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THE ESTIMATION OF SULFATES IN A CONCENTRATED ELECTROLYTE AND THE DETERMINATION OF SULFUR IN FOODS.

BY VERNON K. KRIEBLE AND AUTREY W. MANGUM.

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While one of us[1] was engaged in a study of general metabolism in the department of physiological chemistry at the Jefferson Medical College, great difficulty was experienced in the determination of sulfur by the sodium peroxide method in the composite sample of food used. Many of the samples either exploded or caught fire during the oxidation. Our greatest difficulty, however, was due to the fact that we could not get complete precipitation of the barium sulfate. Out of 9 experiments, 7 gave an additional precipitate in the filtrate when it became diluted with wash water, in spite of the fact that the solutions had stood 48 hours after the barium chloride had been added. When the second precipitates were added to the first the totals showed such a wide divergence that it was impossible to tell whether the sulfur balance was positive or negative. It was consequently decided at the suggestion of Professor Hawk to study the problem a little more thoroughly. The present investigation was, therefore, directed to a study of the oxidation of foods by sodium

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[1] V. K. Krieble and O. Bergeim, in press.

peroxide and the precipitation of sulfates as barium sulfate in solutions containing large amounts of sodium chloride.

The first objective was soon reached in a very satisfactory manner by mixing a suitable quantity of sodium carbonate with the second addition of sodium peroxide in the fusion and subsequently heating just one side of the nickel crucible in order to start the oxidation locally and keep the rest of the mixture in the crucible relatively cool.

The second problem is not an easy one, for it involves the precipitation of barium sulfate in the presence of electrolytes. Many papers have been published on this subject and the general conclusion seems to be that no direct method is satisfactory. This seems especially clear from the recent work of Johnston and Allen,[1] Johnson and Adams,[2] and of Blumenthal and Gurnsey.[3] Johnston and Adams showed that barium sulfate precipitated in a solution containing a large amount of electrolyte had a relatively large amount of foreign substance occluded in the precipitate, and consequently estimation as barium sulfate in such a medium did not give accurate results. They showed, further, that this occlusion was much less if the barium sulfate was precipitated in a solution of high acid concentration. Under such conditions, a certain amount of barium sulfate remained in solution so that the solubility had to be taken into consideration. They got, however, a granular precipitate and very concordant results in fairly strong hydrochloric acid solutions so that a correction could be applied and accurate results obtained. We therefore tried to apply this method to solutions high in sodium chloride such as are obtained in a sodium peroxide fusion.

EXPERIMENTAL.

Materials, Apparatus and Technique.

All the samples of solutions for analysis were measured in either a 10 cc. or a 50 cc. pipet. The same two pipets were used in all the determinations. Either "non-sol" or Jena glass beakers were used. Distilled water was used, which did not give a test for sulfates. Mallinckrodt's C. P. sodium chloride was found to be free from sulfates. When not otherwise stated, precipitation was made with 10 cc. of 10% barium chloride solution without stirring during the addition of the precipitant. The barium chloride was added by means of a calcium chloride drying tube, with a small opening at the bottom which would allow the solution to drop at the rate of about 10 cc. in 4 minutes. If not otherwise stated, the precipitates were washed with 300 cc. of hot water. During ignitions a platinum lid was placed under the Gooch crucible and another one over

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[1] J. Johnston, and E. T. Allen, THIS JOURNAL, 32, 588 (1910).

[2] J. Johnston and L. H. Adams, *Ibid.*, 33, 829 (1911).

[3] P. L. Blumenthal and S. C. Guernsey, *Res. Bull.*, 26, Agr. Exp. Sta., Iowa State Coll., 1905.

it. All weighings were made with the Gooch crucible in a glass-stoppered weighing bottle, counterbalanced by another one of about the same size and shape. The results in the tables are all expressed in milligrams.

We used a solution of potassium sulfate as our standard sulfate solution. We had two specimens of the salt, one manufactured by Schuchardt and the other by Baker & Adamson. Both were recrystallized several times from water and then thoroughly dried in a hot air oven at 250°. Two solutions were made up and equal amounts analyzed for sulfates, under identical conditions, with the following results:

$BaSO_4$. Mg.

Schuchardt's: 248.1, 248.0, 248.0, 248.3, 248.2, 248.1.

