

Collaborative Study of the Microanalytical Oxygen Flask Sulfur Determination with Dimethylsulfonazo III as Indicator

LAVERNE H. SCROGGINS

*Agricultural Research Service, U.S. Department of Agriculture,
600 E. Mermaid Lane, Philadelphia, Pa. 19118*

The volumetric, microchemical oxygen flask sulfur determination using dimethylsulfonazo III as the sulfate indicator and standard barium perchlorate as the titrant was tested by 21 collaborators. The samples studied were sulfanilamide, benzyl-isothiurea hydrochloride, cystine, potassium sulfate, and potassium sulfate with a phosphate additive. Only 5 collaborators reported good results for the potassium sulfate when it was contaminated with phosphate. Overall statistical evaluation of the data for the 4 pure compounds gave satisfactory values—average standard deviation 0.10, overall average deviation of the mean from theoretical value 0.16, and average bias 0.10. However, a statistical analysis of the reproducibility among analysts showed 10 of the 21 laboratories had an overall average deviation of the mean from the theoretical value greater than 0.20. A critical factor was the necessity for vigorous, efficient stirring during the titration to overcome indicator lag-time by hastening the fading of the pseudo-end point color. Thus, many collaborators reported the titration to be slow and tedious. It is recommended that the study of the microanalytical oxygen flask sulfur determination be continued.

Last year's collaborative studies (1) of the oxygen flask microchemical sulfur determination indicated that titrimetric procedures generally gave good results. In that study collaborators had been asked to use the procedure currently employed in their laboratory. The tetrahydroxyquinone sulfate indicator, which requires the use of a titration assembly, gave good results even in the presence of potassium ions, but results were poor for the samples contaminated with phosphate ions. For those samples contaminated with potassium or phosphate ions, dimethylsulfonazo III gave the best results. Four collaborators had used a sulfonazo-type indicator.

The objective of this year's work was to fully test the procedure, using dimethylsulfonazo III, to see if it was sufficiently accurate, precise, and

dependable to warrant a recommendation for adoption as official first action. The details of the procedure were based on the overall results of the statistical study of all data from the previous study. The evolved method was used successfully in the author's laboratory; excellent accuracy and reproducibility were obtained. Results were also acceptable for potassium sulfate in the presence of phosphate ions. No colorimetric apparatus, comparators, visual aids, or spectrophotometers were employed. In the presence of potassium ions, the platinum baskets must be dropped into the absorption solution just before the shaking period to insure complete absorption. During the titration and long before the end point is reached, the blue barium salt of the indicator forms. This produces pseudo-end points which, with vigorous stirring, slowly disappear as the barium associated with the indicator reacts with the remaining sulfate ions. The true end point is that point where no fading of the barium-indicator color occurs. It is necessary to use a magnetic stirring apparatus for this titration because vigorous and continuous stirring is essential.

Collaborative Study

The collaborators were asked to make duplicate determinations, adhering strictly to the method described herein. The 4 samples submitted to each were benzyl-isothiurea hydrochloride, sulfanilamide, cystine, and potassium sulfate. In addition, the collaborators were asked to contaminate 2 potassium sulfate samples with approximately 2 mg monobasic potassium phosphate before combustion. They were required to leave both the potassium and the phosphate ions in the solutions throughout the determination. Comments on the method were requested from the collaborators.

METHOD

Reagents and Apparatus

(a) *Cation exchange resin*.—Dowex 50W-X8, H⁺ form (Dow Chemical Co.).

(b) *Hydrogen peroxide*.—30%.

(c) *Barium perchlorate standard solution*.—About 0.01M. Dissolve 4.0 g Ba (ClO₄)₂·3H₂O in 1 L water and adjust pH to 3.0 with 0.5N HCl.

(d) *Dimethylsulfonazo III indicator solution*.—About 0.1%. Dissolve 100 mg dimethylsulfonazo III in 30 ml water. Elute solution through column of ion exchange resin, (a) (pretreated with 100 ml 3N HCl). Dilute eluate to 100 ml with water.

(e) *Titration lamp*.—Stirrer-lamp or any similar source of glare-free fluorescent illumination with flat white background. Recommended.

