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AFML-TR-66-147

THE DETERMINATION OF SULFUR IN ORGANIC COMPOUNDS

THOMAS M. DOWNER, JR.

and

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UNIVERSITY OF CINCINNATI

TECHNICAL REPORT AFML-TR-66-147

MAY 1966

AIR FORCE MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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NOTICES

300 - July 1966 - 773-43-1071

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FOREWORD

This report was prepared by the University of Cincinnati under Contract Number AF 33(615)-2746. Dr. Michael Hoch served as principal investigator. This contract was initiated under Project No. 7360 "The Chemistry and Physics of Materials", Task No. 736005 "Composition, Atomic and Molecular Analysis". The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command. Mr. F. F. Bentley was the project engineer.

This report covers the work carried out from December 1964 to December 1965. The work was performed at the Analytical Branch, Physics Laboratory by Mr. Thomas M. Downer, Jr. and Mr. Charles R. Riber, Jr.

This manuscript was released by the authors, Thomas M. Downer, Jr. and Charles R. Riber, Jr. on 28 April 1966 for publication as an RTD technical report.

This technical report has been reviewed and is approved.

Freeman F. Bentley

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Chief, Analytical Branch
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ABSTRACT

A rapid method for the determination of Sulfur is described. The method is applicable to the sulfate ion formed following an oxygen flask combustion procedure. The percentage of sulfur is determined by titrating the sulfate ion with barium perchlorate using a complexing indicator, Thorin to detect the end-point. Compounds containing carbon, hydrogen, nitrogen, chlorine and sulfur were successfully analyzed.

INTRODUCTION

The Microchemical Group of the Analytical Branch has adapted the method of J. S. Fritz and M. Q. Freeland (Reference 1) for the determination of sulfur in organic compounds. The procedure involves the combustion of the sulfur compound in a Schoniger flask, and the titration of the sulfate ion formed with barium perchlorate, using a complexing indicator to detect the equivalence point.

REAGENTS

Barium perchlorate: (Baker "Desicclora") or G. F. Smith 0.01 Molar

Isopropyl Alcohol: C. P. Reagent

Thorin: o-2(2-Hydroxy-3,6,-disulpho-1-naphthylazo)benzenearsonic acid: 0.2% aqueous

Methylene Blue: 0.0125% aqueous

Sulfuric acid: 0.01N Standardized

Hydrogen peroxide: 30%

APPARATUS

Microtitration assembly is composed of the following:

(1) 5 or 10 ml burette graduated in 0.01 ml intervals which can be read accurately to 0.005 ml.

(2) Magnetic stirrer.

(3) 100 ml beakers and teflon stirring bars.

DETERMINATION OF BLANK VALUES

In the combustion of the organic compounds in an oxygen flask, according to the procedures of Schöniger, it has been found that a very small amount of sulfate ion is produced from the ashless filter paper. In addition, a small quantity of the titrant, $Ba(ClO_4)_2$, is consumed in the reaction with the thorin indicator to produce the color change, (yellow to pink), used as a criterion of the equivalence point. A blank value, therefore, must be taken which includes the indicator blank and the blank which comes from the combustion of the organic sample holder. This blank value, when subtracted from the apparent volume of barium perchlorate used in a titration, will give a true volume of titrant necessary to titrate the sulfur content of the organic compound in question. At least two blanks should be run along with every batch of samples which are to be analyzed. Included below is a series of blank values obtained in evaluating the blank, with procedures for the experiment.

1. Titrate 10 ml distilled water, 40 ml of isopropyl alcohol, 3 drops "Thorin" (0.2% aqueous) and 2 drops of methylene blue (0.0125% aqueous) with 0.01 N barium perchlorate.
    - a) 0.030 ml $Ba(ClO_4)_2$ used
    - b) 0.034 ml $Ba(ClO_4)_2$ used
    - c) 0.030 ml $Ba(ClO_4)_2$ used
    - d) 0.035 ml $Ba(ClO_4)_2$ used
2. Titrate same solution as above but add 3 drops 30% hydrogen peroxide.
    - a) 0.034 ml $Ba(ClO_4)_2$ used
    - b) 0.035 ml $Ba(ClO_4)_2$ used
    - c) 0.035 ml $Ba(ClO_4)_2$ used
    - d) 0.037 ml $Ba(ClO_4)_2$ used

3. Combust Schöniger sample holder (ashless filter paper flag) with 10 ml water, 3 drops 30% hydrogen peroxide. Transfer resulting solution with 40 ml isopropyl alcohol, add indicator and titrate with barium perchlorate (0.01N).

   a) 0.060 ml $Ba(ClO_4)_2$ used

   b) 0.050 ml $Ba(ClO_4)_2$ used

   c) 0.050 ml $Ba(ClO_4)_2$ used

   d) 0.050 ml $Ba(ClO_4)_2$ used

The third series of values indicates a small quantity of sulfate ion is present in the Schöniger flask and should be taken into consideration.