Baker and Adamson: 248.6, 248.7, 247.0.

As the two samples agreed we assumed that both were pure.

The asbestos for the Gooch crucibles was prepared in a manner similar to that recommended by Folin.[1] It was placed in a suction flask with equal quantities of water and concentrated hydrochloric acid. Air was drawn through it for several hours. The asbestos was then removed, washed with water and the process repeated. After again washing thoroughly with water the asbestos was placed in the crucibles a little at a time and well packed with a glass rod after each addition. A thickness of about $^1/_6$ of an inch was used.

We first tried the precipitation of sulfates as barium sulfate in the presence of large amounts of hydrochloric acid without any sodium chloride present. 50 cc. of our potassium sulfate solution, equivalent to 251 mg. of barium sulfate, was diluted to 350 cc. with water and 50 cc. of conc. hydrochloric acid. Precipitation was made near the boiling point with 10 cc. of 10% barium chloride solution. The solutions stood 48 hours before filtering.

Table I.

Precipitation of Barium Sulfate in the Presence of 50 Cc. of Conc. Hydrochloric Acid without Sodium Chloride.

Wt. in mg., 249.5, 250.8, 249.8, 250.2, 250.0, 250.8, 250.1, 250.5, 250.0, 250.4, Average, 250.4.

This table confirms the view of Johnston and Adams that it is possible to get very concordant results in the presence of high acid concentration. We also found that the precipitate was very granular and easy to manipulate. It is interesting to note that the errors caused by occlusion of potassium sulfate and the solubility of barium sulfate balance each other so that theoretical results are obtained.

The experiments recorded in Table II were carried out in the same way except that 50 g. of pure sodium chloride was added to the solution before the volume was brought up to 350 cc. In Cols. 1 and 2 only 10 cc.

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[1] *J. Biol. Chem.*, 1, 147 (1905).

of the potassium sulfate solution was used, which is equivalent to 50.2 mg. of barium sulfate.

TABLE II.

Precipitation of Barium Sulfate in the Presence of 50 g. of Sodium Chloride in 350 cc. of the Solution.

10 cc. of potassium sulfate solution.		50 cc. of potassium sulfate solution.
2 cc. of conc. HCl. Mg	10 cc. of conc. HCl. Mg.	50 cc. of conc. HCl. Mg.
52.6	51.6	248.0
51.7	50.5	248.3
53.3	..	248.2
52.2	..	248.7
53.5	..	248.1
..	..	248.0
..	..	248.1
Average, 52.7	51.1	248.2

This table shows several important facts. First, it confirms the results of former investigators that in the presence of 2 cc. of conc. hydrochloric acid. which is the usual procedure, the weights obtained are invariably too high. Second, it seems to show that very constant results can be obtained even in a very high concentration of sodium chloride. These results were gratifying, as from them it appeared that our chief difficulty had been solved.

We next investigated the solubility of barium sulfate in the filtrate; the occlusion of sodium and potassium sulfate and the occlusion of chlorides in the barium sulfate. We used the method given by Johnston and Allen[1] for determining the solubility of barium sulfate. The results were as follows:

TABLE III.

Solubility of Barium Sulfate in 350 cc. containing 50 cc. of Conc. Hydrochloric Acid.

Without sodium chloride. Mg.	With 50 g. of sodium chloride. Mg.
6.5	6.9
6.0	5.1
5.3	...
6.3	...
6.4	...
6.1	...
Average, 6.1	Average, 6.0

We agree with Johnston and Allen that the solubility of barium sulfate is not appreciably affected by the presence of sodium chloride. Our results are very much lower than their results as they give about 30 mg. for the same volume, but this discrepancy is no doubt explained by the fact that we used a greater excess of barium chloride which would necessarily decrease the solubility of barium sulfate.

The determination of the occlusion of sodium and potassium sulfate in the barium sulfate was also done by a method suggested by Johnston

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[1] *Loc. cit.*

and Allen.[1] The method is briefly as follows: The precipitate is dissolved in conc. sulfuric acid, the solution diluted with a large amount of water, the barium sulfate filtered out, and the filtrate evaporated down and ignited. We added 10% to our actual results, as Johnston and Adams find that only 90% of the occluded sulfate is obtained in one solution and precipitation. The results are given in the following table:

TABLE IV.

