

Microchemical Determination of Sulfur by Oxygen Flask Combustion

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A collaborative study was conducted on the use of oxygen flask combustion in the micro-determination of sulfur. Eighteen collaborators performed duplicate analyses on 5 samples. In conjunction with the oxygen flask combustion, collaborators used gravimetric, colorimetric, and a variety of titrimetric procedures. All those employing gravimetric analysis used BaCl_2 to precipitate BaSO_4 ; the one analyst who employed the colorimetric technique used a recorded transmission at 530 nm with $\text{Ba}(\text{ClO}_4)_2$ and a Thorin-methylene blue indicator. Several indicators were used in the titrimetric procedures: sulfanazo III, dimethylsulfanazo III, Thorin-methylene blue, carboxyarsenazo-methylene blue, Thorin, and tetrahydroxyquinone. The differences in the precision and accuracy of the various methods were small except in the presence of potassium or phosphate ions. In the presence of these ions, dimethylsulfanazo III gave better results than any other indicator. It is recommended that the study be continued.

The official AOAC microchemical methods for sulfur determination include procedures using either the Carius or catalytic method of combustion. It is now an established fact that the oxygen flask combustion technique greatly reduces analysis time by facilitating complete combustion in seconds while minimizing the strong effects attributed to manual error. These factors together with the overwhelming popularity which the oxygen flask combustion procedure enjoys today in sulfur analysis made it advisable that a collaborative study be conducted to establish eventually a basis for official adoption of an alternative method of this kind.

In this study, the collaborators were asked to make duplicate determinations using the oxygen flask procedure normally employed in their laboratories. The 4 samples submitted to each were benzylisothiurea hydrochloride, sulfanilamide, cystine, and potassium sulfate. In addition, the collaborators were given a sample of monobasic potassium phosphate and were instructed to analyze duplicate samples of potassium sulfate after

adding 2 mg of the phosphate compound to each of the duplicates. A questionnaire designed to determine details of the procedure which might vary from laboratory to laboratory was included. Literature references were also requested and are listed.

Results and Discussion

Eighteen collaborators reported sulfur data totaling 194 determinations, using oxygen flask combustion. The majority (15) used a titrimetric method of analysis (Table 1) involving oxygen flask combustion with 3-6% aqueous hydrogen peroxide solution as absorbent. In general, this

Table 1. Details of methods used by collaborators in the oxygen flask microchemical determination of sulfur

Condition	No. of colls.
Combustion aids:	
Sucrose, <i>n</i> -dodecanol, potassium perchlorate	5
Combustion product absorbent:	
3-6% aqueous H_2O_2 solution	15
0.1N NaOH+15 drops 30% H_2O_2	1
2N NH_4OH +5 drops 30% H_2O_2	1
0.1N NaOH	1
Post-combustion treatment (after shaking and standing period):	
Boil or evaporate	10
Solvents used in volumetric analysis:	
Isopropanol	5
Acetone	3
Ethanol	6
Methanol	1
Pretitration pH adjustment (pH 2-3)	5
K cation removal—column	4
Phosphate removal (MgCO_3 +column, AgO +column, or FeCl_3)	6
Indicator:	
0.1% Sulfanazo III	2
0.1% Dimethylsulfanazo III	2
0.2% Thorin+methylene blue (0.01-0.05%)	4
0.15% Carboxyarsenazo+5% methylene blue chloride	1
0.2% Thorin	4
Tetrahydroxyquinone	2
Colorimetric analysis	1
Gravimetric analysis for K_2SO_4 + KH_2PO_4 sample only	2
Gravimetric analysis for all compounds	3
Titrimetric analysis:	
$\text{Ba}(\text{ClO}_4)_2$	11
BaCl_2	3

was followed by a shaking period (average time 10 min), a standing period before opening the flask (average time 20 min), a boiling period which leaves the solution relatively peroxide- and carbon dioxide-free, the dilution of the sample $\geq 50:50$ with acetone, ethanol, or isopropanol, and, finally, the addition of indicator and titration with $0.01N$ $Ba(ClO_4)_2$. Two of the 3 collaborators who used $BaCl_2$ as titrant also used tetrahydroxyquinone (THQ) as indicator. Most collaborators (Table 1) used either a sulfanazo-type indicator (dimethylsulfanazo III or sulfanazo III) or a Thorin-type indicator (Thorin and methylene blue, carboxyarsenazo and methylene blue, or Thorin alone).

