Determination of Sulfur in Bone Char [1]

By Victor R. Deitz, Helen R. Higginson,[2] and Cola Parker

In sugar technology the established analytical procedures were found to give erroneous results for the "sulfide" sulfur and "total" sulfur in bone char. The error was found to be caused by the presence of organic sulfur in the carbonaceous component. Solution of the total sulfur in bone char was obtained by three independent methods: (1) After oxidation with nitric and perchloric acids, (2) after air oxidation in an intimate mixture with sodium carbonate and magnesium oxide, (3) after oxidation with nitric acid in a modified Carius tube. The precipitate of barium sulfate was found to be contaminated with calcium and phosphate from the bone char. It was discovered in the present work that barium sulfate was easily and completely soluble in hot 70-percent perchloric acid, thus making possible a purification by reprecipitation. Quantitative precipitation was verified by using known mixtures of calcium chloride, phosphoric acid, and sulfuric acid. The distribution of the total sulfur between the carbonaceous residue and the filtrate resulting from the conventional acid treatment of bone char was determined after digestion in three mixtures: nitric and hydrochloric acids, potassium chlorate and hydrochloric acid, and hydrochloric acid alone. It was shown that the sulfur contained in the gases evolved with hydrochloric acid (determined by combustion with air followed by gravimetric barium sulfate) was greater in most samples than that determined as sulfide-sulfur (precipitated as cadmium sulfide and determined iodometrically). The distribution of the total sulfur between filtrate, residue, and evolved gases was influenced by deliberate variations in the acid leaching process.

I. Introduction

In sugar technology the established methods of determining sulfur in bone char have been concerned with the calcium sulfate and calcium sulfide. The general procedure outlined by Spencer and Meade [1][3] is substantially the same as that of the original methods outlined in 1881 by Tucker [2]. Discordant results obtained by these methods made it desirable to make a critical study of the procedures for determining sulfur in bone char.

According to the old procedure, a sample of bone char was heated with hydrochloric acid, cooled, and diluted to a known volume. The residual carbonaceous matter was removed by filtration. A barium sulfate determination was then made in an aliquot part of the filtrate. The result was calculated as percentage "calcium sulfate" of the original sample of char. In order to determine "calcium sulfide", a sample of the original char was first digested with either nitric acid or a mixture of potassium chlorate and hydrochloric acid. The subsequent procedure was the same as that given for the calcium sulfate. Subtracting from the result of this determination, the barium sulfate already found in the calcium sulfate determination gave the barium sulfate equivalent to the calcium sulfide. One object of this paper is to show that these methods may give erroneous results for the sulfide sulfur and the total sulfur in bone char. It will also be shown that this is due to a significant quantity of organic

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sulfur contained in the carbonaceous component of bone char.

An accurate determination of the sulfur in bone char is important in a study of its revivification. In kilns using direct firing, the bone char is in contact with the products of combustion of the fuel, which may have several possible effects on the char.

The total sulfur content of service bone char may be of the order of magnitude of 1 percent, when expressed as SO_4. The gross heterogeneity of char and the difficulty of obtaining uniform samples are factors that limit the reproducibility of the analytical results. For aliquot parts of a given well-mixed powdered sample, it is possible to realize a precision adequate for this work.[4]

II. Precipitation of $BaSO_4$ in the Presence of Ca and PO_4 Ions

Many investigations with contaminated barium sulfate precipitates in analytical chemistry have shown the difficulties attending the exact determination of sulfur as barium sulfate. An interesting discussion of the possible compensation of considerable plus and minus errors has been given by Hillebrand and Lundell [3]. Kolthoff and Sandell [4] have also reviewed the evidence for the contamination of barium sulfate precipitates by coprecipitation under various conditions.

A great deal of difficulty was experienced in precipitating the sulfate quantitatively from known solutions containing the sulfate, calcium, and phosphate ions. For bone char the problem is that of determining about 1 percent of total sulfur, expressed as SO_4 in the presence of about 40 percent of calcium ion and 50 percent of phosphate ion. The extensive literature on the barium sulfate determination has unfortunately not dealt with this situation.

The precipitation of barium sulfate from known solutions of calcium chloride, phosphoric acid, and sulfuric acid was first investigated in some detail. The weights of calcium chloride and phosphoric acid in each solution were maintained constant, and the values were chosen so as to give 1.75 g of calcium ion and 2.75 g of phosphate ion in each test solution. These weights correspond approximately to the weight of calcium and phosphate

ions contained in a solution of 5 g of a bone char.

In these investigations, the precipitation of barium sulfate was conducted at an acidity between pH 1 and 2. It was found possible to obtain an easily filterable precipitate and to avoid excessive loss of barium sulfate by solution. This value for acidity is in agreement with the value of 0.05 N hydrochloric acid recommended by Kolthoff and Sandell [4]. Fortunately, the solutions prepared from the bone char samples were readily filterable at pH 1, although they were almost nonfilterable at pH 2. A glass electrode and pH meter, calibrated with a buffer of pH 3.0, were used in determining the pH of all solutions.

Data for the weights of barium sulfate precipitated from known amounts of sulfuric acid in mixtures of calcium chloride and phosphoric acid are given in table 1. The precipitation was made by the slow addition of 50 ml of a 5-percent solution of barium chloride. The first four determinations were with mixtures of the sulfuric acid in calcium chloride only, and the results indicate a

TABLE 1. *Weights of barium sulfate derived from a single precipitation in a mixture of sulfuric acid, calcium chloride, and phosphoric acid, adjusted with hydrochloric acid to pH 1*

Conditions of precipitation	Weight of precipitate		
	Found	Theory	Difference
CALCIUM CHLORIDE AND SULFURIC ACID			
	g	*g*	*Percent*
4 hr stirring at 30° C	0.3273	0.3239	+1.05
Do	.3228	.3239	−0.33
Do	.3263	.3239	+.74
Do	.3278	.3239	+1.20
PHOSPHORIC ACID AND SULFURIC ACID			
4 hr stirring at 30° C	0.3346	0.3239	+3.30
Do	.3440	.3239	+6.21
CALCIUM CHLORIDE, PHOSPHORIC AND SULFURIC ACIDS			
4 hr stirring at 50° C, stood overnight	0.3044	0.2790	+9.10
Do	.3081	.2790	+10.43
6 hr stirring at 90° C, stood overnight	.3375	.3244	+4.0
Do	.3387	.3244	+4.4
4 hr stirring at 50° C, stood overnight	[a].2961	.2790	+6.13
Do	[a].3009	.2790	+7.85
Do	[a].2979	.2790	+6.77
Do	[a].3010	.2790	+7.88
Do	[a].3056	.2790	+9.53

[a] Saturated barium hydroxide used instead of 5-percent solution of barium chloride.