Standardization of Barium Perchlorate Solution

Accurately weigh 5–7 mg freshly dried K₂SO₄ and transfer to 200 ml tall-form graduated beaker. Dissolve in 50 ml water. Adjust pH to 3.0±0.2 with ca 4 drops 0.5N NH₄OH solution. Add 6 drops (0.3 ml) dimethylsulfonazo III indicator solution and 50 ml acetone. With vigorous stirring, titrate with 0.01M barium perchlorate solution to permanent sky blue which persists while stirring for ≥30 sec. Light blue may appear at start of titration but normal purple will return upon continued titration. Titration end point is permanent change from mauve-purple to azure-blue. Subtract reagent blank. Repeat standardization ≥ 3 times. Normality = mg K₂SO₄ / (mol. wt × ml barium perchlorate solution).

Determination

Weigh sample containing 0.75–1.5 mg S and fold in paper carrier. Add 10 ml water and 6 drops 30% H₂O₂ to flask. Combust sample. If Na or K is present in sample, allow Pt basket to fall into absorption solution just before beginning shaking period. Shake closed flask 10 min on mechanical shaker. Let stand 20 min. Open flask and rinse stopper and sample carrier with water. Boil solution vigorously ca 10 min (solution should be relatively free of CO₂ and H₂O₂). Cool to room temperature and transfer quantitatively with water rinses to 200 ml tall-form graduated beaker. (Total volume should be <50 ml.) Proceed as in standardization, beginning "Adjust pH to 3.0±0.2 . . ." Subtract paper blank from volume used.

$$\text{Factor} = (\text{mg K}_2\text{SO}_4 \times 0.1840) / (\text{ml Ba}(\text{ClO}_4)_2 - \text{blank})$$

$$\% \text{ Sulfur} = [\text{ml Ba}(\text{ClO}_4)_2 - \text{blank}] \times \text{factor} \times 100 / \text{mg sample}$$

Results and Recommendation

Twenty-one collaborators reported sulfur data. Table 1 contains the mean, difference between duplicate values, and the deviation of the mean from the theoretical value for each of the 5 samples analyzed. In a population of 105 values, 25% (including 8 sulfanilamide, 5 *S*-benzyl, 7 cystine, and 7 phosphate-free potassium sulfate values) had deviations of the mean from theoretical greater than 0.20. Five collaborators submitted a total of 10 values for potassium sulfate (phosphate added) which were acceptable in both accuracy and precision. However, 76% of the collaborators submitted an average deviation of the mean from the theoretical value greater than 0.20 for this sample. Two collaborators reported they did not have detachable baskets and thus were unable to comply with the part of the procedure which specified that the platinum baskets be dropped into the absorption solution just prior to shaking; their results were among those whose deviations were greater than 0.20 for the potassium sulfate samples (both pure and adulterated).

Within-laboratory precision, calculated from the difference between duplicates, bias, and average deviation of the mean from theoretical values, is shown in Table 2. Ten of the 21 laboratories had values greater than 0.20 for the deviation of the mean from theoretical.

Collaborators reported that the procedure itself was straightforward but most had some comment on titration with dimethylsulfonazo III indicator. The solicited comments from the collaborators included the following: (1) The majority found the end point reproducible; (2) 4, however, found the end point difficult to see; (3) 2 collaborators reported the end point was both difficult to detect and unstable in the presence of phosphate contamination; (4) collaborators noted the very vigorous stirring required to overcome indicator lag-time; (5) the fading end point forced many collaborators to titrate at a fairly slow rate to prevent overshooting the end point; (6) 3 collaborators indicated titration with this indicator was too tedious for routine analysis; (7) several collaborators indicated titration with this indicator made the procedure dependent on the training and experience of the individual who performed the analysis.

The statistics in Table 3 summarize the data from all 5 compounds. In the total population of

Table 1. Collaborative results for microanalytical oxygen flask sulfur determination using dimethylsulfonazo III indicator