STANDARDIZATION OF 0.01 MOLAR BARIUM PERCHLORATE SOLUTION

An approximate 0.01 M $Ba(ClO_4)_2$ solution is prepared by dissolving 3.3627 grams of anhydrous $Ba(ClO_4)_2$ in 200 ml of distilled water in a one liter volumetric flask. Add isopropyl alcohol nearly to the mark and add, dropwise, perchloric acid until pH is between 2.5-4.0. Check pH by taking small aliquotes and using regular laboratory pH meter. Then dilute to mark with isopropyl alcohol. Standardize against 0.01 N sulfuric acid as given below.

To a 100 ml beaker add 5 ml of 0.01 N H_2SO_4 and 5 ml of water. Add 40 ml of C.P. isopropyl alcohol. Add 3 drops of Thorin and 2 drops of methylene blue to give a greenish-yellow solution. Titrate with 0.01 M barium perchlorate until the color changes from yellow to pink. Note: The color change is very sharp but the titration should be performed slowly near the end-point and with rapid stirring.

<u>Calculations:</u>

$$\text{Reaction - } Ba(ClO_4)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HClO_4$$

At equivalence point: Moles H_2SO_4 = Moles $Ba(ClO_4)_2$

$$M_{H_2SO_4} \frac{\text{Moles}}{\text{Liter}} \times \frac{V_{H_2SO_4}}{1000} \text{ (liters)} = M_{Ba(ClO_4)_2} \frac{\text{Moles}}{\text{Liter}} \times \frac{V_{Ba(ClO_4)_2}}{1000} \text{ liter}$$

Where:

$M_{H_2SO_4}$ = Molarity of H_2SO_4

$M_{Ba(ClO_4)_2}$ = Molarity of $Ba(ClO_4)_2$

$V_{H_2SO_4}$ = Volume of H_2SO_4 (aliquot) ml taken

$V_{Ba(ClO_4)_2}$ = Volume (ml) of $Ba(ClO_4)_2$ used in titration

$$\therefore M_{Ba(ClO_4)_2} = M_{H_2SO_4} \times \frac{V_{H_2SO_4}}{V_{Ba(ClO_4)_2}}$$

Typical standardization values are summarized below. A standard solution of H_2SO_4 = 0.006402 M.

Aliquot of H_2SO_4 used	Volume $Ba(Cl)_4)_2$	Molarity $Ba(ClO_4)_2$
5 ml	3.452	0.009267
5 ml	3.462	0.009243
5 ml	3.461	0.009246
5 ml	3.440	0.009300
5 ml	3.460	0.009248
5 ml	3.463	0.009240
5 ml	3.460	0.009248
Average 5 ml	Average 3.457	Average 0.009256

Note: This standardization procedure should be performed with the utmost care in view of the dependence of all subsequent sulfur determinations on these results.

SELECTION OF SAMPLE SIZE

In the determination of the sulfur content of an organic compound containing organic sulfur, the selection of the sample size is made so as to minimize, insofar as is possible, the various errors that are involved in the determination. The major aim is to adjust the volume of titrant consumed so that it is relatively large compared with the errors associated with end-point determination and burette reading. If the volume of titrant consumed is 5.00 ml., then an error of 0.05 ml in the end-point evaluation and burette reading is found. This leads to an error of 1% in the percent sulfur. An error of 0.05 ml is regarded as considerably greater than one should encounter in end-point evaluation or burette reading. Consider the following equation:

$$\text{(I)} \quad \%\ \text{sulfur} = \frac{M_s V_s}{1000} \times \frac{32.066}{\text{wt. sample (g.)}} \times 100$$

where: M_s = Molarity of barium perchlorate solution

V_s = Volume (ml.) of barium perchlorate solution

32.066 - Atomic weight of sulfur

Substitute the following values into Equation (I): $M_s = 0.01$; $V_s = 4.50$ ml.; and solve for the weight of the sample.

$$\text{(II)} \quad \text{weight of sample (grams)} = \frac{0.144}{\%\ \text{sulfur}}$$

or

$$\text{(III)} \quad \text{weight of sample (mgs.)} = \frac{144}{\%\ \text{sulfur}}$$

Equation (III) provides a very simple means for selecting sample size provided some idea of the magnitude of the sulfur content is available. In some cases, due to insufficiency of sample, it may not be possible to select the size of the sample by the above considerations. In such cases, it would be well to utilize as large a sample as can be obtained, short of the above criterion.