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[4] A coefficient of variability of 1.65% as a measure of the precision was calculated from the data of table 5.

percentage difference of about 1 percent. With sulfuric acid in solutions of phosphoric acid, the indicated contamination was greater. With mixtures of calcium chloride, phosphoric acid, and sulfuric acid the positive error has been found to be as much as 10 percent. Qualitative examination showed that the precipitates from the phosphate mixtures were contaminated with phosphate ion.

In the course of the experiments to be described on the total oxidation of the carbonaceous matter in bone char, it was discovered that the barium sulfate precipitate was freely soluble in hot perchloric acid.[5][6] It was thus possible to purify the precipitate by a reprecipitation from perchloric acid. The only other solvent for barium sulfate to which reference has been found is hot concentrated sulfuric acid. Its use here is obviously not feasible.

The procedure for reprecipitating the barium sulfate was as follows: The first precipitate was obtained from a known volume of the standard solution of sulfuric acid in solutions of calcium chloride and phosphoric acid by the slow addition in drops of 50 ml of a 5-percent solution of barium chloride to the stirred mixture at 50° C. The pH was adjusted with ammonium hydroxide with the aid of a glass electrode to either pH 1 or 2, as designated in table 2. The precipitate was separated by filtration through analytical-grade filter paper and washed with 200 ml of distilled water. Both precipitate and paper were digested with concentrated nitric acid until the paper was decomposed. Perchloric acid was then added, and the mixture boiled in a covered beaker until a clear colorless solution was obtained. Distilled water was added slowly to the warm solution until the volume was approximately 400 ml; 5 ml of a 5-percent solution of barium chloride was added, and the stirred mixture was adjusted to pH 1 with ammonium hydroxide. The precipitate was allowed to stand overnight at room temperature and then filtered through a porcelain filtering

TABLE 2. *Weights of barium sulfate after double precipitation*

pH	Weight of precipitate		
	Found	Theoretical	Difference
	g	*g*	*Percent*
2.0	0.1336	0.1298	+2.93
2.0	.1306	.1298	+0.62
1.0	.1283	.1298	−1.16
1.0	.1348	.1298	+3.85
1.0	.2907	.2790	+4.19
1.0	.2912	.2790	+4.37
1.0	.2923	.2790	+4.77
1.0	.2897	.2790	+3.84
2.0	.3286	.3244	+1.29
2.0	.3328	.3244	+2.59
2.0	.3360	.3244	+3.58
2.0	.3333	.3244	+2.74
1.0	.3384	.3244	+4.31
1.0	.3376	.3244	+4.06
1.0	.3352	.3244	+3.33
2.0	.6478	.6488	−0.15
2.0	.6506	.6488	+.28
2.0	.9873	.9732	+1.44
2.0	1.0000	.9732	+2.75

crucible. It was ignited at 600° C for at least 2 hours.

The results for the double precipitation are shown in table 2. The quantity of standard sulfuric acid was varied over a wide range. An analysis of the results in table 2 was made, disregarding the two values for pH. A measure of precision and also of accuracy was obtained and found to be very satisfactory. A very slight contamination of the barium sulfate precipitate was found equal to about 1 percent.[7]

The better agreement realized on double precipitation could be attributed to either a purging of the barium sulfate of the contaminants or to the closer compensation of the minus errors (for example, the possible loss of barium sulfate in the acid solution because of the additional analyti-

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[5] Throughout this paper, whenever acids are mentioned, perchloric acid will mean the concentrated acid of commerce 70 to 72 percent; hydrochloric acid, the concentrated acid of specific gravity 1.18; nitric acid, the concentrated acid of specific gravity 1.42. Diluted acids will be designated as follows: For example, diluted hydrochloric acid (1+20) will mean 1 volume of the concentrated acid of specific gravity 1.18 diluted with 20 volumes of water. Ammonium hydroxide will mean the concentrated solution of specific gravity 0.90.

[6] Because of the possible explosive nature of perchloric acid mixtures, care must be taken that excess nitric acid be always present before adding perchloric acid.

[7] The authors are indebted to J. Mandel and W. V. Loebenstein for the following analysis of the data in table 2. They have plotted the weight of the precipitate found against the corresponding weight as calculated from the volume and the normality of the standard sulfuric acid. The plot of 19 points appeared to be sufficiently linear to warrant a fit by the method of least squares. The intercept of the resulting line was not significantly different from zero as indicated by a "Student's" *t* value of 1.64. This is smaller than the 2.11 value, corresponding to the 5-percent significance level for 17 degrees of freedom (R. A. Fisher, Statistical Methods for Research Workers). The slope of the fitted line was found to be only slightly different from 1, since the *t* value in this case was 2.14 compared to 2.11. This might indicate a contamination in the second precipitation of the order of 1 percent of the theoretical value. The standard deviation from regression is 0.0062 when expressed in grams of precipitate.

cal step) with the plus errors (the gain due to contamination). In order to test the latter possibility, an additional precipitation of the barium sulfate was made. The procedure for the second reprecipitation was exactly the same as for the first. The results are shown in table 3 where a comparison is made with those for a single and for a double precipitation. The results of a spectro-chemical analysis of the second and third precipitates did not show any appreciable difference in the presence of calcium or any other possible contaminants. This would indicate that the observed smaller plus error obtained in the third precipitation might be attributed to a closer compensation of the plus and minus errors.

