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## DETERMINATION OF SULPHUR AND SULPHATE IN WOOL

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## ABSTRACT

Methods of known precision and accuracy for the quantitative determination of total sulphur and sulphate sulphur in wool are given in this paper and the experimental bases for them are described.

Sulphur is present in wool as an essential constituent of the wool substance, presumably in one constituent of the molecule, the amino acid, cystine. The amount varies with the type and quality of the wool and with the severity of processing. Thus cystine sulphur is of considerable practical significance. Sulphate sulphur is formed in wool through the action of light and other agencies on this sulphur and is acquired by wool from solutions used in carbonizing, dyeing, or finishing. Therefore it is necessary to distinguish between the cystine sulphur of the wool and sulphate sulphur.

The total sulphur in wool is determined by completely oxidizing a specimen in an oxygen bomb, absorbing the oxidized sulphur in ammonium carbonate solution, precipitating and weighing it as barium sulphate. The sulphate sulphur is determined by dissolving a specimen of the wool in hydrochloric acid, precipitating and weighing the sulphate as before. Under the conditions recommended, the dissolved wool does not interfere and the cystine sulphur is not precipitated.

The results reported indicate that with these methods either form of sulphur can be determined to within 2 percent of the amount present.

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## I. INTRODUCTION

Wool protein contains from 3 to 4 percent of sulphur, all of it presumably in one constituent of the molecule, the amino acid, cystine. The amount of this sulphur has been found to vary with the type and quality of the wool. Some of the sulphur is oxidized when wool is damaged by the action of light, sulphuric acid being the end product. Wool is also liable to damage in wet processing with a loss of some of its cystine sulphur. Thus the amount of sulphur in wool has come to be regarded as of considerable practical significance.<sup>1</sup>

Wool may absorb sulphurous and sulphuric acid from air and from solutions used in carbonizing, dyeing, or finishing. The sulphurous acid is readily oxidized to sulphuric acid. The sulphate ion is held tenaciously and cannot be removed completely by extraction with

<sup>1</sup> S. G. Barker. Wool Quality, p. 209 to 223 and literature cited on p. 284 to 328 (1931), His Majesty's Stationery Office, London.

water or even with dilute bases without seriously damaging the wool.<sup>2</sup> Therefore, it is often necessary to distinguish between the cystine sulphur of the wool and the sulphate sulphur formed from it or acquired from other sources.

Methods of known precision and accuracy for the determination of total sulphur and sulphate in wool, which are rapid and convenient, were needed in work on the analysis of wool-cotton textiles and on the system wool—sulphuric-acid—water.<sup>3</sup> A number of methods for the determination of the sulphur content of other organic materials have been considered. Most of them require several hours for the destruction of organic material and preparation of the oxidized sulphur for precipitation as barium sulphate. Many require the addition of nonvolatile salts which lower the rate of precipitation of barium sulphate and introduce errors by contaminating the precipitate or which necessitate reprecipitation.

This paper describes the methods for total sulphur and sulphate sulphur which have been found to be satisfactory for the analysis of wool and gives experimental results which indicate the precision and accuracy to be expected.

## II. PREPARATION OF WOOL FOR ANALYSIS

The wool for the experiments was chosen from a lot which had been put through a commercial scouring process but had not been carbonized. The remaining visible foreign material was removed by hand and the wool agitated for  $\frac{1}{2}$  hour in a 1-percent solution of a neutral soap at 70° C. It was rinsed with distilled water at the same temperature, extracted with alcohol for 16 hours in a Soxhlet extraction apparatus and then with ether for 6 hours. It was air dried, rinsed with distilled water at 70° C, and again dried and conditioned at 70° F and 65-percent relative humidity. The fibers were cut into short lengths and mixed thoroughly.

Sulphate sulphur was introduced into some of this wool by immersing it for 20 minutes in sulphuric acid of about 72-percent concentration, at room temperature. The wool was then extracted with water in an apparatus operating similarly to a Soxhlet extraction apparatus but with the wool at room temperature at all times. The extraction was continuous for 15 hours or more with a total of about 15 liters of distilled water.

The treated wool was air dried and conditioned as before. Wool fibers thus treated lose a portion of their substance, as evidenced by a coloration of the acid solution, and retain sulphur as sulphate which is not removable by extraction with water without serious decomposition of the fiber.

