

MICRODETERMINATION OF SULFUR AND HALOGENS IN NONVOLATILE SUBSTANCES IN SOLUTION BY THE SCHÖNIGER FLASK METHOD

CLARA MCGREW AND CECIL H. VANETTEN
Northern Regional Research Laboratory, Peoria, Illinois

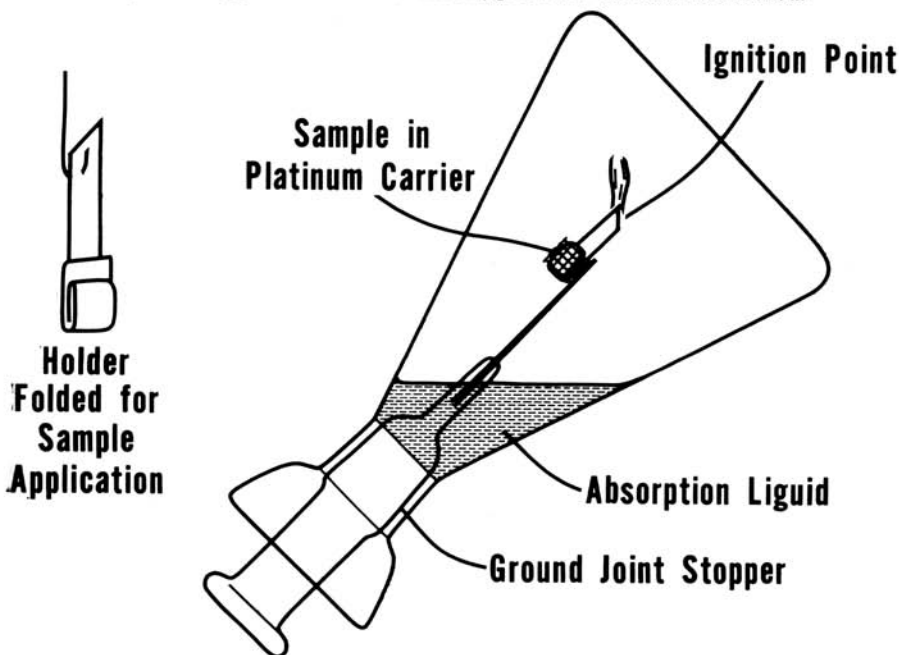
ABSTRACT.—A simple procedure is described for the analysis of solutions for sulfur and halogen content by the oxygen flask method. The method gives an average recovery of 100.32% with a standard deviation of 1.376 for 22 sulfur determinations on solutions of S-benzylthiuronium chloride. Good results are also obtained on solutions of other known compounds, extracts from natural products, and of commercial preparations. Three compounds boiling below 200°C. gave low results.

In 1955, Schöniger reintroduced the use of the oxygen flask for de-

composing organic material before analysis. He first described this flask as used in an analytical method for halogen (1955) and later extended its use to include analysis for sulfur (1956).

Either a 250- or 500-ml. Erlenmeyer flask is modified by a funnel-like extension of the top. The flask is fitted with a ground glass stopper shaped into a sample holder. The top of the holder extends above the flask to form a handle. A platinum net or basket is fused into the lower part of the holder (Fig. 1).

Figure 1. Apparatus used for the oxygen flask combustion method.



The sample to be analyzed is weighed onto a 1-inch square ashless filter paper that has a narrow wicklike extension of one side. The sample is wrapped in the paper and placed in the platinum net.

The flask is first charged with a suitable absorbing solution and then filled with oxygen. The paper wick is ignited, and the sample holder immediately thrust into the flask. When combustion is complete, the gases are dissolved by the absorbing solution, which is then analyzed.

The use of this oxygen flask has greatly simplified the method of analysis of organic compounds for elements such as sulfur or halogen. In 1961, MacDonald discussed absorption solutions and methods of analyzing these solutions for 13 elements.