Tables 2 and 3 contain the following information for each of the 4 samples studied: mean, difference between duplicate values, and deviation of the mean from the theoretical value. An

Table 2. Statistical analysis of collaborative results for microchemical determination of sulfur

Coll.	Mean, %	Diff., ^a %	Dev., ^b %
Benzylisothiurea HCl, 15.82% S			
8	15.79	0.04	-0.03
15	15.90	0.27	0.08
20	15.82	0.08	0.00
13	15.92	0.01	0.10
18	15.95	0.08	0.13
2	15.94	0.01	0.12
16	15.86	0.08	0.04
11	15.82	0.07	0.00
1	15.90	0.15	0.08
6	16.27	0.22	0.45
23	15.70	0.50	-0.12
17	15.95	0.10	0.13
7	15.88	0.09	0.06
4	15.82	0.05	0.00
5	15.88	0.26	0.06
22	15.98	0.15	0.16
9	15.95	0.20	0.13
14	15.88	0.07	0.06
Sulfanilamide, 18.62% S			
8	18.87	0.12	0.25
15	18.73	0.18	0.11
20	18.50	0.08	-0.12
13	18.72	0.24	0.10
2	18.63	0.14	0.01
16	18.64	0.03	0.02
18	18.62	0.60	0.00
11	18.65	0.12	0.03
1	18.52	0.30	-0.10
6	18.86	0.19	0.24
23	18.64	0.00	0.02
17	18.55	0.04	-0.07
7	18.50	0.07	-0.12
4	18.61	0.02	-0.01
5	18.68	0.15	0.06
22	18.66	0.08	0.04
9	18.84	0.11	0.22
14	18.48	0.14	-0.14

Table 2. (Continued)

Coll.	Mean, %	Diff., ^a %	Dev., ^b %
Cystine, 26.69% S			
8	26.52	0.03	-0.17
15	26.56	0.03	-0.13
20	26.67	0.02	-0.02
13	26.98	0.01	0.29
18	26.72	0.03	0.03
2	26.65	0.28	-0.04
16	26.66	0.03	-0.02
11	26.66	0.09	-0.04
1	26.48	0.12	-0.21
6	26.84	0.01	0.15
23	26.58	0.11	-0.11
17	26.62	0.06	-0.07
7	26.64	0.09	-0.05
4	26.68	0.01	-0.01
5	26.73	0.20	0.04
22	26.58	0.24	-0.11
9	26.59	0.28	-0.10
14	26.92	0.54	0.23
Potassium sulfate, 18.40% S			
15	18.31	0.42	-0.09
15 ^c	18.41	0.04	0.01
20	18.47	0.06	0.07
13	18.32	0.15	-0.08
8	13.96	2.18	-4.44
8 ^d	17.62	0.36	-0.78
18	6.00	7.78	-12.40
2 ^e	17.10	0.07	-1.30
16	17.20	0.23	-1.20
16 ^f	18.60	0.06	0.10
11	17.72	0.27	-0.68
1	17.18	0.14	-1.22
6	16.86	0.00	-1.54
6 ^d	18.23	0.08	-0.17
23 ^c	18.52	0.01	0.12
17 ^c	18.43	0.10	0.03
7	17.18	0.16	-1.22
7 ^c	18.41	0.12	0.01
5	18.40	0.15	0.00
5 ^d	18.38	0.01	-0.02
22 ^f	18.35	0.12	-0.05
9 ^f	18.42	0.19	0.02
14 ^f	18.37	0.06	-0.03

^a Difference between duplicate values.

^b Deviation of mean from theoretical value.

^c Employed column separation for potassium.

^d K_2SO_4 sample not combusted.

^e Colorimeter used.

^f Used gravimetric determination.

examination of the data for K_2SO_4 in Tables 2 and 4 shows a large statistical variation among the values for the deviation of the mean from the theoretical, ranging from 0.00 to 12.40. Eight of these determinations for per cent sulfur in K_2SO_4 were not acceptable. Collaborators 8 and 6 showed marked improvement in results when they determined per cent sulfur in K_2SO_4 without combustion. Yet Collaborator 5, who used THQ indicator, reported results for both combusted and uncombusted K_2SO_4 samples which were accu-

Table 3. Statistical analysis of collaborative results for potassium sulfate (KH₂PO₄ added), 18.40% S

Coll.	Mean, %	Diff., ^a %	Dev., ^b %
Dimethylsulfanazo III and sulfanazo III indicators			
15	18.31	0.24	-0.09
15 ^c	18.41	0.03	0.01
8	19.60	0.86	1.20
8 ^d	18.72	0.02	0.32
13 ^e	18.20	0.17	-0.20
Thorin, Thorin-methylene blue, and carboxyarsenazo-methylene blue indicators			
2 ^f	21.16	0.62	2.76
16	19.30	1.41	0.90
1	9.38	0.13	-9.02
7	21.12	0.04	2.72
11	17.90	0.03	-0.50
11 ^f	17.60	0.13	-0.80
6	3.42	2.82	14.98
6 ^d	19.96	1.14	1.56
17 ^f	18.35	0.10	-0.05
23 ^d	18.57	0.30	0.17
18	29.16	5.37	10.76
Final step—gravimetric			
9	18.54	0.05	0.14
14	18.94	0.45	0.54

^a Difference between duplicate values.