## III. ANALYSIS OF WOOL FOR TOTAL SULPHUR

Two methods of analysis for total sulphur in wool received special attention. The well-known Carius method<sup>4</sup> and the oxygen bomb method.<sup>5</sup> The Carius method is generally recognized to be reliable

<sup>2</sup> R. T. Mease and D. A. Jessup. *Analysis of wool-cotton textiles*. BS J. Research 9,669(1932)RP498.

<sup>3</sup> M. Harris. *The carbonization process: A study of the system wool—sulphuric-acid—water*. BS J. Research 12,475(1934)RP673.

<sup>4</sup> Ludwig Gattermann, *Practical Methods of Organic Chemistry*, 3d American ed. translated from 11th German ed. by William B. Schober and S. Vahan, 390 pp.(1916). The Macmillan Co., New York.

<sup>5</sup> F. Garelli and B. Saladini. *The determination of sulphur in organic compounds with an oxygen bomb*. Atti accad. sci. Torino (classe sci. fis.) Mat., Nat. 66,163(1931).

for the determination of sulphur in organic compounds, and Barritt and King found it to be the best of several methods for the determination of sulphur in wool.<sup>6</sup>

The specimen to be analyzed by the Carius method is heated in a sealed glass tube with fuming nitric acid to destroy organic matter and to oxidize the sulphur. The nitric acid remaining after the action is complete is removed by evaporation and the sulphur is precipitated and weighed as barium sulphate. In order to obtain accurate results the nitric acid must be removed completely. Sulphur may be lost during the evaporation of the nitric acid through creeping of the solution up the sides of the evaporating dish and through the reducing action of particles of dust which may fall into the dish. The addition of sodium carbonate solution in excess of the amount estimated to be necessary to combine with the sulphur was found to prevent losses.

Although the Carius method is reliable and is free from errors caused by the presence of nonvolatile salts, it has the disadvantages of requiring a small specimen, unusual skill in sealing, heating, and handling the tubes, and a long time for completion of an analysis. The oxygen bomb method offered advantages in these respects.

The oxygen bomb method has been used with success by Garelli and Saladini for the analysis of a variety of organic compounds<sup>7</sup> and by McPherson and Cummings for the accurate determination of sulphur in rubber-sulphur compounds.<sup>8</sup> The specimen to be analyzed is ignited in an atmosphere of oxygen under pressure, the sulphur absorbed in a solution of ammonium carbonate, precipitated, and weighed as barium sulphate.<sup>9</sup>

The oxygen bomb used in this work is of an all-metal type. The combustion chamber has a diameter of approximately 6.5 cm and a depth of 11.5 cm. Too great a pressure of oxygen results in a spattering of partially-decomposed wool on the sides of the chamber where ignition is incomplete. Pressures of 150 to 180 lb/in.<sup>2</sup>, were found to produce satisfactory combustion, provided the wool fibers were tightly packed in a small filter paper capsule, and so placed that on ignition the heat of combustion was not too rapidly dissipated by metal parts touching the paper container.

Table 1 gives the results of analyses for the sulphur content of the scoured and extracted wool.

The results for the two methods are in good agreement and indicate that the accuracy and precision are nearly the same for both methods.

#### IV. PROPOSED METHOD FOR TOTAL SULPHUR IN WOOL

Detailed instructions follow for the determination of the total sulphur content of wool in the absence of substances forming sulphates insoluble in dilute hydrochloride acid.

<sup>6</sup> Mease and Jessup, Analysis of wool-cotton textiles BS J. Research 9,669(1932)RP498.

<sup>7</sup> F. Garelli, and B. Saladini. *The determination of sulphur in organic compounds with an oxygen bomb.* Atti acad. sci. Torino (classe sci. fis.) Mat., Nat. 66,163(1931).

<sup>8</sup> Unpublished results obtained at the National Bureau of Standards.

<sup>9</sup> It is probable that the direct titration method described by W. C. Schneider could be applied here for the determination of sulphate. See Ind. Eng. Chem., anal. ed., 5,403-6(1933).