PROCEDURE

(1) Solid samples are weighed accurately on an appropriate microchemical

balance in a closed charging tube. Liquid samples are weighed in a sealed capillary tube and the samples are transferred to an ashless Schöniger combustion paper and combusted according to the procedures outlined by Schöniger.

(2) To a 500 ml. combustion flask add 10 ml. distilled water and 3 drops of 30% hydrogen peroxide.

(3) The samples are combusted and allowed to remain untouched until no further vapors are observed in the flasks. As a precaution against leakage, a small volume of isopropyl alcohol may be added to the lip of the flasks.

(4) Transfer the combustion products to a 100 ml beaker with isopropyl alcohol keeping the total volume at 50 ml.

(5) One should check the apparent pH of the solution to be titrated to insure a pH of 2.5-4.0. The pH adjustments should be made with 0.01 N perchloric acid or 0.01 NH_4OH.

(6) Add 3 drops of thorin and 2 drops of methylene blue.

(7) Titrate to the first color change with 0.01 M barium perchlorate.

Calculations of experimental results

Available data:

(1) M = Molarity of barium perchlorate

(2) V = Volume of barium perchlorate used in titration

(3) Weight of Sample in milligrams

$$\% \text{ Sulfur} = \frac{M \times V \times 32.066}{\text{Sample Weight}}$$

INTERFERENCES

Several authors have reported no interference from chloride, bromide, iodide, nitrate or phosphate ions after combustion in the Schöniger flask, but fluoride must be masked with some agent to prevent interference. A. M. G. McDonald (Reference 2.) recommends the use of boric acid, while several other authors (Reference 2.) use aluminum, and iron.

Hydrogen peroxide added to convert all sulfur to the SO_4^{--} form need not be destroyed prior to titration.

PRECISION AND ACCURACY OF THE SULFATE DETERMINATION

An evaluation of the precision and accuracy of the determination of sulfur by the barium perchlorate-thorin indicator method has been made. In Table I are listed a series of results obtained for cystine, a National Bureau of Standards certified standard, and chloropropamide, a Quality Control working standard.

The precision and accuracy data are summarized below:

Compound	% Sulfur Found (Average Value ± 1.96 x Std. Deviation)	% Sulfur, Theory
Cystine	26.74 ± 0.27%	26.69
Chloropropamide	11.79 ± 0.14%	11.59

TABLE I. SULFUR DETERMINATION OF CYSTINE AND CHLOROPROPAMIDE

A. Cystine
Source: National Bureau of Standards

% Sulfur	Deviation From Average	(Deviation)^2
26.87	+.13	.0169
26.50	-.24	.0576
26.65	-.09	.0081
26.66	-.08	.0064
26.86	+.12	.0144
26.80	+.06	.0036
26.85	+.11	.0121
Average Value: 26.74	Total	.1191

$$\sigma = \pm\sqrt{\frac{.1191}{6}} = \pm\sqrt{.0199} = \pm 0.14$$

$$\text{Average Value} = 26.74 \pm 1.96 \times 0.14$$
$$= 26.74 \pm 0.27\%$$

Theory = 26.69

B. Chloropropamide
Source: Quality Control Standard

% Sulfur	Deviation From Average	(Deviation)^2
11.81	+.02	.0004
11.89	+.10	.0100
11.70	-.09	.0081
11.84	+.05	.0025
11.71	-.08	.0064
11.77	-.02	.0004
11.78	-.01	.0001
Average Value: 11.79	Total	.0279

$$\sigma = \pm\sqrt{.0047} = \pm 0.07$$

$$\text{Average Value} = 11.79 \pm 1.96 \times 0.07$$
$$= 11.79 \pm 0.14$$

Theory = 11.59

REFERENCES

1. J. S. Fritz and M. Q. Freeland, Anal. Chem. 26, 1593 (1954).

2. C. L. Wilson and D. W. Wilson, Comprehensive Analytical Chemistry, Elsevier Publishing Co., p. 534-35, 1960.

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* University of Cincinnati Cincinnati, Ohio	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP

3. REPORT TITLE

THE DETERMINATION OF SULFUR IN ORGANIC COMPOUNDS

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Work covers period from December 1964 to December 1965.

5. AUTHOR(S) *(Last name, first name, initial)*

Thomas M. Downer, Jr., and Charles R. Riber, Jr.

6. REPORT DATE May 1966	7a. TOTAL NO. OF PAGES 9	7b. NO. OF REFS 2

8a. CONTRACT OR GRANT NO. AF 33(615)-2746 b. PROJECT NO. 7360 c. Task No. 736005 d.	9a. ORIGINATOR'S REPORT NUMBER(S) AFML-TR-66-147 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*

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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Air Force Materials Laboratory Research & Technology Division Wright-Patterson AFB, Ohio 45433

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DD FORM 1 JAN 64 1473

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Schöniger Combustion method						
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