

average errors resulting from the use of an arbitrary figure (like 5.38 per cent. as representing hydrogen in pure coal) in calculation of available hydrogen, and fuel value, compared with other methods.

H indicated by calories — H of ultimate analysis = 0.18 per cent.

H by Prof. Parr's curve — H of ultimate analysis = 0.20 "

H by Prof. Parr's curve — H indicated by calories = 0.17 "

H from arbitrary figure — H of ultimate analysis = 0.15 "

H from arbitrary figure¹ — H indicated by calories = 0.15 "

¹ Corrected 0.17 per cent., as explained in the preceding paragraph.

It is noticeable that the averages from an arbitrary simple figure are a little better than any of the more complicated ones from a curve. In view of the uniformity of these results, it is quite remarkable that the several curves and calculations that Prof. Parr has devised, did not lead even farther from the actual figures.

Summary.

In all bituminous coal, and black and brown lignite, the proximate analysis and estimation of total carbon are sufficient data for a calculation of an ultimate analysis, in which no error seems to be above 1.00 per cent., and the average, much less. The high errors are in nitrogen and oxygen, where they are of slight consequence.

The hydrogen of ash-and water-free coal is 5.38 per cent., with an average error of only about 0.16 per cent. In a limited coal field, the maximum error is undoubtedly often less than 0.51 per cent. When an arbitrary figure like this gives such close results, the uselessness of any further calculation of hydrogen is apparent.

If it is possible to obtain the carbon percentage and proximate analysis more easily than to get the fuel value, a fairly close fuel value may be calculated by Dulong's formula, and the estimated ultimate analysis suggested above. Inasmuch as recent careful work indicates that Dulong's formula and the ultimate analysis give slightly low results, it is suggested that 0.17 per cent. be added to the per cent. of available hydrogen in the ash- and water-free coal, before applying the formula. A similar correction should be applied to the estimated ultimate analysis. Then, aside from a complete ultimate analysis, this estimated ultimate analysis gives the best foundation known for calculating fuel values. But the value of such calculation seems to be confined to cases where the carbon estimation is found easier than the calorimetric work.

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THE FORMATION OF VOLATILE SULPHUR COMPOUNDS IN MEAT AND THEIR INFLUENCE ON THE DETECTION OF ADDED SULPHITES.

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Sulphites are commonly detected in meat products by distillation with phosphoric acid into dilute bromine water and precipitation of the sul-

phuric acid, formed by the oxidation of the sulphurous acid, with barium chloride. To avoid oxidation in the distilling flask the distillation may be conducted in a current of carbon dioxide or steam. The sulphurous acid is quantitatively determined by weighing the barium sulphate or by collecting the distillate in standard iodine solution and titrating with standard thiosulphate solution.

It is well known that this process, because of the oxidation to sulphate which goes on continually on exposure of the meat to the air, does not give the full amount of sulphurous acid originally added to the meat; on the other hand meat to which no sulphite has been added but which has undergone decomposition responds to the test. The latter error, if not duly considered, is liable to lead to serious injustice in the official inspection of meat products, especially in cases where samples must be sent a considerable distance in warm weather. If possible, samples should be examined while still fresh, but if decomposition has set in, only such amounts of sulphurous acid as considerably exceed that obtained by decomposition should be regarded as from added sulphites. To obtain data for use in this connection, we have conducted experiments to determine the amount of volatile sulphur compounds formed in meat and what part of this sulphur is in the form of sulphurous acid or similar combination.

The distillations were carried on in all cases in a 500 cc. flask provided with a triple-bored rubber stopper. The first hole served to introduce a stream of carbon dioxide into the liquid, the second was fitted with a funnel tube with stop-cock for the introduction of phosphoric acid, while the third carried the exit tube which in turn was connected with a vertical condenser. A 200 cc. flask served as a receiver, the distillate in all cases being passed into the bromine solution by means of a tube broadened at the lower end. Experiment proved that no sulphurous acid escaped from this receiving flask.