TABLE 1.—*Comparison of results obtained by Carius and oxygen-bomb methods for total sulphur in the prepared wool*

Percent sulphur	
Carius method	Oxygen-bomb method
2.95±.09	3.00±.03
2.98	3.04
3.05	3.05
3.06	3.07
3.08	3.08
3.09	3.09
3.10	3.09
3.11	3.13
Average....3.05±.03	Average....3.07±.01

Weigh accurately about 0.5 g of the dry or conditioned wool to be tested. Wrap the specimen compactly in a piece of filter paper, or in a filter-paper capsule if the specimen is in the form of loose, unspun fibers, and bind it with pure silk. Place the specimen on a rectangular piece of filter paper larger enough so that when laid on the concave side of a platinum crucible cover the four corners will rest on the rim and support the remainder of the paper free of any metal. Avoid the use of too much paper for it consumes oxygen which may be needed for complete combustion of the wool. Place the platinum cover thus loaded on the ignition platform of a calorimeter bomb. Attach the fusible ignition wire to the electric leads with which the bomb is equipped and have it touch the center of the top of the paper specimen container. Place about 50 ml of a 2-percent aqueous solution of ammonium carbonate in the bomb, fasten the cover securely in place and introduce sufficient oxygen into the bomb to produce a pressure of 150 to 180 lb/in<sup>2</sup>. Care must be taken not to permit wetting of the paper and specimen.

Ignite the specimen and permit the bomb to stand, with occasional shaking, for 10 minutes to permit all of the sulphur to be absorbed by the ammonium carbonate solution. Open the bomb and filter the solution to remove globules of the fused ignition wire and collect the filtrate in a 300 ml beaker. Acidify the solution with concentrated hydrochloric acid (sp gr 1.18) using about 2 ml in excess, dilute to a volume of 250 ml, heat on the steam bath and add 10 ml of a 5-percent solution of barium chloride (prepared by dissolving 50 g of BaCl<sub>2</sub>·2H<sub>2</sub>O in 1 liter of distilled water containing about 3 drops of concentrated hydrochloric acid). Allow the solution to stand, preferably overnight, until the precipitate has settled. Collect the barium sulphate by filtration through paper or other suitable filtering medium. Wash the paper and precipitate with small portions of hot distilled water until the wash water gives no test for chlorides. Transfer the precipitate and filter paper to a weighed crucible and ignite in an electric muffle or other suitable furnace, at such a rate that from 1½ to 2 hours are required to heat the crucible from room temperature to redness. Cool the precipitate in a desiccator and weigh. Then:

$100 \frac{.1314w}{W}$  is the percentage of sulphur in the specimen where  $w$  is the weight of the barium sulphate found and  $W$  the weight of the dried or conditioned specimen.

## V. ANALYSIS OF WOOL FOR SULPHATE

Two convenient methods for the destruction of wool fiber without oxidation of cystine sulphur but with liberation of the sulphate sulphur preparatory to its quantitative determination seemed applicable: (1) Digestion with aqueous potassium hydroxide solution, and (2) digestion with concentrated hydrochloric acid. The first had been used by the author<sup>10</sup> for the purpose of sulphate determination in wool but without a critical study of its probable precision or accuracy.

Analyses of solutions of known composition were made as a basis for determining the accuracy to be expected in the determination of sulphate by these methods. A solution of known sulphur content was prepared by dissolving an accurately weighed amount of pure dry sodium sulphate in a measured volume of water. Aliquot parts were acidified and the sulphate was precipitated and determined in the usual way. The results obtained are given in table 2, experiments 1 to 5, inclusive. They serve to indicate the degree of accuracy to be expected in the absence of complicating substances. On of these is the acid which is present when the wool substance is digested in hydrochloric acid. Experiments 6 to 10 were the same as 1 to 5, except that the precipitation of barium chloride was made in the presence of the amount of hydrochloric acid necessary to dissolve wool and free the adsorbed sulphate when present. The values obtained are in reasonably good agreement with those of experiments 1 to 5. If the wool specimen were digested in potassium hydroxide solution, the potassium chloride formed when the solution is acidified would be a complicating factor. Potassium hydroxide of amount and concentration convenient to dissolve wool was added to the solutions for experiments 11 to 15 of table 2. With one exception, these results are in good agreement with those of experiments 1 to 5.

