trioxide in the substance. The oil (B) after long treatment with concentrated hydrochloric acid and potassium chlorate yielded 0.0124 gram barium sulphate, corresponding to 0.0187 per cent. sulphur trioxide in the substance.

The bottom of the retort was then broken out, and the charred mass (C) was detached as completely as possible from the glass. It was then powdered, together with some of the broken glass from which the substance could not be removed, and burnt in the combustion tube used by me, in an oxygen stream, sodium carbonate being used as absorbing substance. This yielded 0.3015 gram barium sulphate, corresponding to 0.455 per cent. sulphur trioxide. The ash in the boat (D) gave 1.3251 gram barium sulphate, corresponding to 1.99 per cent. sulphur trioxide in the substance.

The resume of the results is as follows:

			Per cent. sulphur trioxide in substance.
Lost.	During evaporation and charring (*A*)	0.136	0.154
	" " " " (*B*)	0.018	
	During the burning of the charred mass to an ash in an oxygen stream (*C*)		0.455
	Remaining in the ash (*D*)		1.990
		Total	2.60
	Actual per cent. sulphur trioxide (mean of two analyses)		2.869

It is hardly to be expected, considering the nature of the above experiment, that the sum of the two losses above (0.6 per cent.)

should correspond with the average loss by Fraps' method actually observed (0.375 per cent.), (see Table III).

CONCLUSIONS.

A. *Special Conclusions.*—The conclusions with regard to the various methods tested have been given in Section 2. The following additional points, of more theoretical interest and importance, seem worthy of fuller consideration here.

1. *Effect of Addition of Sodium Carbonate before Ashing.*— The effect varies greatly with different substances. (Compare peas and oats in Table VII.) That the gases from the charring, after addition of alkali, actually contain sulphur is shown (*a*) indirectly, by the low results, and (*b*) directly, by the following experiments. Several determinations of sulphur in mustard seeds were made according to my method except that varying amounts of sodium carbonate were mixed with the substance in the boat before the combustion. Sulphuric acid was found both in the ash and in the absorption column, the amount volatilized being greater when smaller quantities of soda were used.

Table VII gives the results obtained by ashing the various substances with varying amounts of sodium carbonate. The figures on the right-hand side of columns *a*, *b*, *c*, etc., give the percentage of the total sulphur trioxide which was retained in each case. Thus, by ashing mustard seeds without sodium carbonate:

True content of sulphur trioxide	2.862
Found in this case	0.363
Percentage of whole .... $\frac{0.363 \times 100}{2.862}$ =	12.68

The results given in Table VII are more clearly expressed graphically in Fig. 3. The amounts of sodium carbonate added are given as abscissae *a*, *b*, *c* and *e*, corresponding to the amounts of sodium carbonate in columns *a*, *b*, etc., in Table VII. The figures on the right-hand sides of columns *a*, *b*, etc., are laid off as ordinates.

Two facts are clearly expressed by the curves, in spite of their incompleteness: (1) The effect of the sodium carbonate in retaining sulphur is much more marked in the first than in the succeeding stages, the curves quickly growing flatter.

(2) None of the curves show a certainty of ever reaching the line A B which corresponds to the retention of all the sulphur.

The addition of more than twice the substance's weight of sodium carbonate would evidently have no perceptible effect. Accurate analytical results by this process are probably impossible, since the addition of ten or twenty times the weight of sodium carbonate, in the hope of retaining all the sulphur, would lead to analytical difficulties.

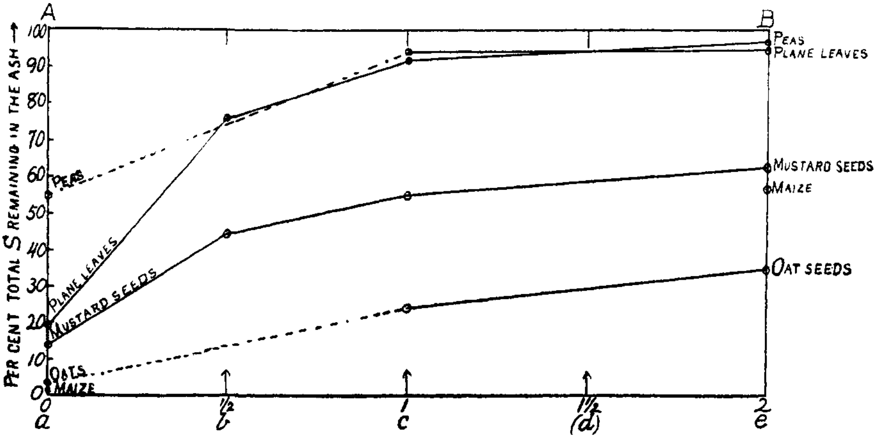

Fig. 3.—Effect of addition of sodium carbonate in ashing.

2. *The Loss of Sulphur when the Substance is Burnt Alone.*—The loss varies greatly with different substances. With plant-stuffs, from 20.43 per cent. of the whole (in the case of leaves) to 99.43 per cent. (in the case of maize) was lost. With coal the loss varied from 75 to 96 per cent. In the case of albuminous substances, no sulphur was left in the ash. The numerical relations are clearly shown in Table VIII. The numbers are calculated from the results of combustions according to the method described above, since the sulphur left in the ash by burning in an oxygen stream is practically the same as that left when the substance is burned in air in an open dish. (For example, leaves ashed in air gave 1.037 per cent. sulphur trioxide, and in the combustion tube 1.084 per cent.) The volatile sulphur is expressed as SO_3 for the sake of comparison. The figures for the plane tree-leaves are especially interesting. This was the only substance examined in which the sulphur retained in the ash was greater in amount than that volatilized. The youngest leaves show the greatest proportion of volatile sulphur, and the oldest the