Coll.	Mean, %	D ^a	X ^b
Sulfanilamide, 18.62% Sulfur Theor.			
1	18.58	0.05	-0.04
2	18.64	0.01	0.02
3	18.68	0.03	0.06
4	18.50	0.17	-0.12
5	18.78	0.17	0.16
6	18.62	0.28	0.00
7	18.54	0.19	-0.08
8	19.08	0.19	0.46
9	18.32	0.29	-0.30
10	19.00	0.19	0.38
11	18.76	0.16	0.14
12	19.00	0.00	0.38
13	18.66	0.15	0.04
14	18.56	0.28	-0.06
15	18.97	0.06	0.35
16	18.95	0.04	0.33
17	18.90	0.27	0.28
18	18.62	0.15	0.00
19	18.55	0.05	0.06
20	18.76	0.16	0.14
21	19.14	0.03	0.52
Benzyl-isothiurea HCl, 15.82% Sulfur Theor.			
1	15.86	0.09	0.04
2	15.88	0.05	0.06
3	15.87	0.02	0.05
4	15.35	0.03	-0.47
5	15.86	0.15	0.04
6	15.70	0.09	-0.12
7	15.71	0.26	-0.11
8	16.06	0.05	0.24
9	15.86	0.01	0.04
10	15.96	0.12	0.14
11	15.90	0.07	0.08
12	16.00	0.00	0.18
13	15.88	0.02	0.06
14	16.02	0.55	0.20
15	15.98	0.09	0.16
16	16.22	0.05	0.40
17	15.50	0.79	-0.32
18	15.70	0.10	0.12
19	15.86	0.03	0.04
20	15.94	0.43	0.12
21	16.30	0.25	0.48
Cystine, 26.69% Sulfur Theor.			
1	26.58	0.00	-0.11
2	26.62	0.07	-0.07
3	26.70	0.04	0.01
4	26.54	0.32	-0.15
5	26.66	0.25	-0.03
6	26.79	0.28	0.10
7	26.52	0.19	-0.17
8	27.10	0.19	0.41
9	26.76	0.11	0.07
10	26.72	0.15	0.03
11	26.86	0.01	0.17
12	26.85	0.10	0.16
13	26.92	0.01	0.23
14	26.74	0.14	0.05
15	27.12	0.56	0.43

Table 1. (Continued)

Coll.	Mean, %	D ^a	X ^b
16	27.25	0.06	0.56
17	26.85	0.01	0.16
18	26.48	0.11	0.21
19	26.76	0.06	0.07
20	27.70	1.90	1.01
21	27.37	0.62	0.68
Potassium Sulfate, 18.40% Sulfur Theor.			
1	18.43	0.06	0.03
2	18.37	0.01	-0.03
3	18.30	0.17	-0.10
4	18.21	0.02	-0.19
5	18.08	0.07	-0.32
6	18.18	0.06	-0.22
7	14.10	0.35	-4.30
8	18.32	0.09	-0.06
9	18.08	0.03	-0.32
10	18.31	0.22	-0.09
11	17.89	0.04	-0.51
12	18.25	0.10	-0.15
13	18.24	0.06	-0.16
14	18.46	0.13	0.06
15	18.18	0.12	-0.22
16	18.61	0.04	0.21
17	18.58	0.25	0.18
18	18.50	0.06	0.10
19	18.40	0.80	-0.04
20	18.36	0.09	0.08
21	18.48	0.01	0.04
Potassium Sulfate (KH ₂ PO ₄ Added), 18.40% Sulfur Theor.			
1	18.56	0.13	0.16
2	18.64	0.31	0.24
3	19.70	1.85	1.30
4	18.90	2.05	0.50
5	19.24	0.27	0.84
6	20.07	0.46	1.67
7	18.36	0.36	-0.04
8	18.54	0.15	0.14
9	18.80	0.15	0.40
10	18.74	0.58	0.34
11	19.10	0.08	0.70
12	20.95	0.30	2.55
13	18.84	0.03	0.44
14	18.86	0.21	0.46
15	19.01	0.16	0.61
16	22.57	0.16	4.17
17	19.68	0.41	1.28
18	20.96	0.03	2.56
19	18.41	0.00	0.00
20 ^c	—	—	—
21	19.66	0.46	1.26

^a D = difference between duplicate values.

^b X = deviation of mean from theoretical.

^c No end point.