TABLE 2.—Effect of condition of precipitating medium on SO<sub>4</sub> determination in sodium sulphate

Experiment no.	Condition of precipitating solution	Wool present	SO <sub>4</sub>	
			Present	Found
1.....	Acidified with 0.2 ml 35 percent hydrochloric acid.....	g		
2.....		None	0.0847	0.0844
3.....		None	.0847	.0844
4.....		None	.0847	.0843
5.....		None	.0847	.0842
6.....	Same as experiments 1 to 5, but acidified with 20 ml 30-percent hydrochloric acid.	None	.000	.0001
7.....		None	.0847	.0847
8.....		None	.0847	.0846
9.....		None	.0847	.0840
10.....		None	.0847	.0845
11.....	Contained 100 ml of 3½-percent potassium hydroxide and acidified with HCl with 2 ml excess.	None	.000	.0001
12.....		None	.0847	.0842
13.....		None	.0847	.0846
14.....		None	.0847	.0859
15.....		None	.0847	.0841
16.....	Same as 11 to 15, but contained decomposition products of wool..	None	.000	.0001
17.....		1.00	.0847	.0846
18.....		1.00	.0847	.0868
19.....		1.00	.0847	.0856
20.....		1.00	.0847	.0865
21.....	Same as 16 to 19, but contained no added sulphate.....	1.00	.000	.0015
22.....		1.00	.000	.0029
23.....		1.00	.000	.0013
24.....		1.00	.000	.0018
25.....		1.00	.000	.0019

<sup>10</sup> R. T. Mease and D. A. Jessup. *Analysis of wool-cotton textiles*. BS J. Research 9,669(1932)RP498.

TABLE 2.—*Effect of condition of precipitating medium on SO<sub>4</sub> determination in sodium sulphate—Continued*

Experiment no.	Condition of precipitating solution	Wool present	SO <sub>4</sub>	
			Present	Found
26.....	Same as 6 to 10, but contained decomposition products of wool.....	0		
27.....		1.00	0.0847	0.0847
28.....		1.00	.0847	.0841
29.....		1.00	.0847	.0842
30.....		1.00	.0847	.0852
31.....	Same as 26 to 29, but contained no added sulphate.....	1.00	.000	.0001
32.....		1.00	.000	.0003
33.....		1.00	.000	.0001
34.....		1.00	.000	.0001
34.....		1.00	.000	.0001

These experiments indicate that either potassium hydroxide or hydrochloric acid may be used to dissolve the wool. However, when an alkali solution of wool is acidified preparatory to precipitation of sulphur, the organic matter present becomes colloidal. It is difficult to remove, slows filtration, and interferes with the washing of the precipitate. This may result in a loss of some of the sulphur or contamination of the precipitate by salts held by the organic matter. The predominance of the latter factor is indicated by the results of experiments 16 to 19, and a comparison of the result obtained for experiment 15 with those for 20 to 25 of table 2.

A solution of wool in hydrochloric acid is nearly clear and gives no difficulty in filtration. That it is also to be preferred for accuracy is concluded from a comparison of the results of experiments 26 to 29, and 16 to 19, also experiments 20 to 25, and 30 to 34 of table 2. The last group mentioned also shows that the cystine sulphur of wool is not precipitated with barium chloride when hydrochloric acid is used for digesting the wool for sulphate-sulphur determination.

The results given in table 3 were obtained by analyzing the sulphuric-acid-treated wool described in section II using potassium hydroxide for one group of results and hydrochloric acid for the other to dissolve the wool.

TABLE 3.—*Comparison of results obtained using the potassium-hydroxide and hydrochloric-acid methods for determining SO<sub>4</sub> in wool*

[The sulphuric-acid-treated wool described in sec. II was analyzed]

Percentage of SO <sub>4</sub>	
Potassium hydroxide	Hydrochloric acid
7.76±.13	7.69±.05
7.92	7.84
8.09	7.83
8.26	7.86
Average...8.00±.07	Average...7.81±.03

## VI. PROPOSED METHOD FOR THE DETERMINATION OF SULPHATE IN WOOL

Detailed instructions follow for the determination of the sulphate sulphur in wool in the absence of substances forming sulphates insoluble in hydrochloric acid.

Accurately weigh 1 to 1.5 g of the conditioned or dried wool to be tested and place it in a pyrex-glass test tube about 19 cm long and 75 ml capacity. Add 20 ml of a 30-percent (by weight of HCl) solution of hydrochloric acid and heat in a water bath at 95 to 100° C with occasional agitation until the wool is dissolved. Twenty to thirty minutes is usually sufficient. Cool the solution, dilute with about an equal volume of distilled water, and filter, collecting the filtrate in a 300 ml beaker. Dilute the solution to a volume of 250 ml heat on the steam bath, and add 10 ml of a 5-percent solution of barium chloride. Filter, ignite, and weigh the barium sulphate as described in section

IV. Then the percentage of sulphate in the specimen is  $100 \frac{0.4115 w}{W}$  where  $w$  is the weight of barium sulphate found and  $W$  is the weight of the dried or conditioned specimen.

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