^b Deviation of mean from theoretical value.

^c Employed column separation for K ion.

^d Phosphate removed by AgO precipitation followed by a column separation.

^e Phosphate removed with FeCl₃.

^f Colorimeter used.

rate and precise. Collaborators 23, 17, and 7 obtained acceptable results by passing the combusted sample solution through a cation column before the titration step. The results submitted by Collaborators 15, 20, and 5 were accurate, although they did not pass the samples through a column. They used THQ or dimethylsulfanazo III indicator. Collaborators 16, 22, 9, and 14, who followed the oxygen flask combustion with a time-consuming gravimetric procedure, also generally reported acceptable results.

Table 4 compares the reproducibility among certain analysts who carried out duplicate determinations on all 5 samples submitted; no special treatment was given to the K₂SO₄ samples. Some collaborators did not perform the K₂SO₄ (PO₄ added) determination and others removed the phosphate by precipitation with MgCO₃ or AgO prior to an ion exchange column step. The reproducibility among analysts under those conditions is shown in Table 5.

Only 5 collaborators used combustion aids and 3 of these had at least one incident where poor results were reported. Collaborator 8 used 2 mg

sucrose as combustion aid. The resultant deviation of the mean from theoretical for sulfanilamide was 0.25 and the difference between duplicate values for K₂SO₄ was 2.18 and that for K₂SO₄ (phosphate added) was 0.86. Moreover, the deviation of the theoretical value from the mean for K₂SO₄ was -4.44 and that for K₂SO₄ (phosphate added) was 1.20. When this same collaborator determined per cent sulfur in K₂SO₄ without combustion, the difference between duplicate values decreased greatly: the K₂SO₄ value was 0.36 and the K₂SO₄ (phosphate added) value was 0.02. The deviation of the mean from theoretical also decreased. The K₂SO₄ value was then -0.78, and that for K₂SO₄ (phosphate added) was +0.32. Collaborator 18 who used one drop of dodecanol obtained a relatively high difference between duplicates for sulfanilamide of 0.60. Collaborator 15 also used *n*-dodecanol but submitted good results for all 12 determinations. Collaborator 17 used *n*-dodecanol for *S*-benzyl only and obtained good results for that sample. He also obtained good results for sulfanilamide and cys-

Table 4. Reproducibility among analysts for microchemical determination of sulfur^a

Coll.	Bias ^b	σ^c	χ^d
Dimethylsulfanazo III			
15	-0.006	0.18	0.08
20	0.02	0.04	0.05
Sulfanazo III			
8	-3.20	0.74	0.61
Thorin+methylene blue			
16	-0.27	0.45	0.44
1	-2.09	0.13	2.13
2	0.33	0.22	0.85
7	0.28	0.07	0.83
Carboxyarsenazo+methylene blue chloride			
18	-1.48	3.00	4.66
Thorin			
11	-0.24	0.10	0.25
6	-3.13	0.28	3.47
Gravimetric			
9	0.08	0.13	0.12
14	0.13	0.23	0.20

^a All samples; no special treatment for K₂SO₄ determinations.

^b Average deviation of mean from theoretical value, signs observed.

^c Standard deviation based on difference between duplicates.

^d Average deviation of mean from theoretical value, signs ignored.

Table 5. Statistical comparison among analysts for calculation of per cent sulfur^a

Coll.	Bias ^b	σ^c	\bar{X}^d
15 ^e	0.02	0.13	0.11
15	0.07	0.10	0.10
20 ^e	0.05	0.04	0.05
8 ^e	0.05	0.05	0.15
8 ^f	-0.41	0.12	0.31
13 ^e	0.16	0.10	0.16
13 ^f	0.04	0.10	0.15
2 ^{e,g}	0.06	0.13	0.06
16 ^e	0.006	0.04	0.02
16 ^h	0.03		0.05
1 ^e	-0.08	0.14	0.13
7 ^e	-0.04	0.06	0.08
7 ^e	-0.03		0.06
18 ^e	0.05	0.25	0.05
11 ^e	-0.003	0.07	0.02
6 ^e	0.28	0.12	0.28
6 ^f	0.51		0.51
23 ^e	0.07	0.21	0.08
23 ⁱ	0.08	0.19	0.11
17 ^e	-0.003	0.05	0.12
17 ^e	0.006	0.06	0.07
4 ^e	0.04	0.02	0.04
5 ^e	0.05	0.15	0.05
22 ^{e,h}	0.03	0.12	0.10
9 ^{e,h}	0.08	0.15	0.15
14 ^{e,h}	0.05	0.23	0.14

^a Determined after removal of potassium and phosphate ion, or when all results for potassium sulfate determinations are eliminated.

^b Average deviation of mean from theoretical value, signs observed.