210 values studied, 8 values were outliers according to the Dixon test (2). The overall statistical results showed acceptable standard deviations and deviations of the mean from theoretical value for all compounds studied except the phosphated potassium sulfates. However, overall considera-

Table 2. Reproducibility among analysts

Coll.	σ^a	Bias ^b	X ^c	X ^d	σ^e
1	0.06	0.04	0.08	0.06	0.04
2	0.10	0.04	0.08	0.04	0.03
3	0.59	0.26	0.30	0.07	0.06
4	0.66	-0.09	0.29	0.23	0.13
5	0.14	0.14	0.28	0.14	0.12
6	0.19	0.29	0.42	0.11	0.14
7	0.20	-0.94	0.94	1.16	0.18
8	0.11	0.24	0.26	0.29	0.10
9	0.10	-0.02	0.23	0.18	0.11
10	0.21	0.16	0.20	0.16	0.12
11	0.06	0.12	0.32	0.22	0.06
12	0.10	0.62	0.68	0.22	0.05
13	0.15	0.12	0.19	0.12	0.17
14	0.21	0.14	0.17	0.09	0.23
15	0.19	0.27	0.35	0.29	0.21
16	0.06	1.13	1.13	0.38	0.03
17	0.30	-0.52	0.44	0.24	0.31
18	0.07	0.47	0.60	0.11	0.08
19	0.03	0.02	0.04	0.04	0.03
20	—	0.25	—	0.33	0.75
21	0.26	0.60	0.60	0.44	0.24

^a Standard deviation calculated from difference between duplicates for all 6 samples.

^b Average deviation of mean from theoretical values, observing signs.

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

^d Average deviation of mean from theoretical values, signs ignored and results from potassium sulfate-phosphate added eliminated.

^e Calculated from difference between duplicates, phosphated potassium sulfate results eliminated.

tions, including the large number of individual laboratories exhibiting borderline or unacceptable average values, preclude acceptance of the method using dimethylsulfonazo III indicator as universally dependable.

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

Acknowledgments

The Associate Referee wishes to express appreciation to the following collaborators:

R. C. Anderson, The Upjohn Co., Kalamazoo, Mich.

W. M. Barbour, E. I. DuPont de Nemours & Co., Wilmington, Del.

R. N. Boos, Merck & Co., Inc., Rahway, N.J.

L. M. Brancone and G. P. McTernan, Lederle Laboratories, Pearl River, N.Y.

The recommendation of the Associate Referee was approved by the General Referee and by Subcommittee C and was accepted by the Association. Their reports will appear in (1974) *JAOAC* 57, March issue.

Table 3. Summary of statistical results for 5 samples studied^a

Compound	σ^b	X ^c	Bias ^d
Sulfanilamide	0.12	0.19	0.12
S-Benzyl	0.10	0.16	0.06
Cystine	0.11	0.16	0.08
Potassium sulfate	0.09	0.15	-0.08
Potassium sulfate + PO ₄ ⁻³	0.20	0.98	0.98

^a Statistical outliers eliminated.

^b Standard deviation calculated from the difference between duplicates.

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

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

C. E. Childs and T. M. Stickney, Parke Davis & Co., Ann Arbor, Mich.

R. Conroy and J. J. Kobliska, American Cyanamid Co., Bound Brook, N.J.

J. Corliss, Department of the Army, Edgewood Arsenal, Md.

G. M. Elsea, Tennessee Eastman Co., Kingsport, Tenn.

H. W. Galbraith and G. R. Hutchens, Galbraith Laboratories, Inc., Knoxville, Tenn.

G. M. Gustin and M. Tefft, Norwich Pharmaceutical Co., Norwich, N.Y.

D. F. Ketchum, Eastman Kodak Co., Rochester, N.Y.

R. G. Lade, Rohm & Haas Co., Bristol, Pa.

R. Leith and A. M. Morwitz, Inmont Corp., Clifton, N.J.

J. M. Lockard and J. Nemeth, University of Illinois, Urbana, Ill.

G. M. Maciak, Eli Lilly & Co., Indianapolis, Ind.

G. F. Morris, Chemistry and Biology Research Institute, Canada Department of Agriculture, Ottawa, Ontario

M. Myers, Ciba-Geigy Corp., Ardsley, N.Y.

J. J. Neumayer, 3M Co., St. Paul, Minn.

R. B. Nunemaker, The Dow Chemical Co., Midland, Mich.

R. C. Rittner, Olin Research Center, New Haven, Conn.

D. J. St. Maurice, Pennwalt Corp., Rochester, N.Y.

REFERENCES

- (1) Scroggins, L. H. (1973) *JAOAC* 56, 892-896
- (2) Dixon, W. J., & Massey, F. J. (1957) *Introduction to Statistical Analysis*, 2nd Ed., McGraw-Hill, New York