TABLE 3. *Triple precipitation of the barium sulfate from known solutions of sulfuric acid containing calcium chloride and phosphoric acid*

| Method | Weight of precipitate | | |
	Found	Theoretical	Difference
	g	*g*	*Percent*
Three precipitations	0.2845	0.2790	+1.97
Do	.2798	.2790	+0.29
Do	.2837	.2790	+1.68

The best procedure for the reprecipitation of barium sulfate from its solution in hot perchloric acid has yet to be established. It is, of course, most desirable to avoid the addition of any reagent that will recontaminate the barium sulfate. A few determinations were made in which the precipitate was dissolved in 15 ml of perchloric acid and reprecipitated by dilution with 600 ml of distilled water only (pH of the resulting mixture, 0.3). The results obtained by this procedure are low, as may be seen in table 4. Since barium sulfate was known to be soluble in strong acids, a few determinations were made in which the diluted mixture from the perchloric acid solution was adjusted to pH 1 with ammonium hydroxide. The very low results so obtained indicate the relatively strong effect of ammonium salts. This may have affected the solubility of the barium sulfate or the ammonium ion may have replaced some barium in the precipitate. The results were also low when only 1 ml of a 5-percent solution of barium chloride was added to the mixture containing ammonium hydroxide at pH 1. However, it was possible to obtain a positive error from the diluted mixture with ammonium hydroxide at pH 1 by the addition of sufficient barium chloride (see table 4). The addition of saturated barium hydroxide solution to the diluted mixture (instead of ammonium hydroxide and barium chloride) was tried in order to raise the pH and to depress the solubility by the common ion effect. Unfortunately, a considerable amount of barium hydroxide was required to decrease the acidity to pH 1 and the corresponding amount of barium ion introduced (50 times that contained in 5 ml of a 5-percent solution of barium chloride) was found to yield a large positive error (see table 4).

It would be of interest to ascertain how much barium hydroxide should be added to the diluted mixture in order to compensate for the negative error caused by the solubility. The addition of the barium ion would depress the solubility by the common ion effect alone. Another mode of attack would be to raise the pH by addition of the base of a large organic group and to furnish the barium ion by the barium salt of an organic acid (for example, barium salicylate). The use of large ions that do not coprecipitate has recently been used for the purpose of preparing a crystallographically pure barium sulfate [8]. The precision so far indicated by the work described appears to be sufficient for the present purposes.

TABLE 4. *Effect of some variations in the conditions employed to reprecipitate barium sulfate from solutions in hot concentrated perchloric acid*

[All first precipitates made in same manner]

| Method | pH | Weight of precipitate | | |
		Found	Theory	Difference
		g	*g*	*Percent*
Dilution with water only	0.3	0.2732	0.2790	−2.08
Do	.3	.2688	.2790	−3.66
Dilution+NH₄OH	1.0	.0904	.1298	−30.4
Do	1.0	.1017	.1298	−21.6
Dilution+NH₄OH+1 ml BaCl₂	1.0	.3069	.3244	−5.39
Do	1.0	.3076	.3244	−5.18
Dilution+NH₄OH+10 ml BaCl₂	1.0	.3384	.3244	+4.31
Do	1.0	.3376	.3244	+4.06
Do	1.0	.3352	.3244	+3.33
Dilution+saturated Ba(OH)₂ (400 ml)	1.0	.2990	.2790	+7.17
Do	1.0	.2994	.2790	+7.31
Do	1.0	.2980	.2790	+6.81
Do	1.0	.2925	.2790	+4.84

III. Total Sulfur Content of Bone Char

In order to obtain the complete solution of a sample of bone char, it is necessary to decompose the insoluble carbonaceous component under conditions that insure no loss of the sulfur. Some of the total sulfur is contained as sulfate-sulfur, some as sulfide-sulfur, and some in combination with the carbonaceous component. Three different methods have been employed in this investigation to prepare a complete solution of the sulfur free of organic matter: (1) complete oxidation with nitric and perchloric acids, (2) the Eschka method, i. e., air oxidation in a muffle furnace of the intimate mixture with sodium carbonate and magnesium oxide, (3) nitric acid treatment in a modified Carius bomb.

1. Complete Oxidation With Nitric and Perchloric Acids

The destruction of organic matter by heating with concentrated nitric and perchloric acids has been incorporated in a number of analytical schemes. A 72.4-percent perchloric acid solution in water boils at 203° C (1 atm). This is approximately 100 deg lower than the temperature reached in a boiling sulfuric acid solution at atmospheric pressure. In these experiments, as well as many others, it has been shown that the oxidation with a mixture of nitric and perchloric acids can be performed without fear of dangerous explosions. The only precaution needed is first to heat the mixture at about 100°C until subsidence indicates the destruction of the more easily decomposable portion of the organic matter.

The detailed procedure for the analysis of a bone char for total sulfur by this method follows. A screen test of samples for analysis indicated that 90 percent passed through a U. S. Standard Sieve 80 and that 60 percent passed through a U. S. Standard Sieve 140. The procedure is divided into the numbered paragraphs for convenience in cross reference when the other methods are described. The following procedure is designated as method 1.

1.1. Five grams of the powdered bone char was placed in a weighing bottle and was dried between 105° to 110° C in an air oven for at least 4 hours. The bottle containing the sample was tightly stoppered upon removal from the oven and cooled in a desiccator. The stoppered bottle was weighed, the contents then transferred to an 800-ml beaker, and the bottle weighed again.

1.2. The sample was wetted with about 10 to 15 ml of distilled water, and 25 ml of nitric acid was added. This mixture was boiled gently for 1½ hours in a covered beaker. Fifteen milliliters of perchloric acid (see footnotes 5 and 6) was added and the beaker heated until all fumes of nitric acid had disappeared and the carbonaceous residue was completely oxidized. During this process the mixture changed from the original black to orange, then to brilliant yellow, and finally to a clear solution with a slightly pinkish tinge.

1.3. The clear solution was cooled and diluted with about 100 ml of distilled water. The small residue (insoluble silica) was removed by filtration through a Whatman No. 40 filter paper or its equivalent. The residue was washed thoroughly with 150 to 200 ml of distilled water, and all filtrates were collected in a 1,500-ml beaker.

1.4. Water was added until the volume of filtrate was 750 to 800 ml. The pH of this solution was adjusted to 1.0 by adding ammonium hydroxide dropwise during mechanical stirring (add hydrochloric acid if the pH is greater than 1.0 at first). A glass electrode and pH meter were used in determining the pH.