Sulfur determinations by the oxygen flask method were statistically evaluated by Malissa and Machherndl (1962). The 18 compounds they studied varied in sulfur content from 10 to 55%. There was no significant relationship between the standard deviation and the sulfur content, or between the standard deviation and the nature of the sulfur bond.

Although Ma and Gutterson (1964) discuss in a review article a number of techniques and modifications of the oxygen flask method as applied to specialized analytical problems, we have found no reference to its application to organic substances in solution. Therefore, we are reporting a suitable method for analysis of solutions. We also report the accuracy and precision of our analytical results, possible uses of the method as modified, and some of its limitations.

MATERIALS AND METHODS

The oxygen flask, sample holder, carrier paper, and pipettes are all available from almost any laboratory supply house. Gouverneur and Eerbeek (1962) describe a flask safety jacket which can be made from heavy metal gauze shaped into a cone and fitted into a solid metal base.

Purity of the compounds which were used in testing the procedures were established as follows: S-benzylthiuronium chloride, cystine, methionine, and lysine hydrochloride were pure compounds as indicated within the accuracy and precision of analysis for the elements present. 1-Allyl-2-thiourea was an Eastman white label compound. The inorganic compounds, H_2SO_4 , NH_4SCN , and $Na_2S_2O_3 \cdot 5H_2O$, were of reagent grade. The ethylene chlorohydrin and 3-bromo-1-propanol were indicated by analysis for halogen content to be of 90% purity. The aqueous solution of trichloroacetic acid used for analysis was made from Eastman white label product and the amount of trichloroacetic acid present measured by titration with standard base.

Samples of these compounds were accurately weighed and dissolved in a suitable volume of water or other solvent. A volumetric pipette was used for the 1-ml. samples, and micropipettes for volumes of less than 1 ml. The solutions were pipetted on to paper holders suspended from a rack by a small wire hook as shown in Figure 1. After air drying, the papers were wrapped in a second paper holder and, finally, were dried for at least 1 hour in a vacuum desiccator over P_2O_5 at 20-30 mm. The samples were burned as usual, and the flask contents analyzed for either sulfur or halogen by the methods of D. C. White (1961, 1962).

As a safety precaution, all volatile solvents must be completely removed from the flask before the next combustion. Also, when substances dissolved in organic solvents are analyzed, the solvent must be completely removed before ignition. Using these precautions, we have performed thousands of oxygen flask combustions without a single explosion. Nevertheless, we *always* carry out the combustion with the flask in the metal basket as an added safety measure.

RESULTS AND DISCUSSION

The average sulfur or halogen values and the standard deviation from

analysis of solutions of eight compounds are shown in Table 1. Based on all 22 analyses of S-benzylthiuronium chloride for sulfur, the method gave an average recovery of 100.32% with a standard deviation of 1.376. The accuracy and precision are of the same order we normally obtain for routine microanalytical determinations, and are comparable to the accuracy and precision reported for oxygen flask methods for sulfur (Malissa and Machherndl, 1962).

Table 2 contains the results of analysis of some extracts and commercial products. These samples may suggest use of the method in control

work, analysis of plant extracts, inspection of commercial products, or in research on natural products. No analytical balance is required for these determinations.

Table 3 indicates that the method is not applicable to the analysis of compounds of high volatility when the solvent is removed as described.

Aqueous solutions were quantitatively transferred from the pipette to the paper without difficulty. In some determinations with low-boiling organic solvents, such as acetone, the solute tended to crystallize on the tip of the pipette. This crystallization made quantitative transfer of the material difficult.

TABLE 1.—Compounds of Known Composition.