Occlusion of Potassium Sulfate.

Potassium sulfate found. Mg.	Calc. as barium sulfate. Mg.
8.8	11.8
9.4	12.6
9.8	13.1
Average, 9.3	12.5

The determinations were made on precipitates weighing 500 mg., which were obtained under the same conditions as the results given in Table I. In Table V we have the occlusion in precipitates obtained under the same conditions as those given in Table II, using 50 cc. of conc. hydrochloric acid. These experiments were also made on 500 mg. of barium sulfate.

TABLE V.

Occlusion of Sodium Sulfate.

Calc. as sodium sulfate. Mg.	Calc. as barium sulfate. Mg.
13.7	22.6
13.0	21.3
13.9	22.9
Average, 13.3	22.5

We assumed that the occluded sulfate was sodium sulfate in this series on account of the huge preponderance of sodium in the solution.

The occlusion of chlorides was determined by a method developed by Hulett and Duschak.[2] The ignited barium sulfate is dissolved in conc. sulfuric acid and the hydrochloric acid liberated is extracted with air which then passes through a silver nitrate solution, where the acid is precipitated as silver chloride.

TABLE VI.

Occlusion of Chloride.

Calc. as barium chloride.		
Wt. of barium sulfate used. Mg.	Without sodium chloride. Mg.	With 50 g. of sodium chloride. Mg.
251	8.3	9.2
251	9.2	9.2
50	...	2.8
50	...	2.6
50	...	3.0

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[1] *Loc. cit.*

[2] G. A. Hulett and L. H. Duschak, *Z. anorg. Chem.*, 40, 196 (1904).

Hulett and Duschak have shown that the amount of occluded chlorides does not increase very much if the barium sulfate is precipitated in the presence of hydrochloric acid, and apparently the presence of large amounts of sodium chloride in addition to hydrochloric acid has very little effect.

It is interesting, though perhaps not very instructive, to calculate the total sulfate obtained, allowing for the solubility of the barium sulfate in the filtrate, the occlusion of the potassium or sodium sulfate, and the occlusion of chlorides.

Johnston and Adams[1] assume that in high acid concentration the potassium sulfate is occluded as potassium hydrogen sulfate and that during the ignition the reaction $2KHSO_4 = H_2SO_4 + K_2SO_4$ takes place. The correction to be applied to bring the occluded potassium sulfate to barium sulfate is, therefore, represented by the formula $2\left(\frac{BaSO_4 \times y}{Na_2SO_4}\right) - y$, where y represents the amount of occluded potassium sulfate as determined by experiment. The above authors have made a slight error in their correction, as they calculate it by the formula $2\left(\frac{BaSO_4 - Na_2SO_4}{Na_2SO_4}\right) \times y$. Our results agree much better, however, if we assume that no sulfuric acid is lost. This is quite possible as the sulfur trioxide may have displaced chlorine in the occluded barium chloride which was present in excess. Unfortunately, we were not able to prove that no sulfuric acid came off during ignition, as we did not have the necessary apparatus. All the determinations in the following two tables were made with a volume of 350 cc. and with 50 cc. of conc. hydrochloric acid. The precipitations were made at temperatures near the boiling point of the solutions. The solutions were filtered 48 hours after precipitation. The calculated weight of barium sulfate for the amount of potassium sulfate used is 251.0 mg.

TABLE VII.
Total Sulfate.

	Mg.	Mg.	Mg.	Mg.	Mg.
Wt. of precipitate..........	250.6	250.8	250.0	250.6	249.8
Corr. for occl. of K_2SO_4 (Av.)	1.6	1.6	1.6	1.6	1.6
Solubility of $BaSO_4$ (Av.).....	6.1	6.1	6.1	6.1	6.1
	258.3	258.5	257.9	258.3	257.5
Occlusion of $BaCl_2$ (Av.)....	8.6	8.6	8.6	8.6	8.6
Total sulfate.............	249.7	249.9	249.3	249.7	248.9

If it is assumed that a molecule of sulfuric acid escaped for every molecule of potassium sulfate remaining in the ignited precipitate, another 6.3 mg. would have to be added to the total.

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[1] *Loc. cit.*

It is rather astonishing that by making the same assumption in regard to the occlusion of the sulfate and chloride very good results are obtained when 50 g. of sodium chloride is present. It is hardly plausible, however, that in this case all the occluded sodium should be present as sulfate or all the occluded chloride as barium chloride.