1.5. The solution was heated to a temperature of 50° C, and 50 ml of a 5-percent solution of barium chloride was added dropwise, the solution being stirred mechanically during the entire process. The temperature was maintained at 50° C for 4 hours.

1.6. The solution was then filtered through a Whatman No. 42 filter paper or its equivalent and the precipitate washed with distilled water until only a faint test for chloride was obtained with silver nitrate.

1.7. The filter paper containing the barium sulfate precipitate was transferred to an 800-ml beaker, and 25 ml of nitric acid was added. It was heated gently until the paper had decomposed; 15 ml of perchloric acid was added, and the solution was boiled until the nitric acid had been eliminated and the residue had dissolved. The covered beaker at this point became filled with white fumes, and the constant boiling mixture of perchloric acid and water condensed on the wall of the beaker. This state of reflux was continued for at least 15 minutes. The solution was perfectly clear and colorless or slightly yellow.

1.8. The solution was cooled to room temperature and 400 ml of distilled water was added; 5 ml of a 5-percent barium chloride solution was added, and the pH readjusted to 1.0. It was allowed to stand overnight. The mixture was filtered through a porcelain filtering crucible, washed with 100 ml of distilled water, and ignited for about 2 hours at 600° C, then cooled in a desiccator and weighed. The precipitate was weighed as barium sulfate, and the result was expressed as percentage of SO_4.

2. Eschka Method Applied to Bone Char

The Eschka method is commonly used in the determination of sulfur in coal. An intimate mixture of the sample with sodium carbonate and magnesium oxide is heated to convert all the sulfur into water-soluble sulfate. The method

can be readily applied to the determination of sulfur in bone char. There is little danger of losing oxides of sulfur, since the quantity of sulfur expressed as SO_4 contained in the organic matter to be oxidized is usually less than 1 percent of the weight of bone char.

A modification of the Eschka method described by Treadwell and Hall [5] was used. The following procedure is designated as method 2.

2.1. A 5-g sample of powdered bone char was taken. However, the sample in this case was transferred to a 200-ml evaporating dish instead of an 800-ml beaker.

2.2. The sample was mixed thoroughly in the dish with 10 g of magnesium oxide and 5 g of sodium carbonate. A second mixture containing 6 g of magnesium oxide and 3 g of sodium carbonate was sprinkled over the top of the mixture in the dish. The mixture with the sample should be completely covered. The dish was placed in an electric muffle furnace at room temperature, heated slowly to 600° C, and left overnight.

2.3. The sample was removed from the furnace and allowed to cool. The mixture was transferred to a 1,500-ml beaker with distilled water, stirred mechanically, and 100 ml of saturated bromine water added. The mixture was heated to boiling on a hot plate while continuously stirring; 50 to 80 ml of diluted hydrochloric acid (1+1) was added until the solution was acid to litmus, and the hot mixture was stirred for about an hour. Concentrated hydrochloric acid was then added dropwise until the solids dissolved and the solution became clear yellow with only a small insoluble residue of silica remaining. The amount of hydrochloric acid needed to make the solution clear varied from 100 to 200 ml. After the final addition of hydrochloric acid, the solution was kept on the hot plate an additional hour while continuously stirring.

2.4. The solution was allowed to cool and the silica residue filtered according to the procedure used in paragraph 1.3. The analysis of the filtrate was performed exactly as in paragraphs 1.4 through 1.8 of the perchloric-acid method (method 1).

3. Complete Oxidation in a Modified Carius Tube

A Carius combustion tube as modified by Gordon [6] and the technique described by Gordon, Schlecht, and Wichers [7] for the use of sealed tubes in preparing acid solutions of samples for analysis were employed in these analyses. The sealed tube was placed in a protective shell of cold-rolled steel, made by drilling a 1-in. hole into 1 4-in. length of 1¼-in. hexagonal stock and surrounded with solid carbon dioxide to provide a compensating pressure that served to reduce the probability of bursting the tube. It was found possible to oxidize the carbonaceous matter in bone char completely with fuming nitric acid and to reuse the tubes for several analyses.

The following analytical procedure is designated as method 3:

3.1. A 5-g sample of powdered bone char was taken. However, the sample in this case was transferred to a Carius tube [6]. The tube was cooled in liquid air, and 5 ml of fuming nitric acid was added. This was done to freeze the acid in order to delay any reaction. The tube was sealed while it was still immersed in the cooling mixture. The tube was placed in the steel shell and surrounded with 50 g of dry ice and the top screwed on securely. The steel shell was tested for leaks by immersing it in water to note the escape of gas bubbles. It was then placed in a muffle furnace at 215° C, slightly inclined so that the seal of the glass tube was elevated. The tube was left overnight in the furnace.

3.2. The steel shell was cooled to room temperature (about 2 hours) and the carbon dioxide cautiously released by unscrewing the cap. The Carius tube was taken out and the contents frozen by placing it in liquid air.[8] It was opened by heating with a tiny gas flame from a blow torch at the very end of the seal. The material inside the Carius tube usually had a deep blue color that disappeared soon after the tube was opened. The residue in the tube was transferred to an 800-ml beaker with a stream of hydrochloric acid. The analysis was continued exactly as in paragraphs 1.3 through 1.8.

4. Percentage of Total Sulfur

The method of determination for a given service bone char (Y–1) was further tested by making a number of determinations with the addition of known quantities of standard sulfuric acid to the bone char. The determinations were made according to method I in which the total sulfur was oxidized to sulfate-sulfur with a mixture of nitric and perchloric acids. The results are summarized in table 5. The amount of standard sulfuric acid was varied from 5 to 25 ml (0.1112N). With the smallest addition of sulfuric acid, approximately 20 percent of the barium sulfate came from the acid and 80 percent from the char. With the largest addition of sulfuric acid, approximately 60 percent came from the acid and 40 percent from the char. The average value of the total sulfur for the eight determinations was 1.91 percent expressed as SO_4. There is no apparent correlation of the individual results with the total amount of barium sulfate involved in the determination.

