

grams per 100 cc. of water. If the reagent is not in solution, the liberation of nascent oxygen occurs at the solid surface and the oxidizing efficiency is low.

TABLE IV. RESULTS OF ANALYSES

SUBSTANCE	CO ₂ CALCD.		CO ₂ FOUND	RECOVERY
	Mg.	Mg.		%
Acetic acid	176	175		99.4
Propionic acid	132	130		98.5
Butyric acid	176	173		98.3
Chloroacetic acid ^a	88	83		94.3
Thiourea	44	43		97.7
Ethyl alcohol	150	150		100
Succinic acid	176	173		98.3
Dextrose	150	150		100
Dextrose + NH ₄ Cl	100	99		99.0

^a Eastman's c. p. chloroacetic acid used; could not be further purified.

The results of analyses made on solutions containing representative compounds obtained by fermentation of carbo-

hydrates are shown (chloroacetic acid and thiourea are also included in Table IV). From Table IV it can be seen that the presence of sulfur, nitrogen, and chlorine has no serious effect.

LITERATURE CITED

- (1) Birkinshaw, J. H., and Raistrick, H., *Trans. Roy. Soc. (London)*, **B220**, B11-15 (1931).
- (2) Cain, J. R., *J. IND. ENG. CHEM.*, **6**, 465-8 (1914).
- (3) Franz, A., and Lutze, H., *Ber.*, **57B**, 768-70 (1924).
- (4) Friedemann, T. E., and Kendall, A. I., *J. Biol. Chem.*, **82**, 45-55 (1929).
- (5) Grey, E. C., *J. Chem. Soc.*, **105**, 2204-10 (1914).
- (6) Heck, A. F., *Soil Sci.*, **28**, 225-32 (1929).
- (7) Truog, E., *J. IND. ENG. CHEM.*, **7**, 1045 (1915).

RECEIVED July 7, 1932. Coöperative project with Department of Bacteriology, Iowa State College. Project IF 12.

Sulfur Content of Foods

Modification of Turbidimeter for Determination of Small Quantities of Sulfur

K. S. KEMMERER AND P. W. BOUTWELL, Beloit College, Beloit, Wis.

THE necessity for an accurate knowledge of the mineral constituents of our common foodstuffs has increased in recent years. So far as the present authors have been able to find, the data on the sulfur content of foods are fragmentary and are based on different methods of analysis. Sherman (5) has compiled a table listing the sulfur content of many foods. The data are gathered from various sources and the methods used are undoubtedly varied. It is the purpose of this paper to describe a modification of the sulfur turbidimeter adapted to the determination of small quantities of sulfur in foods and biological material following oxidation of the sample with nitric and perchloric acids according to the method of Toepfer and Boutwell (6), and to give the sulfur content of a number of our common foods as determined by this method.

The earlier work (1, 6) from this laboratory was carried out with the old model of the sulfur photometer. The present authors have used a modification of the new model of the Burgess-Parr turbidimeter. The new instrument offers advantages over the old in simplicity, accuracy, and speed, but it requires from 4 to 6.5 mg. of sulfur in a volume of 200 cc. in order to obtain suitable readings. In the case of materials low in sulfur, this would often require too large a sample for oxidation. The authors have modified the instrument so as to make it suitable for use with a working

volume of 25 cc. containing from 0.7 to 1.3 mg. of sulfur. This modification was accomplished by using black hard rubber tubing of a smaller diameter in place of the larger tubes furnished with the instrument as described by Parr and Staley (3). The stationary tube C, in Figure 1 in their description, is replaced by a hard rubber tube of 13 mm. inside diameter with an optical glass bottom immediately above the light L. This tube holds the turbid solution to be examined and is suitable for use with a volume of 20 to 25 cc. The inner plunger tube, P, is replaced by a smaller hard rubber tube of 8 mm. outside diameter, also fitted with an optical glass bottom. The small diameter of the plunger tube gives a small field for comparison but adds to the sharpness of the end point. Suitable metal collars are used to hold the smaller tubes in place in the instrument. This modification is of especial value for work on materials low in sulfur. It has made possible an accurate determination of sulfur in a sample one-sixth to one-seventh as large as would have been necessary if the original instrument had been used. This modification is recommended for the turbidimetric determination of sulfur in urine (1).