Table VIII.

Total Sulfate with 50 g. of Sodium Chloride.

	Mg.	Mg.	Mg.	Mg.	Mg.
Wt. of precipitate..............	248.1	248.0	248.1	248.0	248.3
Corr. for occl. of Na_2SO_4 (Av.)...	4.6	4.6	4.6	4.6	4.6
Solubility of $BaSO_4$ (Av.)........	6.0	6.0	6.0	6.0	6.0
	258.7	258.6	258.7	258.6	258.9
Occlusion of $BaCl_2$ (Av.)........	9.2	9.2	9.2	9.2	9.2
Total sulfate...............	249.5	249.4	249.5	249.4	249.7

We, however, were not primarily interested in the mechanism of the precipitation of barium sulfate, but rather a satisfactory method for the estimation of sulfur in food. We therefore tried next to improve the oxidation sufficiently to avoid explosions and fires during the fusion with sodium peroxide. We began our experiments using powdered blood albumen. Two g. of the material was placed in the bottom of a nickel crucible holding about 100 cc. Two cc. of water was added and the mixture stirred with a nickel stirring rod. Five g. of sodium carbonate was then added and the whole well mixed. Sodium peroxide, about 8 g., was now added in small amounts with stirring until the mass became dry and granular. The crucible was then carefully heated with a Barthel alcohol lamp and the mixture constantly stirred until a brown homogeneous fused mass was obtained. Then the lamp was removed and the crucible cooled, after which another 8 g. of sodium peroxide and 2 g. of sodium carbonate were added. The crucible was again heated with the flame pointing at one side of the crucible opposite the inside level of the contents. The object was to get the ignition started locally without getting the whole crucible and contents warmer than necessary. After the ignition started, the lamp was quickly removed and the crucible covered with a lid. Usually the reaction continued until all the contents were fused but sometimes more heat had to be applied. After the mass had thoroughly fused, the lamp was put under the crucible and the heating continued for 10 minutes, during which the crucible was turned from side to side in order to make sure that all the fragments adhering to the sides were thoroughly oxidized. After the crucible and contents were cool, they were placed in a beaker containing about 100 cc. of water, and placed on a hot plate and digested until all the material was dissolved. The crucible was removed and washed, and the wash water run into the beaker. The solution was then carefully neutralized with conc. hydrochloric acid, and the desired amount of excess hydrochloric acid added. This method worked fairly well on blood albumen—about one explosion in 4 fusions—but was quite unsatisfactory with composite food samples having an average amount of fat. One of these samples was made up of 2 parts of milk, 2 of meat, 2 of corn flakes, one of egg yolk and 4 of soda biscuit. The second sample was the same as the first, except that potato chips were substituted for the egg yolk. The ingredients, however, came from a different source. The materials had all been dried at 110° before they were mixed. In these experiments the explosions were much more numerous. We, therefore, increased the amount of sodium peroxide to 26 g. and the sodium carbonate to 8 g. The procedure remained the same until the first heating was completed, then instead of adding about 8 g. of sodium peroxide enough was always added to bring the total for each oxidation to 26 g. After this 3 g. of sodium carbonate instead of 2 was added and mixed with the peroxide. The second heating was then carried out as before, *i. e.*, by starting the ignition at one point instead of heating the whole crucible. We found that this method is quite satisfactory for from 2 to 3 g. of organic material. It was tried on some 50 samples of oats, hay and straw without a single fire or explosion. With composite food samples it was very nearly as successful, the loss being one in 10 to 12 fusions. The method was submitted to one of the American Agricultural Experiment Stations, where it has been used with success for some time.

TABLE IX.

Analyses of Organic Materials.

Mg. $BaSO_4$. Excess conc. HCl. 2 cc.	Mg. $BaSO_4$. 50 cc.
Blood Albumen.	
163.2	157.2
161.4	155.8
166.9	155.2
Composite Food I.	
...	38.3
...	39.2
...	39.6
...	39.7
Composite Food II.	
47.6	19.5
48.0	14.9
37.5	21.1
46.8	21.4
49.6	35.3
44.5	33.5
42.4	34.3
49.5	34.0
50.6	...
44.5	...
52.0	...