In view of the consideration already given to the reprecipitation of the barium sulfate (derived from known solutions of sulfuric acid, calcium chloride, and phosphoric acid) after solution in perchloric

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[8] As a safety precaution, it is recommended that the steel shell be cooled in dry ice and the transfer of the Carious tube to the liquid air be made behind a window of safety glass.

TABLE 5. *Determinations by the nitric-perchloric acid method of the total sulfur in samples of a service bone char (Y–1) with additions of standard sulfuric acid*

Volume of standard H_2SO_4 (0.1112N)	Weights of barium sulfate			Weight of char	Total sulfur in char expressed as SO_4
	Total	From the H_2SO_4[a]	From the char		
ml	*g*	*g*	*g*	*g*	*Percent*
5	0.2901	0.0649	0.2252	4.8465	1.91
10	.3645	.1298	.2347	4.9098	1.96
20	.4883	.2596	.2287	4.8937	1.92
25	.5545	.3244	.2301	4.8797	1.94
5	.2920	.0649	.2271	4.9799	1.88
10	.4447	.1298	.3149	6.9572	1.86
20	.5169	.2596	.2573	5.5377	1.91
25	.5497	.3244	.2253	4.8260	1.92
Avg					1.91

[a] Weights calculated from the normality and quantity of the standard sulfuric acid in column 1.

acid, it is important to study the effect of multiple precipitation employing bone char alone. Accordingly, several determinations were made of the total sulfate after a nitric-perchloric acid oxidation of the char sample in which the barium sulfate was reprecipitated twice. The results are contained in table 6, in which a comparison is made with the results from a single and double precipitation. Included, also, are some determinations in which the initial oxidation of the bone char was effected by the Eschka method already described. It is apparent from table 6, and can be shown by statistical considerations, that a significant difference exists between the average values for single and double precipitations, namely, 1.97 and 1.91 percent, respectively. The average value for the determinations employing triple precipitation is 1.89 percent, which can be shown not to be significantly smaller than 1.91 percent. It appears, therefore, that while a single reprecipitation of the barium sulfate precipitate is justified, there is not much to be gained by another similar operation.

Table 7 contains the results for the determination of total sulfur (expressed as SO_4) in six different service bone chars. The sulfur in each char was completely oxidized to sulfate-sulfur by the three methods already outlined. The results by initial oxidation with nitric acid in a Carius tube (method 3) appear to be higher than the results by methods 1 and 2. This may be due to unknown factors inherent in the methods of analysis

TABLE 6. *Single, double, or triple precipitation of the barium sulfate in the determination of total sulfur in bone char (expressed as SO_4)*

[All determinations were made with a service bone char, Y–1]

Single precipitation	Double precipitation	Triple precipitation
COMPLETE OXIDATION OF THE SAMPLE WITH NITRIC AND PERCHLORIC ACIDS		
Percent	*Percent*	*Percent*
[a] 2.01	1.89	1.89
[a] 1.97	1.90	1.90
1.97	1.91	1.88
1.96	1.92	----
ESCHKA'S METHOD APPLIED TO BONE CHAR		
1.98	1.92	----
1.96	1.92	----
Avg 1.97	1.91	1.89

[a] Standard sulfuric acid added, and the corresponding amount of barium sulfate subtracted from the quantity determined experimentally.

TABLE 7. *Total sulfur (expressed as SO_4) in six service bone chars by three methods*

[Values in italic type are average values]

Char	method 1	method 2	method 3	Average of methods 1, 2, and 3
	Percent	*Percent*	*Percent*	*Percent*
Y–1	*1.91*	*1.92*	*1.96*	1.93
36	*1.98*	1.99	2.04	2.00
P–1	1.01	*0.95*	*1.00*	0.99
P–2	0.80	.81	0.85	.82
R–22	.96	.95	*1.00*	.97
R–23	.97	.94	*1.04*	.98

rather than to loss of sulfur during the oxidation step.

Further discussion of these results will be postponed until presentation of the analyses according to methods 4, 5, and 6.

IV. Sulfur in the Residue and in the Filtrate From Acid Leaching

When bone char is digested with nitric acid, it is well known that the carbonaceous residue takes on a different appearance than when hydrochloric acid alone is used. The treatment with nitric acid leaves a definite brownish residue that has been attributed to organic oxidation reactions. It is also known that the inorganic sulfides or sulfites are completely oxidized to sulfates. It is possible

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also to oxidize sulfides and sulfites to sulfates with a dilute mixture of potassium chlorate and hydrochloric acid. This does not appear to alter the carbonaceous matter to the extent that the nitric acid treatment does. Dilute hydrochloric acid alone may be expected to oxidize the carbonaceous matter to the least extent. The extent to which the above three acid mixtures oxidize the carbonaceous residue in bone char should determine the amount of sulfur that is extracted from the residue, providing, of course, there is appreciable sulfur in the residue. Thus, the sulfate-sulfur contained in the filtrate need not be derived solely from the inorganic salts in bone char.

Three independent analytical procedures will now be described in which the sulfur may be determined in both the residue and the filtrate obtained in acid leachings of bone char.

1. Digestion With Nitric Acid and Hydrochloric Acid

The following procedure will be designated as method 4 for the determination of sulfur in bone char:

4.1. A 10-g sample of finely powdered bone char was taken.

4.2. The sample contained in the 800-ml beaker was wetted with 25 ml of distilled water; 25 ml of concentrated nitric acid was added dropwise and the mixture allowed to evaporate slowly to dryness on the hot plate. It was necessary to remove the mixture from the hot plate immediately after the evaporation was completed so that no carbonaceous matter would be lost by oxidation. Three additional evaporations to dryness were then made using 15 ml of diluted hydrochloric acid $(1+1)$ each time. This was done in order to expel the nitric acid completely. After the third evaporation, 40 ml of diluted hydrochloric acid $(1+1)$ was added and the mixture boiled gently for about 1 hour.

4.3. The mixture was cooled and transferred to a volumetric flask, where it was made up to exactly 250 ml. The mixture was filtered through a No. 40 Whatman filter paper or its equivalent and exactly 200 ml collected in a second volumetric flask. The remaining solution, the residue and filter paper, and the funnel washings were transferred to an 800-ml beaker.