The accuracy of the results secured with the modified turbidimeter is shown by the ability to reproduce the calibration curve of the instrument between the optimum range of 0.7 to 1.3 mg. of sulfur with an average error of about

TABLE I. RESULTS ILLUSTRATING USE OF MODIFIED TURBIDIMETER

Wt. of sample, grams Volume (made up to), cc. Aliquot taken, cc. Turbidimeter reading	SULFUR 1			SULFUR 2			SULFUR 3			RED RADISHES			APPLE		
	0.3163 500 20			0.5565 200 7			0.5060 250 14			25.81 100 15			82.5 50 10		
	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
	86	84	84	67	67	67	64	65	67	69	69	67	61	60	61
	87	84	83	64	65	67	64	63	64	69	68	68	61	61	60
	85	83	85	65	67	71	63	65	66	69	67	67	61	62	62
	85	84	84	65	67	68	65	65	65	69	68	68	60	60	61
	85	82		65	67	68			65				64		
				64		68							61		
Mean	85.6	83.4	84.6	65	66.8	68.1	64	64.9	65.3	69	67.5		61.3	60.9	61
Average		84.5			66.6			64.5		67.3				61.07	
Sulfur found, grams		0.00078			0.00095			0.00099		0.00097				0.00101	
Sulfur present, grams		0.000783			0.000945			0.00099							
Error, grams		-0.000003			+0.000005			0.00000							
Sulfur found, %		6.165			4.93			3.53		0.025				0.012	
Sulfur present, %		6.188			4.84			3.53							
Error, %		0.32			1.6			0.00							

1 to 2 per cent. This represents the limit of accuracy in reading the instrument and applies in any determination. The earlier papers (1, 6) from this laboratory show the ability to recover added sulfur by this method and a comparison of the turbidimetric results with those obtained by the standard gravimetric methods.

TABLE II. SULFUR CONTENT OF FOODS

MATERIAL	SULFUR %	MATERIAL	SULFUR %
Apple (crab)	0.018	Meat (cont'd)	
Apple (Rome beauty)	0.012	Ham (pig)	0.130
Asparagus	0.065	Heart (pig)	0.125
Banana	0.013	Kidney (pig)	0.155
Barley	0.137		
Beans (lima, dry)	0.187	Lamb chop	0.174
Beans (navy, dry)	0.250	Pork liver	0.266
Beans (shell)	0.070	Pork loin	0.242
Beans (soy, dry)	0.290	Steak (round)	0.202
Beans (string, yellow)	0.017	Shoulder (pork)	0.174
		Veal chop	0.069
Beets (red)	0.017	Milk (condensed)	0.126
Beets (sugar)	0.015	Milk (whole)	0.028
Bread (bran)	0.011	Molasses	0.032
Bread (white)	0.011	Muskmelon	0.031
Bread (whole wheat)	0.104	Mustard seed	1.175
Cantaloupe	0.031	Nut meats (hickory)	0.166
Cabbage	0.046	Nut meats (English walnut)	0.135
Carrot	0.016	Oats	0.160
Cauliflower	0.056	Oatmeal	0.233
Celery	0.025	Orange (California)	0.014
Cheese (American Kraft)	0.198	Parasnip	0.036
Cherries (maraschino)	0.041	Peach	0.005
Chocolate (bitter)	0.196	Peanut	0.208
Cocoa	0.236	Pear	0.016
Coffee (bean)	0.131	Peas (dried)	0.154
Corn (yellow, maize)	0.120	Peas (green)	0.031
Corn (sweet, dried)	0.131	Plums (purple)	0.004
Corn (sweet, green)	0.051	Plums (red)	0.005
Corn (gluten)	0.607	Potato (early Ohio)	0.049
Cornflakes	0.114	Potato (sweet)	0.017
Cracker (white)	0.094	Prunes	0.022
Cucumber	0.009	Pumpkin	0.018
Egg (total)	0.167	Pepper	0.035
Egg (yolk)	0.108	Radish (white)	0.019
Egg (white)	0.169	Radish (red)	0.025
Egg plant	0.036	Raisins (seedless)	0.046
Garlic	0.506	Rice (white)	0.136
Grapes (with skins)	0.012	Shredded Wheat	0.164
Hemp seed	0.291	Spinach	0.030
Honey	0.004	Spinach (New Zealand)	0.045
Horse radish	0.221	Squash (Table Queen)	0.029
Jelly (grape)	0.006	Squash (summer)	0.053
Kohlrabi	0.036	Sirup (Karo)	0.029
Lettuce (southern)	0.013	Tapioca	0.012
Lettuce (northern)	0.016	Tea	0.217
Macaroni	0.143		
Meat		Tomato	0.017
Calves' liver	0.225	Wheat	0.145
Brain (pig)	0.113	Wheat flour (40% gluten)	0.470

TREATMENT OF SAMPLE

It is desirable to have sufficient sulfur in the oxidized sample to make possible check determinations. In the course of this work three sets of readings were taken on each sample, so it was necessary to have from 3 to 5 mg. of sulfur in each sample oxidized. The samples used varied in weight from 0.5 gram for materials high in sulfur to 120 grams for materials such as honey which contain little sulfur. The per cent of sulfur in all cases is reported on the wet basis or on the condition in which the sample was offered in the market for food consumption. This was done in order to obtain a more representative sample of the material. It is difficult in many cases to dry a sample of food high in moisture and then obtain a satisfactory sample for analysis. Volatile compounds other than water may be lost at the temperature of the drying oven or even at low temperatures. Peterson (4) has shown a 10 to 20 per cent loss of the volatile sulfur in rutabagas and cabbage on drying the green material in the oven. The figures presented in this paper do not represent the sulfur content of these foods in general, but only the sulfur content of the particular sample analyzed. Only when a large number of samples grown in different

localities and under different conditions have been analyzed will it be possible to state the average sulfur content of any foodstuff.