The clear solutions obtained from the above fusions by neutralization and filtration were diluted with water to a volume of 350 cc. after adding the stated amount of hydrochloric acid. 10 cc. of 10% barium chloride solution was added when the temperature was near the boiling point and the solutions were allowed to stand for 48 hours before filtering.

Until the results given in Table IX were obtained, it was thought that precipitation made in high acid concentration would insure complete precipitation of barium sulfate in the presence of a large amount of sodium chloride. The filtrates from the first 4 determinations given in the above table under Composite Food II with 50 cc. of conc. hydrochloric acid contained barium sulfate after they had stood for several days. The same was true of many determinations with 2 cc. of conc. hydrochloric acid. Apparently small amounts of sulfate are not completely nor uniformly precipitated in a conc. hydrochloric acid and sodium chloride solution, although precipitation seems to be complete under the same conditions when the amount of sulfate is much larger. To make sure that this incomplete precipitation was not due to something present in either the chemicals used or the food itself which might act as an anticatalyst, we performed a series of experiments with pure sodium chloride and potassium sulfate. The experiments were carried out under the same conditions as those of Table II, except that we used 10 cc. of our potassium sulfate solution, which is equivalent to 50.2 mg. of barium sulfate. The results are given in the following table:

TABLE X.

Precipitation of Small Amounts of Barium Sulfate in the Presence of 50 g. of NaCl, and 50 cc. of conc. HCl, in 350 cc.

Mg. $BaSO_4$.	
46.7	48.1
45.1	46.1
36.6	37.6
37.6	42.4
44.3	

It is quite evident from these results that the incomplete precipitations noted in Table IX were not due to any substance in the food. As we had such excellent results with larger amounts of sulfate present, it was considered possible that better results might be obtained by slightly changing the conditions under which the precipitation was made.

In Table XI are given the results obtained by adding the barium chloride at various temperatures. In the last 3 determinations the solutions were kept near the boiling point on the hot plate for at least 5 hours after the barium chloride was added. All the experiments were made in the presence of 50 g. of sodium chloride and 50 cc. of conc. hydrochloric acid. All the solutions stood 48 hours before filtering.

TABLE XI.

Temperature Effect on Barium Sulfate Precipitation.

Volume. Cc.	Temperature. Degrees.	Barium sulfate found. Mg.
500	23	34.4
500	23	29.8
500	23	32.5
350	80	39.1
350	80	40.1
350	80	40.0
350	b. p.	46.7
350	b. p.	46.1
350	b. p.	45.8
350	b. p.	51.6
350	b. p.	50.5
350	b. p.	42.4
350	b. p.	44.3
350	Precipitated near b. p., stood 96 hrs.	47.3
350	Precipitated near b. p., stood 96 hrs.	46.1
350	Precipitated near b. p., stood 96 hrs.	47.6
350	Precipitated at b. p. and heated 5 hrs.	17.6
350	Precipitated at b. p. and heated 5 hrs.	27.6
350	Precipitated at b. p. and heated 5 hrs.	37.2
	Calc..........................	50.2

The above determinations indicate that the best results are obtained when the barium chloride is added at the boiling point of the solution, but that even at this temperature precipitation is not always complete. No great advantage is gained by letting the solutions stand an extra 24 hours. Since most of the barium sulfate is precipitated in those experiments where the barium chloride was added at the boiling point, it is astonishing that keeping the solutions at this temperature for several hours and then allowing them to stand for some 40 hours at the room temperature gives such poor results.

In a few experiments the solution was stirred for 3 hours after the barium chloride was added and then allowed to stand for 48 hours, but no great advantage is gained by this procedure. The quantities used were the same as in the last table. The barium chloride, however, was added at the room temperature. The results on two experiments were 41.6 and 42.6 mg., respectively.

Having found no conditions under which complete precipitation of small amounts of sulfate in the presence of large amounts of sodium chloride could always be obtained, it was decided to resort to an evaporation method. Johnston and Adams[1] have stated that evaporation immediately after precipitation will give satisfactory results. This, no doubt, is true under all ordinary circumstances, but it apparently does not hold in a concentrated electrolyte, according to our results in Table

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[1] *Loc. cit.*

XII. Precipitation was made near the boiling point in a volume of 350 cc. containing 50 g. of sodium chloride and 50 cc. of conc. hydrochloric acid. The evaporations were made immediately on a hot plate in Jena glass beakers.