4.4. The filtrate contained in the 200-ml volumetric flask was transferred to a 1,500-ml beaker and this part of the analysis concluded according to paragraphs 1.4 through 1.8.

4.5. Twenty-five milliliters of nitric acid was added to the beaker containing the residue, the paper, and remaining filtrate and heated until the filter paper had disintegrated; 15 ml of perchloric acid was added, and the procedure outlined in paragraphs 1.2 through 1.8 was then followed.

4.6. The percentage total sulfate in the sample was calculated from the sum of the weights of barium sulfate obtained in 4.4 and 4.5. The volume of the residue was estimated from the weight of the residue and a value of 1.8 for the density. The weight of the residue was determined by the acid washing of independent samples. Subtracting the small volume of the residue from 250 ml yielded the total volume of the filtrate. The total sulfur in the filtrate, expressed as SO_4, was the value obtained for 200 ml (paragraph 4.4) multiplied by the ratio of the total volume of filtrate to 200 ml, approximately 1.25. The total sulfur expressed as SO_4 in the residue was calculated by subtracting the value for the filtrate from the value for the total sulfate.

2. Digestion With Potassium Chlorate and Hydrochloric Acid

The following procedure is designated as method 5 for the determination of sulfur in bone char:

5.1. A 10-g sample of finely powdered bone char was taken.

5.2. The sample contained in the 800-ml beaker was wetted with 25 ml of distilled water and 50 ml of a solution of potassium chlorate (10 g of potassium chlorate in a liter of water) was slowly added. The solution was heated to about 80° to 90° C, and 100 ml of diluted hydrochloric acid $(1+1)$ was added dropwise from a buret, while stirring mechanically. The acid must not be added too rapidly lest sulfur escape as hydrogen sulfide. After the addition of all the acid, the mixture was boiled gently in the covered beaker for 1½ hours.

5.3. The analysis was concluded according to paragraphs 4.3 through 4.6.

3. Digestion With Hydrochloric Acid

The following procedure is designated as method 6 for the determination of sulfur in bone char:

6.1. A 10-g sample of finely powdered bone char was taken.

6.2. The sample contained in the 800-ml beaker was wetted with 25 ml of distilled water and 100 ml of diluted hydrochloric acid $(1+1)$ slowly added. The solution was heated in a covered beaker for about 1½ hours at 80° to 90° C.

6.3. The analysis was concluded according to paragraphs 4.3 through 4.6. However, when separating the residue from the 200 ml of filtrate, No. 42 Whatman filter paper, or its equivalent was used.

4. Distribution of the Sulfur Between Residue and Filtrate

The results of a number of analyses by methods 4, 5, and 6 have shown good checks for the *sum* of the sulfur contained in the residue and that contained in the filtrate. The data for the six service bone chars already mentioned are given in table 8. The values for total sulfur contained

TABLE 8. *Distribution of the total sulfur (expressed as SO₄) between the residues and filtrates derived from the acid-leaching of service bone chars*

Char	Average total sulfur	HNO₃ and HCl			KClO₃ and HCl			HCl (alone)			
		Filtrate	Residue	Total	Filtrate	Residue	Total	Filtrate	Residue	Evolved[a] gases	Total
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
Y-1	1.93	1.78	0.13	1.91	1.65	0.22	1.87	0.99	0.68	0.17	1.84
					1.65	.26	1.91	1.09	.58	.17	1.84
36	2.00	1.77	.23	2.00	1.53	.48	2.01	1.41	.35	.13	1.89
P-1	0.99	0.94	.04	0.98	0.98	.05	1.03	0.78	.16	.07	1.01
P-2	.82	.66	.15	.81	.72	.12	0.84	.52	.30	.05	0.87
		.73	.09	.82				.54	.25	.05	.84
R-22	.97	.88	.10	.98	.76	.23	.99	.48	.40	.08	.96
		.86	.06	.92							
R-23	.98	.89	.08	.97	.83	.11	.94	.57	.29	.10	.96
								.54	.33	.10	.97

[a] Determined by combustion of evolved gases in air.

in column 2 are those given in table 7, and these are inserted for comparison. The use of nitric and hydrochloric acids (method 4) resulted in the least value for the sulfur in the residue. It is of interest to note that the sulfur contained either in the residue or in the filtrate was found to vary considerably for individual determinations. When the sulfur was lower in the residue, it was higher in the filtrate; however, as mentioned above, the sum of that in the residue and that in the filtrate was constant.

Without exception the sulfur contained in the residue was greatest when the char was extracted with hydrochloric acid (method 6). There is evidence which points to some oxidation of the sulfur contained in the carbonaceous matter even when this acid alone is used. Samples of the same char (P–2) were digested in diluted hydrochloric acid (1+1) for different periods of time. Three samples after digestion for 1½ hours gave residues in which the result for sulfur (as SO₄) were 0.307, 0.262, and 0.246; two values after 8 hours were 0.234, and 0.222; one value after 50 hours was 0.226. These results indicate that for contact periods up to approximately 8 hours the hot hydrochloric acid is gradually leaching the sulfur from the carbonaceous residue. Because of the loss of volatile sulfur compounds (principally hydrogen sulfide) during the hydrochloric-acid leaching, the sum of the sulfur contained in the residue and in the filtrate does not equal the total sulfur.

V. Analysis of Gases Evolved With HCl

The presence of hydrogen sulfide is readily apparent in the gases evolved from bone char by the action of hydrochloric acid. The hydrogen sulfide has been attributed to the decomposition of inorganic sulfides in the char. Some may possibly result from an acid hydrolysis of an organic-sulfur component in the carbonaceous residue. If the latter possibility exists, there may be other volatile sulfur-containing gases in those evolved with hydrochloric acid.

With this possibility in mind, the gases derived from bone char by evolution with hydrochloric acid were analyzed by two methods. First, the hydrogen sulfide was determined alone; second, the evolved gases were burned in air and a gravimetric determination for barium sulfate made in the products of the reaction.