OXIDATION OF SAMPLE

The method of oxidation was essentially that described in an earlier paper (6). The sample was weighed in its natural condition and was introduced into an 800-cc. Pyrex Kjeldahl flask and digested on the steam bath with 50 cc. of concentrated nitric acid until solution took place. The flask was then transferred to a digestion rack and boiled very gently until the evolution of nitrogen dioxide ceased. If violent bumping occurred, 15 cc. of fuming nitric acid were added. As a rule, this caused sufficient oxidation to prevent further bumping. After the evolution of nitrogen dioxide had stopped, the solution was boiled until nearly all the nitric acid had been distilled off. Then 10 cc. of 70 per cent perchloric acid were added and the boiling continued until approximately one cc. of solution was left. In some cases further treatment with perchloric acid was required. The oxidation up to this point requires from 4 to 6 hours depending on the type of material and the size of the sample. The excess of nitric and perchloric acids was destroyed by adding 10 cc. of concentrated hydrochloric acid and again evaporating to near dryness. The remaining acid was neutralized by adding dilute ammonium hydroxide and boiling to remove the excess of ammonia. The solution was made slightly acid with hydrochloric acid and filtered into a 50-cc. volumetric flask. The correct hydrogen-ion concentration for the subsequent precipitation of barium sulfate was obtained by making the solution alkaline with ammonium hydroxide and then just acid to litmus with hydrochloric acid. The solution was then made up to volume.

A blank determination was made for the sulfur present in the reagents used by running a determination on a solution containing 5 mg. of sulfur. This correction averaged 0.00006 mg. of sulfur.

USE OF MODIFIED TURBIDIMETER

The turbidimeter readings using the modified instrument were obtained by running a suitable aliquot of the solution prepared as above into a 25-cc. volumetric flask. Three cubic centimeters of a solution containing 240 grams of sodium chloride and 15 cc. of concentrated hydrochloric acid per liter were added and the whole diluted to 25 cc. The solution was transferred to a 50-cc. Erlenmeyer flask, 0.1 gram of solid sized barium chloride added, and the solution shaken for about one minute. Turbidimetric readings were taken within the following 5 minutes as described in the bulletin (2) furnished with the instrument. Practice in reading the instrument is essential and frequent checking of the calibration curve is recommended. The instrument should be calibrated by each operator. In the determination of sulfur in urine this same procedure should be substituted for that previously described (1) if the modified turbidimeter is used.

Results illustrating the use of the modified turbidimeter are given in Table I. The data in the "sulfur found" column were obtained from the calibration curve of the instrument. The figures given under the "sulfur" heads represent data on analyzed samples of known sulfate content. No oxidation was involved in their analysis. In no case did the operator know the sulfate content of these samples until after the analysis was complete.

In Table II the sulfur content of ninety-six foodstuffs is given. The results in both Tables I and II are corrected for the blank determination.

LITERATURE CITED

- (1) Boutwell, P. W., and Toepfer, E. W., *IND. ENG. CHEM., Anal. Ed.*, 4, 117 (1932).
- (2) Burgess-Parr Company, 111 West Monroe St., Chicago, Ill., *Booklet 112*.
- (3) Parr, S. W., and Staley, W. D., *IND. ENG. CHEM., Anal. Ed.*, 3, 66 (1931).
- (4) Peterson, W. H., *J. Am. Chem. Soc.*, 36, 1290 (1914).
- (5) Sherman, H. C., "Chemistry of Food and Nutrition," 4th ed., pp. 554-9, Macmillan, 1932.
- (6) Toepfer, E. W., and Boutwell, P. W., *IND. ENG. CHEM., Anal. Ed.*, 2, 118 (1930).

RECEIVED June 13, 1932.