Determinations were first made in sodium sulphite to test the accuracy of the method of distillation. The sodium sulphite used in the experiments was ground to a fine powder and carefully mixed. As it changed considerably in composition on exposure, comparative experiments in each case were made without delay on aliquot portions of the same solution. The amounts of sulphur as sulphurous acid obtained in this material directly by titration with iodine solution and, after distillation, by the barium sulphate method follow:—

S as SO ₂ By direct titration mg.	S as SO ₂ By gravimetric method after distillation mg.	Error mg.
6.9.	7.1 ¹	+ 0.2
14.4	14.2 ¹	—0.2
29.3	29.0 ¹	—0.3
60.9	59.6 ¹	—1.3

59.3	60.4 ¹	+1.1
60.4	60.32 ¹	-0.1
120.1	121.0 ¹	+0.9
120.1	119.7 ¹	-0.4
7.0	6.6 ²	-0.4
14.4	14.1 ²	-0.3
111.0	110.3 ²	-0.7

¹ Only water used in distilling flask.

² Distilled in the presence of 50 g. of fresh meat.

The following amounts of total volatile sulphur were obtained by the method described from 50 g. portions of chopped beef, mutton, veal and pork, when fresh and after standing in the laboratory for 14 days :

	Beef mg.	Mutton mg.	Veal mg.	Pork mg.
1st day	0.0	0.0	0.1	0.0
14th	1.4	2.1	4.0	2.4

In these experiments no appreciable amount of sulphur, liberated by phosphoric acid, was present in the fresh meat, but decided amounts were formed during decomposition. No attempt was made to learn the nature of these sulphur compounds. From the literature it would appear that they consist chiefly of hydrogen sulphide, ethyl sulphide, and methyl and ethyl mercaptans. Sulphites would probably be formed as intermediate products in the oxidation of sulphides to sulphates.

Search was next made for a suitable metallic salt, through a solution of which the steam from the distilling flask could be passed to precipitate hydrogen sulphide and mercaptans without affecting sulphurous acid. Sodium arsenite, lead acetate, and mercuric chloride, both in neutral and acid solutions, although removing completely hydrogen sulphide were found to hold back considerable amounts of sulphurous acid and were therefore entirely unsuited for the purpose. Dilute copper sulphate solution, (one per cent.), however, met the requirements, as it precipitated completely the hydrogen sulphide without retaining any considerable amount of sulphurous acid. The following results were obtained on aliquot portions of a solution of sodium sulphite following the usual process except that the steam from the distilling flask, before entering the condenser, was passed through 40 cc. of distilled water or of one per cent. copper sulphate. To prevent the CuSO_4 being carried over mechanically into the condenser during the vigorous ebullition, the exit tube was provided with a bulb and a goose neck turn.

S as SO_2 by distillation through distilled water ¹ mg.	S as SO_2 by distillation through CuSO_4 mg.	Error mg.
8.7	8.1	-0.6
8.7	7.9	-0.8
8.7	7.9	-0.8

¹ By previous experiment it was proved that the results by distillation through water were the same as by direct titration.

Two series of determinations of "S as SO_2 " (that is of volatile sulphur not removed by copper sulphate) and of "S as H_2S " (including sulphides and mercaptans) were next made on 50 g. portions of the four principal kinds of meat in different stages of decomposition following the method outlined. At the outset the meat was chopped and the weighed portions introduced into the flasks used later for the distillation. These flasks were kept unstoppered at the room temperature and the meat allowed to decompose. The SO_2 was weighed as BaSO_4 , the H_2S as Cu_2S . Series I is incomplete as neither qualitative nor quantitative tests for S as H_2S were made until the 9th day, whereas in series II in every case both the barium sulphate and the cupric sulphide precipitates were filtered and weighed.

VOLATILE SULPHUR COMPOUNDS FORMED BY DECOMPOSITION IN 50 GRAMS OF MEAT
SERIES I.