^c Standard deviation.

^d Average deviation of mean from theoretical, signs ignored.

^e Results for K₂SO₄ determination eliminated in statistical calculation.

^f Potassium salts not combusted.

^g Colorimeter used.

^h Gravimetric analysis of K₂SO₄+KH₂PO₄ mixture.

ⁱ Phosphate removal by MgCO₃ or AgO precipitation followed by column separation of cation.

tine without using a combustion aid. Other collaborators who did not use combustion aids submitted comparable or better results. There are indications that Collaborator 6 also had combustion difficulties. The deviation of the mean from the theoretical value for *S*-benzyl was 0.45, and for sulfanilamide 0.24, while that for K₂SO₄ was -1.54 when combusted but an improved 0.17 when determined without combustion. The presence of phosphate generally increased the value obtained for per cent sulfur. This was true for Collaborator 6 when the K₂SO₄ samples were not combusted; however, when the K₂SO₄-phosphate mixture was combusted, very low values were obtained by this collaborator. In the final overall statistical analysis of the K₂SO₄ determinations

the results for Collaborators 8, 6, and 18 were excluded for the aforementioned reasons.

Statistical comparisons of results obtained under variation in the method (choice of absorbent concentration, choice of solvents, and shaking-standing period) determined that no one variation was significantly better than another. Statistical variations due to indicator were significant only in the presence of the potassium or phosphate ions. Only dimethylsulfanazo III, sulfanazo III, and THQ gave good results in the presence of potassium ion, and dimethylsulfanazo III alone gave good results in the presence of the phosphate ion. Two collaborators (9, 16) obtained good results for K₂SO₄ and K₂SO₄+phosphate, using a gravimetric analysis. However, Collaborator 14 reported high results for the gravimetric analysis of K₂SO₄+phosphate. The difference between duplicates was 0.45 and the deviation of the mean from theoretical was 0.54 (Table 3).

The statistics in Table 6 summarizes the data for all 5 samples and compare data received from the 4 different types of determinations. The overall average deviation of the mean from the theoretical value was ≤ 0.15 for *S*-benzyl, sulfanilamide, and cystine. Those who used the Thorin-type indicator without removal of the potassium or phosphate ion obtained high results; average deviation of mean from theoretical value was 0.74 for K₂SO₄ and 2.12 for K₂SO₄+phosphate. The average value for the 4 collaborators who used the sulfanazo-type indicator was 0.10.

Overall consideration and evaluation of the data obtained indicated that the oxygen flask procedures for sulfur determination generally gave good results. It has been this author's experience that the presence of potassium or sodium in the sulfur sample promotes low results when the oxygen flask method of combustion is used. Therefore, after combustion, the platinum basket is dropped into the absorbent before the shaking period. The number of collaborators who reported low results in the K₂SO₄ samples indicates a need for such a precaution. The collaborative results also indicate that dimethylsulfanazo III is the preferred indicator when the sulfate sample is contaminated with phosphate ions.

It is recommended that the study of the micro-analytical oxygen flask determination of sulfur be continued.

Table 6. Summary of statistical results for the 5 samples studied

Procedure	No. of colls.	σ^a	Av. ^b bias	Av. ^c X
Benzylisothiourea HCl				
Sulfanazo III	4	0.10	0.04	0.05
Thorin	9	0.13	0.10	0.13
THQ	2	0.13	0.03	0.03
Gravimetric	3	0.10	0.12	0.12
Total	18	0.12	0.09	0.10
Sulfanilamide				
Sulfanazo III	4	0.12	0.12	0.14
Thorin	9	0.17	0.04	0.07
THQ	2	0.08	0.03	0.04
Gravimetric	3	0.08	0.09	0.13
Total	18	0.14	0.06	0.09
Cystine				
Sulfanazo III	4	0.02	-0.008	0.15
Thorin	9	0.08	-0.04	0.08
THQ	2	0.10	0.02	0.02
Gravimetric	3	0.27	0.007	0.15
Total	18	0.13	0.02	0.10
K₂SO₄				
Sulfanazo III	4	0.18	-0.02	0.06
Thorin	8	0.13	-0.69	0.74
Thorin (K removed)	3	0.07	0.05	0.05
Gravimetric	4	0.09	-0.01	0.01
Total	17	0.12	-0.41	0.46
K₂SO₄ (PO₄⁻³ added)				
Sulfanazo III	3	0.10	0.08	0.10
Thorin	8	0.46	-0.48	2.12
Thorin (K and PO ₄ ⁻³ removed)	3	0.14	-0.19	0.34
Gravimetric	2	0.32	0.34	0.34
Total	13	0.37	0.25	1.38

^a Standard deviation based on difference between duplicates.

^b Average deviation of mean from theoretical value, signs observed.

^c Average deviation of mean from theoretical value, signs ignored.

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