1. Iodometric Determination of the Hydrogen Sulfide

The sulfide sulfur was separated from the char by evolution with hydrochloric acid in a closed apparatus and by washing the gases in ammoniacal cadmium sulfate solution.[9] A schematic apparatus is illustrated in figure 1. The cadmium sulfide was determined without removal from the gas wash bottle by a subsequent titration with standard iodine in the acidified solution.

[9] The stock solution of ammoniacal cadmium sulfate contained 168 g of cadmium sulfate, 960 ml of concentrated ammonium hydroxide, and 1,046 ml of distilled water.
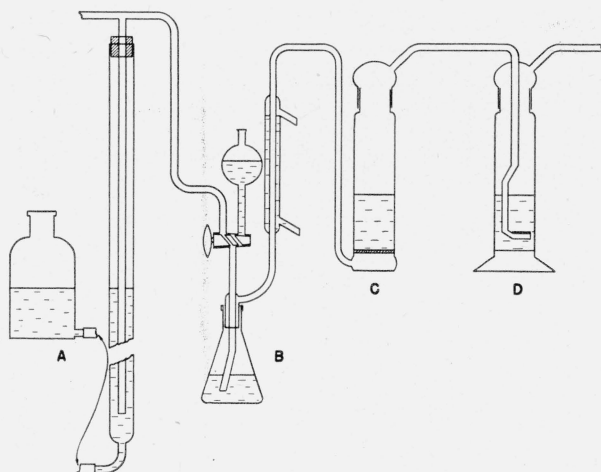
FIGURE 1. *Apparatus for the evolution of hydrogen sulfide.*
A, Pressure regulator for carrier gas; *B,* evolution unit with Erlenmeyer flask equipped with interchangeable ground joint; *C* and *D,* gas-wash bottles with fritted disks charged with solution of ammoniacal cadmium sulfate.

Two gas-wash bottles with fritted disks were used in series and charged with a dilute solution of ammoniacal cadmium sulfate made by diluting 1 ml of the stock solution to 100 ml of water. A 5-g sample of bone char was introduced into the Erlenmeyer flask, the interchangeable joint wetted, and the apparatus assembled. A test for possible leaks was made by application of air pressure. Fifty milliliters of diluted hydrochloric acid (1+1) was slowly added, and, as soon as the reaction slowed down, the system was swept with a flow of compressed air. The flask was heated gently for 20 minutes. The first gas-wash bottle was cooled with ice water. If the first gas-wash bottle alone contained a yellow precipitate of cadmium sulfide, then only this mixture was titrated with iodine. Before titration the mixture was acidified with 25 ml of hydrochloric acid. The heat evolved was usually sufficient to bring the solution to room temperature. The titration with standard iodine solution was made after adding 5 ml of a freshly made starch solution. As the end point was approached the solution appeared yellowish red, orange, purplish red, and finally a deep permanent blue. A blank was run to determine the amount of iodine necessary to color a similar solution containing no sulfide.

A number of results for six service bone chars are given as part of table 9. Considerable fluctuations were observed in repeated runs with aliquot parts of the same sample. A possible expla-

nation will be given after the presentation of the second method for determining sulfur in the evolved gases. A number of measurements of the hydrogen sulfide liberated from steel (National Bureau of Standards Samples 9d and 8g) were made. The average of 10 determinations for samples of 9d was 0.036 percent of sulfur as compared with the standard value of 0.036 percent of sulfur. The average of five determinations of 8 g was 0.024 percent of sulfur as compared with the standard value of 0.026 percent of sulfur.

The results of table 9 indicate a possible oxidation of the sulfur gases with the carrier gas used to sweep out the apparatus. It appears that the results are higher when the carrier gas contains oxygen. However, the differences may also be due to variable action of the hydrochloric acid on the carbonaceous component of the bone char.

TABLE 9. *Determination of sulfur (expressed as SO_4) in the gases evolved from bone char by treatment with hydrochloric acid*

Sample	Iodometric determination of the hydrogen sulfide displaced with carrier gas noted		Gravimetric determination after combustion in air in a quartz furnace
	Percent		*Percent*
	0.135	Air	0.176
	.118	Commercial N_2	.151
Y-1	.105	do	.160
	.108	do	.217
	.117	do	.163
	[a] .148	N_2 and O_2	.174
			.151
			Avg 0.170
	.102	Commercial N_2	
36	.103	do	0.104
	.131	do	.132
	[a] .126	N_2 and O_2	
P-1	.028	Air	
	.040	Commercial N_2	.072
	[a] .035	N_2 and O_2	
P-2	.031	Commercial N_2	.046
	[a] .036	N_2 and O_2	
R-22	.046	Commercial N_2	.077
	[a] .071	N_2 and O_2	
R-23	.047	Commercial N_2	
	.062	Air	.095
	[a] .057	N_2 and O_2	

[a] Independent values by R. M. Thompson.

2. Gravimetric Determination of the Evolved Sulfur by Combustion in Air

In this determination the gaseous products of evolution were directed by a stream of air to pass through a quartz tube, 1-cm inside diameter and 10 cm long, in which pieces of solid quartz rod were packed snugly. The quartz tube covered with wire gauze was heated to about 800° C with two Meker gas burners for at least 15 minutes before the reaction was allowed to take place in the evolution flask. While the quartz tube was heating, the system including two gas-wash bottles containing a 5-percent solution of sodium hydroxide was swept with air.

An attempt was made to get a very slow evolution of gases by the following procedure for the addition of the hydrochloric acid: (a) The sample was wetted with a few milliliters of distilled water, (b) ten 1-ml portions of diluted hydrochloric acid (1+20) were added during a period of about 20 minutes, (c) ten 2 ml portions of diluted hydrochloric acid (1+20) were added in about 20 minutes, (d) 20 ml of concentrated hydrochloric acid was added in one portion. Finally, the flow of air was increased, and the contents of the flash was boiled gently for 40 minutes. During this process the quartz tube was continually heated with two Meker burners.

At the conclusion of the experiment the quartz tube was allowed to cool. All the connecting Pyrex tubing was washed with 200 ml of distilled water into the first gas-wash bottle. The contents of both gas-wash bottles were transferred to a 2-liter beaker; 100 ml of saturated bromine water was added to oxidize any sulfites to sulfates and concentrated hydrochloric acid added until the solution turned a definite orange. The solution was boiled until colorless, cooled, adjusted to pH 1, and a single precipitation of barium sulfate made.