Compounds	No. of Detns.	Sample Size		Sulfur, %		
				Found		Expected
		ml. ¹	mg.	Av.	Standard Deviation	
S-Benzylthiuronium chloride	18	0.25	6-7	15.86	0.217	15.82
S-Benzylthiuronium chloride ²	4	1.00	8.0	15.90	0.217	15.82
1-Allyl-2-thiourea	5	0.50	4.0	27.35	0.134	27.54
Cystine ³	3	0.50	3.0	26.56	0.201	26.67
Methionine	5	0.50	6.8	21.39	0.136	21.45
NH ₄ SCN	6	0.50	2.5	39.98	1.043	40.45 ⁴
Na ₂ S ₂ O ₃ ·5H ₂ O	4	0.50	5.0	24.60	0.285	25.04 ⁴
S-Benzylthiuronium chloride	6	0.25	6.5	17.04 ⁵	0.105 ⁵	17.49 ⁵
Lysine·HCl	4	0.50	5.0	19.17 ⁵	0.289 ⁵	19.41 ⁵

¹ Water solutions unless otherwise specified.

² Dissolved in 80% ethanol.

³ Dissolved in 1 normal HCl.

⁴ Expected value obtained by analysis of solid.

⁵ Percent chlorine.

TABLE 2.—Extracts and Commercial Products.

Substance	No. of Detns.	Sulfur, mg./ml.		
		Found		Present
		Av.	Standard Deviation	
Aqueous plant extract	6	2.71	0.030	2.74 ¹
CHCl ₃ plant extract	6	0.470	0.010
Sugar substitute	7	6.52	0.117	6.28 ²
Detergent	8	3.44	0.053	3.48 ³
2,4,5,-T ⁴ (brush killer)	6	3.65 ⁵	0.070	3.66 ^{3,5}

¹ Determined by an independent method.² Computed from manufacturer's concentration figure.³ Determined by analysis of solid material or concentrate.⁴ Dissolved in 1-1 pentane-hexane and benzene.⁵ Percent chlorine.

TABLE 3.—Boiling Point versus Recovery of Halogen or Sulfur.

Compound	B. P., °C.	Recovery, %
Ethylene chlorohydrin	128-130	0-1
3-Bromo-1-propanol	170-175	28-38
Trichloroacetic acid	196-197	65-88
Sulfuric acid	340 (decomp.)	98-102

ACKNOWLEDGMENTS

We are indebted to Dr. William F. Kwolek for statistical interpretations and to Mrs. Anita Dirks for technical assistance.

This paper was a contribution to the honorary Symposium for Nicholas D. Cheronis at the Annual Meeting of the Illinois State Academy of Science, Chemistry Section, Northern Illinois University, DeKalb, Illinois, April 23, 1965. The Northern Regional Research Laboratory is a laboratory of the Northern Agricultural Research Service, U.S. Department of Agriculture; the mention of firm names or trade products does not imply that they are endorsed or recommended

by the Department of Agriculture over other firms or similar products not mentioned.

LITERATURE CITED

- GOUVERNEUR, P., and C. C. F. EEBEEK. 1962. A simple safety precaution in oxygen flask combustions. *Anal. Chim. Acta*, 27:303-304.
- MA, T. S., and M. GUTTERSON. 1964. Organic microchemistry. *Anal. Chem.* 36:150R-163R.
- MACDONALD, A. M. G. 1961. The oxygen flask method. *Analyst* 86:3-12.
- MALISSA, H., and L. MACHHERNDI. 1962. Eine Systematische Untersuchung zur Schwefelbestimmung in organischen Substanzen nach der Kolbenmethode von W. Schöniger. *Mikrochim. Acta*: 1089-1094.
- SCHÖNIGER, W. 1955. Eine mikroanalytische Schnellbestimmung von Halogen in organischen Substanzen. *Mikrochim. Acta*: 123-129.
- _____. 1956. Die mikroanalytische Schnellbestimmung von Halogenen und Schwefel in organischen Verbindungen. *Mikrochim. Acta*: 869-875.
- WHITE, D. C. 1961. Micro determinations of chlorine or bromine in organic compounds. *Mikrochim. Acta*: 449-456.
- _____. 1962. Simultaneous determinations of sulphur and chlorine in organic compounds. *Mikrochim. Acta*: 807-811.

Manuscript received August 14, 1965.