Comparative Efficiencies of Gas-Washing Bottles

S. HALBERSTADT, University of Jena, Jena, Germany

DECISION as to the efficiency of various types of gas-washing bottles is an apparently simple matter, but one which proves quite complex on thorough investigation. Friedrichs (2), in 1919, showed that of the various devices known at that date, only the gas washers built on the spiral-pattern principle could insure complete absorption. Since that time, apparatus with sintered-glass filter disks have been developed. In a paper by Sieverts and Halberstadt (5) it was shown that besides the length of passage in which gas and liquid are in contact with each other, the size of the gas bubbles distributed within the liquid is also of decided importance. These results are referred to in a recent paper by Friedrichs (3). He employed mixtures of sulfur trioxide and air, both wet and dry, and tested the absorption with eleven different patterns of gas washers.

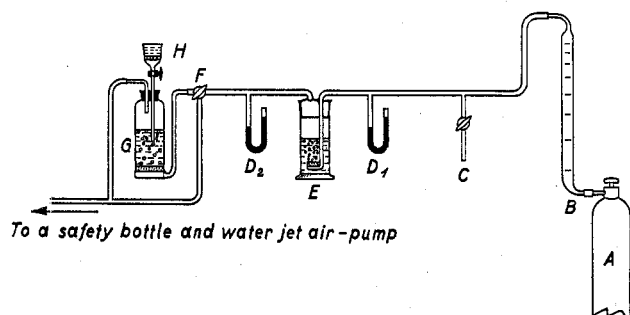


FIGURE 1. MODIFIED APPARATUS

Unfortunately these experiments cannot be compared with former ones because it is well known that wet sulfur trioxide is likely to form a nebula in air and that these nebulas behave quite differently from real gases. It is difficult to absorb them in liquids, but easy to retain them by the action of filters. This is clearly shown by Friedrichs' results. When using a moist mixture of air and sulfur trioxide, a glass-filter gas washer and a spiral gas washer filled with glass grains are most efficient, and have approximately the same effect. When using the dry mixture, the spiral gas washer filled with glass grains gives the same efficiency, owing to the considerable thickness of the filtering layer. On the other hand, the glass-filter gas washers of Schott and Gen. are less efficient because the nebulas are produced only in the thin filter disk in which the gas comes into contact with the liquid, but they are still capable of comparison with the best apparatus without glass filters.

Rhodes and Rakestraw (4), who also studied these problems, came to the conclusion that the spiral gas washers of Greiner and Friedrichs and the pattern 101 of Schott and

Gen. (apparently G1 porosity) gave about the same good results. They employed air containing 13.4 and 5.1 per cent of carbon dioxide, with velocities of flow up to 16 cc. per second—i. e., about 60 liters per hour. They mention that for the glass-filter gas washers, a comparatively higher pressure must be used.

The following experiments were made in accordance with the last-mentioned paper. The gas mixture, contained in a steel cylinder, A (Figure 1), was passed through a flowmeter (Rotameter), then through a gas washer, E, filled with a solution of potassium hydroxide (1 to 2), and through a three-way stopcock, F, to a glass-filter gas washer, 101 G3, containing a clear solution of barium hydroxide, G. The outlet from this led to a water-jet pump. On either side of the gas washer being tested there was placed a mercury manometer D₁, D₂. The differences in height between these two manometers are given in Table I as "resistance of the gas washer."

The gas washer containing the solution of barium hydroxide was constructed in the following manner: The usual ground-glass stopper was replaced by a double-bore rubber stopper carrying an outlet delivery tube and a glass-filter dropping funnel, H. With the three-way stopcock, F, closed, clear filtered barium hydroxide could be drawn into the bottle from this funnel. After every experiment, the filter and the gas-washing bottle were cleaned with hydrochloric acid and carefully washed with distilled water. Then a fresh portion of 75 cc. of barium hydroxide was introduced in the same manner.

The results of these experiments are shown in Table I.

TABLE I. RESULTS OF EXPERIMENTS WITH DIFFERENT TYPES OF APPARATUS

TYPE	HT. OF LIQUID COLUMN Mm.	AV. RESISTANCE OF GAS WASHER Mm. Hg	VELOCITY GIVING REACTION WITH Ba(OH) ₂ WITHIN 5 MIN.		
			17% CO ₂	3% CO ₂	0.67% CO ₂
			L./hr.	L./hr.	L./hr.
Drechsel	65	10	20	20	20
	95		20	20	20
Greiner and Friedrichs	(200 cc. KOH) length of way about 880 mm.	10	60	60	60
Schott 83 G1	65	20	30	45	45
	95		30	45	60
Schott 101a G1	40	25	30	45	60
	65		45	45	75
	95		60	60	75
	140		60	75	80
Schott 101 G3	40	90	60	75	100
	60		75	90	100

From these data it may be concluded that the Greiner and Friedrichs gas-washing bottle, as also found by Rhodes and Rakestraw, is useful for very many purposes. In certain cases, however, the glass-filter gas washers proved to be superior, since with this type the lower the concentration of the gaseous component to be absorbed, the greater