The results for the six service chars are contained in the last column of table 9. Although definite fluctuations were observed in repeated determinations with aliquot parts of the same sample, the sulfate values so determined are greater than those corresponding to simple evolution of hydrogen sulfide. In one case, sample 36, the two values are the same.

A reasonable explanation of the fluctuations, apart from inherent inaccuracies in the determi-

nations, is the variable action of the hydrochloric acid on the carbonaceous residue of the char. It would be very difficult to control the extent of the acid hydrolysis of the organic-sulfur component in the residue. It is important, therefore, in the analysis of a bone char by method 6, to determine first the sulfur in the evolved gases, and to use the mixture remaining in the flask to determine the sulfur in the residue and the filtrate. Unfortunately, the values in table 8 were obtained by method 6 with two samples of char, one for the evolution experiment and the other for the distribution of sulfur between residue and filtrate.

Three service chars, however, were analyzed by method 6 with the precaution of using but one sample for analysis. The results for these chars are given in table 10. A satisfactory agreement was obtained between the total sulfate deduced from method 1 (column 2) and the total sulfate derived as the sum of that in the residue, in the filtrate, and in the gases evolved with hydrochloric acid. Independent data for these three samples are available for the sulfate content of the filtrate after hydrochloric acid treatment. These were furnished through the courtesy of H. I. Knowles, chief chemist, Atlantic Sugar Refineries, Ltd., Saint John, N. B., Canada.

TABLE 10. *Determination of sulfur (expressed as SO$_4$) in service bone chars*

Char	Total sulfur (perchloric acid method)	Digestion of sample with HCl				
		Filtrate	Residue	Evolved gases	Total	Filtrate only [a]
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
A	1.07	0.70	0.32	0.049	1.07	0.60
B	1.48	1.00	.45	.051	1.50	.99
C	1.53	1.13	.34	.056	1.53	1.10

[a] Samples and the results in this column were furnished through the courtesy of H. I. Knowles, chief chemist, Atlantic Sugar Refineries, Ltd.

VI. Discussion of Results

The results of analysis of the several bone chars for sulfur show clearly the errors in the existing methods used by sugar refining laboratories. The major error is in the value for so-called calcium sulfide, which is based on a fallacy contained in its definition. The sulfur reported as calcium sulfide is in reality that contained in the sulfides liberated by evolution with hydrochloric acid and a part of the combined organic sulfur in the carbonaceous residue. Other errors are due to the variable

amount of organic sulfur removed from the carbonaceous residue that depends on the oxidation media employed in the analysis.

It is recommended that for practical purposes the sulfur contained in bone char be defined as follows:

Total sulfur.—This value may be determined from either methods 1, 2, or 3. Method 1 is preferred for its convenience.

Inorganic sulfate-sulfur.—The nearest value to this quantity is the sulfate found in the filtrate of a dilute hydrochloric acid treatment of the bone char, method 6.

Sulfide-sulfur.—This value may be obtained from a determination of the hydrogen sulfide evolved by treatment of the char with hydrochloric acid, see section V, 1.

Combined organic sulfur.—The sulfur in the carbonaceous residue may be determined by either of two alternative procedures: the residue obtained after digestion with dilute hydrochloric acid may be so analyzed (method 6); or, the *total sulfur* may be obtained (method 1) and the sum of the *inorganic sulfate-sulfur* and the *sulfide-sulfur* subtracted.

Any proposed definition of the sulfur content of bone char must take into account the rather complex chemical composition. Research purposes, of course, require the best available methods of analysis, and the data obtained thereby may not fit into the three simple categories defined above. For practical considerations of sugar technology work, however, it may suffice to know the sulfur content of bone char with a precision and accuracy sufficient to warrant the proposed definitions.

Interesting changes take place in the sulfur content of bone char during cane-sugar refining operations, and the contrast in the percentage of sulfur of service bone char with that of new bone char should be briefly mentioned. The order of magnitude of the total sulfur expressed as SO_4 in new bone char is 0.15 percent as compared with a maximum of 1 to 2 percent in service char. This would indicate that an important source of the sulfur during char operations in sugar refining is the adsorbed impurities removed from the sugar liquors.

Some of the adsorbed impurities contain protein matter composed in part of sulfur-bearing amino acids. The sulfur could be retained by the carbonaceous residue formed in the reactions that occur in the char kiln. It is also possible that some sulfate-sulfur may be introduced if phosphate defecation was used in the refining operations. Even good technical phosphoric acid may contain approximately 0.3 to 0.5 percent of sulfate. If manufactured by the wet method (sulfuric acid and phosphate rock), it may contain more sulfate than if manufactured by the furnace method (oxidation of phosphorus). The latter product may be preferred for sugar refining. The two mentioned sources of sulfur are independent of the type of kiln used to revivify the char.

VII. References

[1] G. L. Spencer and G. P. Meade, Cane sugar handbook, p. 348, 8th ed. (John Wiley & Sons, Inc., New York, N. Y., 1945).

[2] John Henry Tucker, A manual of sugar analysis, p. 320–322, 1st ed. (D. Van Nostrand Co., Inc., New York, N. Y., 1881).

[3] W. F. Hillebrand and G. E. F. Lundell, Applied inorganic analysis, p. 575–579 (John Wiley & Sons, Inc., New York, N. Y., 1929).

[4] I. M. Kolthoff and E. B. Sandell, Textbook of quantitative inorganic analysis, revised ed., chap. 20, Determination of sulfur as barium sulfate, p. 329–344 (The Macmillian Co., New York, N. Y., 1943).

[5] F. P. Treadwell and W. T. Hall, Analytical chemistry **2**, 322, 6th ed. (John Wiley & Sons, Inc., New York, N. Y., 1924).

[6] C. L. Gordon, J. Research NBS **30**, 107 (1943) RP1521.

[7] C. L. Gordon, W. G. Schlecht, and E. Wichers, J. Research NBS **33**, 457 (1944) RP1622.

[8] G. Walton and G. H. Walden, Jr., J. Am. Chem. Soc. **68**, 1742 (1946).

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