Day	Beef Sulphur as		Mutton Sulphur as		Veal Sulphur as		Pork Sulphur as	
	SO_2 mgs.	H_2S mgs.	SO_2 mgs.	H_2S mgs.	SO_2 mgs.	H_2S mgs.	SO_2 mgs.	H_2S mgs.
1	0.1	..	0.1	..	0.1	..	0.1	..
2	0.2	..	0.2	..	0.1	..	0.2	..
3
4	0.2	..	0.4	..	0.4	..	0.3	..
5	0.5	..	0.5	..	0.5	..	0.4	..
6	0.4	..	0.7	..	0.7	..	0.4	..
7	0.5	..	0.7	..	0.9	..	0.5	..
9	0.6	1.0	0.8	1.2	1.2	1.4	0.8	2.4
11	0.4	0.7	0.9	2.1	1.2	1.6	0.6	1.7
15	0.5	2.4	0.2	1.2	0.5	1.1	0.6	2.9
19	1.0	0.3	0.2	none	0.7	1.9	0.7	1.1
23	0.4	0.5	0.4	none	0.4	0.3	0.2	1.7
27	0.2	0.9	0.5	1.1	0.6	none	0.2	0.5

SERIES II.

Day	Beef Sulphur as		Mutton Sulphur as		Veal Sulphur as		Pork Sulphur as	
	SO_2 mgs.	H_2S mgs.	SO_2 mgs.	H_2S mgs.	SO_2 mgs.	H_2S mgs.	SO_2 mgs.	H_2S mgs.
1	none	none	0.1	none	0.1	none	0.1	none
2	0.2	none	0.1	none
3	0.2	none	0.4	0.1	0.2	none	0.2	none
4	0.1	none	0.8	none	0.5	0.4	0.1	none
5
6	0.6	none	0.5	0.2	0.5	0.5	0.2	0.5
7	0.4	1.0	1.3	0.2	0.8	0.4	0.5	none
9	0.5	0.2	2.1	0.3	1.2	3.4	0.2	1.1
11	0.2	1.0	0.5	0.2	0.8	2.8	0.4	0.6
15	0.6	1.3	1.3	0.3	0.5	2.6	0.4	0.5
18	0.1	0.2	1.0	0.2	1.9	1.8	0.2	1.2
19
23	0.2	1.1	0.2	0.7	0.5	1.5	0.2	0.8

These results, although not always uniform, show that during the first four days the S as SO_2 was in most cases inconsiderable, in only one

case exceeding 0.5 mg., and the S as H_2S , except in the case of veal, was indeterminably small. With or without the use of $CuSO_4$ during these days there would have been no danger of declaring sulphites present when none had been added. After the 4th day somewhat larger amounts of S as SO_2 were obtained, but in no case did the amount exceed 1.9 mg. (from veal, series II).

The maximum amount of S as SO_2 obtained from beef was 1.0 mg. (series I, 19th day) and from pork 0.8 mg. (series I, 9th day). These results are especially valuable since Hamburg steak and sausages are the meat products commonly preserved with sulphites.

The amounts of S as H_2S , were larger than of S as SO_2 , especially in the case of veal, the maximum being 3.4 mg. (series II, 9th day). The largest amount of total volatile sulphur was also obtained from veal, (series II, 9th day) and amounted to 4.6 mg.

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THE DETECTION OF BLEACHED FLOURS.

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All the processes of technical value that are used for the bleaching of wheat flour employ nitrogen peroxide as the active agent.¹ Chlorine, bromine and sulphur dioxide have been suggested, but while they bleach more or less effectively, they offer no advantages over nitrogen peroxide and possess disadvantages that the latter does not.

The results given in this article were obtained in the course of an investigation, the detailed discussion of which is published elsewhere.²

Early in December, 1906, paper-lined sacks were sent to twenty-four different Nebraska mills with the request that, as far as convenient, both bleached and unbleached samples of three grades of flour, *viz.*, patent, straight and bakers', be forwarded. The samples, all freshly milled, were sent by express to Lincoln. The paper linings of the sample sacks prevented sifting of the flours; accordingly the bleached flour did not enter the sacks of unbleached, while in transit. The 127 five-pound samples were placed side by side, in the order of their numbers, on the shelves of a storeroom.

Some of the mills bleach the lower grades of flour while others do not, considering that it injures the appearance of the flour. Some of the latter class, however, were so obliging as to bleach samples of their low-grade flours for the purpose of the investigation.

Besides the flours secured directly from the mills, fifteen samples, some bleached, others unbleached, that had been stored in paper boxes,

¹ Fleurent, *Compt. rend.*, 142, 180 (1906); Avery, *This Journal*, 29, 571 (1907).

² *Bull.* 102, Nebraska Agr. Exp. Sta. (1907).