TABLE XII.

Method of Evaporation of Johnston and Adams.

$BaSO_4$: 266.2, 252.5, 262.8, 250.2, 252.2 mg. Calc., 251.

In the next series of experiments the solutions were allowed to stand for 48 hours after the barium chloride was added before they were evaporated. The other conditions were the same as in the above series except that the amount of potassium sulfate used was cut to one-fifth.

TABLE XIII.

Method of Evaporation.

Evaporation after filtering. $BaSO_4$. Mg.	Evaporation without filtering. $BaSO_4$. Mg.
53.6	55.7
54.9	55.6
..	54.7
..	54.4
..	56.2
..	54.8
..	54.5
..	54.1

Calc., 50.2

In a few cases the barium sulfate was filtered out at the end of 48 hours before the solution was evaporated. The residue from the evaporation was then taken up in water slightly acidulated with hydrochloric acid and filtered through the same filter paper. This extra manipulation, however, is not justified as the results are about the same as those obtained without filtering. All the results are a few mg. too high, but they are sufficiently consistent that a correction can be applied. We feel that results obtained by this method are far more satisfactory than those obtained by the usual procedure. We analyzed composite food II again using the above method, and obtained 47.7, 48.4 and 46.2 mg. of barium sulfate after correcting for the occlusion.

Our Proposed Modification of the Sodium Peroxide Method.

We propose that the determination be carried out in the following way: A suitable quantity (2–3 g.) of the organic material is placed in a nickel crucible which holds about 100 cc. From 2 to 3 cc. of water is added and the mixture well stirred with a nickel stirring rod. 5 g. of sodium carbonate is then added and the whole well mixed. Sodium peroxide is now added in small lots, stirring after each addition until the whole mass becomes dry and granular. The crucible and contents are then carefully heated with a Barthel alcohol lamp until the mixture becomes a homogeneous well-browned fused mass, stirring being continued during the heating. The crucible is then partly cooled and enough sodium peroxide added to make a total of 25–26 g. 3 g. of sodium carbonate is also added and mixed with the peroxide. The crucible is then heated by pointing the flame at a position opposite the level of the contents until the first signs appear that the oxidation has started, when the flame is removed and the lid placed on top of the crucible. When this first ignition does not melt the contents completely, the heating must be continued in a similar way. The heating is usually continued for 10 minutes after the mass is thoroughly fused. During this heating the crucible is inclined from side to side to insure that all the material sticking to the walls is thoroughly oxidized. After the crucible is cool it is put into a large beaker containing about 100 cc. of water, placed on a hot plate, and digested until the contents are all dissolved. The crucible is then washed and removed and the solution neutralized with conc. hydrochloric acid and filtered if necessary. 50 cc. of conc. hydrochloric acid is now added and the solution brought to a volume of 350 cc. The solution is brought to boiling, then removed from the hot plate and precipitation made with 10 cc. of 10% barium chloride solution, added by means of a dropper, at the rate of 10 cc. in about 4 minutes. After standing for 48 hours, the solution is evaporated to dryness on a hot plate and the precipitate taken up with water. One to two cc. of conc. hydrochloric acid is added. After standing for about 18 hours the precipitate is collected in a Gooch crucible, washed, dried, ignited to constant weight, and weighed in the manner which has already been given in this paper.

The results obtained by the method will be high. A correction should be applied, derived from a comparison of the amount of barium sulfate obtained by making a determination on a solution of sodium or potassium sulfate with the calculated amount. This solution should be of such strength that the amount taken should give about the same amount of barium sulfate as obtained from the food. The analysis of this synthetic solution should be made in exactly the same manner as the analysis of the sample of food. It is obvious that if the amount of silica is appreciable it must be removed in the usual manner before precipitation is made.

This method is long and rather tedious and we do not propose that it should be used indiscriminately. Of many substances in which the sulfur content is relatively high, a suitable quantity can be oxidized with much less peroxide and consequently an evaporation may not be necessary to precipitate all the barium sulfate. But we do believe that when the sulfur content of the material is low and when difficulties from fires and explosions are encountered, our modification is a decided improvement both in the oxidation process and in the final estimation of sulfates.

MONTREAL, CANADA