TABLE VII.—EFFECT OF ADDITION OF SODIUM CARBONATE IN ASHING (See Fig. 3)

		(a) Ashing without sodium carbonate.		(b) Ashing with addition of half the weight of sodium carbonate.		(c) Ashing with addition of an equal weight of sodium carbonate.		(d)	(e) Ashing with addition of twice the weight of sodium carbonate.	
Substance.	True per cent. sulphur trioxide in dry substance.	Per cent. sulphur trioxide found.	Per cent. of whole retained.	Per cent. sulphur trioxide found.	Per cent. of whole retained	Per cent. sulphur trioxide found.	Per cent. of whole retained.	With 1½ times the weight of sodium carbonate.	Per cent. sulphur trioxide found.	Per cent. of whole retained.
Mustard seeds	2.862	0.363	12.68	1.223*	42.73	1.44* 1.66* 1.50 —— 1.533 mean	53.56	....	1.79* 1.72 —— 1.755 mean	61.32
Maize	0.35	0.0026	0.73	....	....	....	....	....	0.19	56.06
Peas	0.411	0.0755	18.37	0.306	74.45	0.372	90.51	....	0.398	96.83
Oats	0.475	0.013	2.52	....	....	0.11	23.16	....	0.16	33.68
Leaves, Oct. 24th	2.585	1.95**	75.39	....	....	....	....	....	....	....
Leaves, July 15th	1.388	0.758	54.61	....	....	1.29	92.92	....	1.33*	95.79
Leaves, Aug. 22d	1.681	1.068***	63.53	1.272	75.56	....	....	....	....	....

NOTE.—The numbers in column (*a*), without stars, are the averages of results obtained by combustion in an oxygen stream.

*Conducted over alcohol lamp.

**Mean of one result by Tucker process without calcium acetate and two results by my method.

***Mean of one ashing over Bunsen lamp and two results by my method.

smallest. Further, Table IV shows that the youngest leaves contain the smallest total amount of sulphur, and the oldest the greatest amount. In the case of maize, practically *all* the sulphur was lost.

TABLE VIII.—RELATIONS BETWEEN VOLATILE, NON-VOLATILE AND TOTAL SULPHUR WHEN THE SUBSTANCE IS BURNED ALONE.

Substance.	Ratio of Volatile sulphur.	to	Non-volatile sulphur.	Percentage of volatile sulphur.
Mustard seeds	6.82	:	1	87.1
Leaves, Oct. 24th	0.30	:	1	22.9
Leaves, July 15th	0.84	:	1	45.8
Leaves, Aug. 22d	0.55	:	1	35.5
Peas	0.45	:	1	81.7
Oats	48.9	:	1	97.4
Maize	171.0	:	1	99.4
Brown coal	4.04	:	1	80.0
"Briquette" coal	3.02	:	1	75.0
Anthracite coal	32.2	:	1	96.0

B. *General Conclusions.*—(1) In ashing a plant-substance, a protein, or a coal in the ordinary manner, without addition of alkali, a loss of sulphur always takes place.

This loss is always considerable, and may be, in some cases, enormous, even when precautions are taken to insure a low temperature and a slow and regular ashing. It is caused by the conversion of organic sulphur into volatile sulphur compounds and into sulphur dioxide and trioxide during the charring and ashing. A certain part of these is retained by the bases, especially by the alkalies, but in presence of phosphoric and silicic acids, which expel sulphuric acid at a red heat, the amount retained in the ash may be very small or even nothing.

(2) The loss takes place even when there is a quantity of alkaline base present more than sufficient to combine all the acid.

(3) The loss is diminished (but by no means entirely avoided) by the addition of amounts of sodium carbonate up to twice the weight of the substance to be ashed. The *additional* effect of adding more sodium carbonate is practically nothing.

(4) The loss of sulphur is not entirely prevented *either* by the addition of calcium acetate before ashing (Tucker); *or*, of magnesium oxide and sodium carbonate together (Eschka); *or* by evaporation with potassium hydroxide followed by oxidation with potassium nitrate; *or* by evaporation with nitric acid and potas-

sium nitrate before ashing (Fraps). In all these cases the gases still contain sulphur.

(5) By far the greater part of the loss of sulphur occurs during the preliminary charring, a much smaller part during the burning of the charred mass to ash.

(6) Combustion in a stream of oxygen, with absorption of the sulphur-containing products of charring and combustion either in heated sodium carbonate in the combustion tube or in a special apparatus, gives, under proper conditions, absolute values for the total sulphur. Such results are, however, exceedingly difficult, if not quite impossible, to attain by either the original Berthelot method or the Sauer method. The writer considers that he has ascertained and described the arrangement of apparatus and the details of manipulation which render possible the attainment of such accurate results with ease and certainty. It is essential to burn the escaping gases completely with an excess of oxygen, introduced laterally at a certain point in the combustion tube, before absorbing the sulphuric acid from them.

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[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, NO. 91.]

THE DETERMINATION OF NITROGEN IN FOOD MATERIALS AND PHYSIOLOGICAL PRODUCTS.

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FOR THE determination of nitrogen in ordinary animal and vegetable substances where it exists mainly as proteids or related compounds, some modification of the Kjeldahl method is now almost always employed. The various modifications differ mainly in that different substances are used to facilitate the decomposition of the organic matter by the boiling sulphuric acid.[1] Those which appear to be most extensively used are mercury (with or without potassium permanganate), potassium sulphate, and copper sulphate. The combination of two or more of these reagents has frequently been suggested and has recently been adopted

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[1] Since the literature of the subject is quite extended and quite familiar to those likely to be interested in the present work, specific references are omitted and the processes tested are indicated without detailed description.