[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ARKANSAS]

THE RAPID DETERMINATION OF SULFUR IN ORGANIC COMPOUNDS[1]

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With the exception of certain special cases the determination of sulfur in an organic compound involves (1) oxidation of sulfur to sulfate and (2) determination of sulfate ion. The Carius method and numerous methods which depend upon fusions in open vessels are still in use for the oxidation of sulfur compounds, but are open to objection in that either they are too complicated and time consuming or they are not universally applicable.

These objections can hardly be urged against the fusion method devised by Parr;[2] because of its great rapidity and simplicity this method should be more generally used than seems to be the rule at present. The Parr method was employed in the work described herein.[3]

The estimation of sulfate ion is ordinarily accomplished by the precipitation and weighing of barium sulfate. Accurate results may be obtained but the procedure is necessarily slow. It was considered desirable to supplant this with a volumetric method which would give as accurate results in much less time. A survey of the literature discloses several reliable volumetric methods, the simplest in principle and procedure being the method of Wildenstein.[4]

In this method a solution containing sulfate is titrated with a slight excess of barium chloride solution, the excess being determined with potassium chromate which is added until a yellow color is noted. A solution of a lead salt is used as external indicator when such is necessary. It was found on trial that this method could be applied but only with considerable difficulty.

The method has been modified so as to use ferrous thiocyanate as an external indicator. After removal of carbon dioxide and hydrogen peroxide from the solution as obtained from the bomb, chromate is added until tests with the ferrous thiocyanate indicator match the "standard end-point" hereinafter described. The barium sulfate is then precipitated, after which chromate is again added until tests match the standard end-

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[1] Paper No. 170, Journal Series, University of Arkansas.

[2] Parr, THIS JOURNAL, **30**, 764 (1908).

[3] For details of the method consult the Burgess-Parr Co., Moline, Ill. *Cf.* also Noyes, "Organic Chemistry for the Laboratory," Chemical Publishing Co., Easton, Pa., **1926**, p. 28.

[4] Wildenstein, *Z. anal. Chem.*, **1**, 323 (1862); Sutton, "Volumetric Analysis," Blakiston, **1924**, p. 337 (modification); Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, **1927**, Vol. I, p. 505 (modification). For discussion of the method see Kolthoff, "Volumetric Analysis," John Wiley and Sons, Inc., New York, **1929**, Vol. II, p. 418.

point. With this procedure the end-point is quickly and easily attained. The color at the end-point is very easy to match and the indicator is sufficiently sensitive to show a noticeable change of color upon the addition of 2 or 3 drops of chromate solution to a volume of 200 cc. It is neither necessary to wait for complete settling of the precipitate while adjusting the end-point, nor to repeatedly boil the solution during the analysis as in the Wildenstein procedure.

Procedure

The solution and washings from the bomb are collected in a 600-cc. beaker. A few chips of porous plate are added, the beaker is covered and the contents boiled for fifteen minutes. The solution is then treated with 3 or 4 drops of dilute phenolphthalein solution.[5] Concentrated hydrochloric acid is added until the reaction is distinctly acid. The solution is filtered[6] if necessary, then chromate solution is added from the buret until a slight yellow color is noted; about 10 drops will suffice. The solution is maintained at a temperature of 80–90° for about ten minutes, then allowed to cool to 70–80° and treated with dilute sodium hydroxide solution until a faint pink color is reached. Slight changes in *P*H during the titration will not notably affect the end-point; however, it is well not to add an excess of base. The indicator solution is prepared from potassium thiocyanate, 1.0 g., ferrous sulfate, 1.5 g., water, 50 cc., dilute (1:1) hydrochloric acid, 15 drops. If the solution is colored the color is discharged by the addition of sodium hyposulfite ($Na_2S_2O_4$).[7] About 0.010 g. will be required; an excess should be avoided. A testing solution is prepared from 100 cc. of water plus 10 drops of the standard chromate solution. The "standard end-point" is prepared by adding 4 drops of the testing solution to 2 drops of the indicator on a porcelain testing plate.

The solution being analyzed is now treated with chromate solution until the addition of 4 drops to 2 drops of indicator on the testing plate gives a color matching that of the standard end-point. This result is quickly attained, usually taking but a few moments.[8] Tests are best made from a pipet fitted with a rubber bulb ("medicine dropper" type). When the end-point is satisfactorily adjusted, the solution is held for five minutes and again tested at approximately the same temperature as before (70–80°). In the majority of cases there is no change, all peroxide having been removed by previous treatment. Twenty drops of 1:1 hydrochloric acid are added, after which the calculated amount of barium chloride solution plus an excess of 1 or 2 cc. is delivered from the buret. A large excess of barium solution should be avoided as it will delay the attainment of the final end-point.[9]

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[5] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, **1911,** Vol. I, p. 35.

[6] The total volume at this point should not exceed 200 cc.

[7] The indicator will remain colorless for three or four days if not placed in direct daylight. It may be "revived" several times with sodium hyposulfite without loss of sensitivity.

[8] If by error too much chromate solution is used the excess is removed by the addition of hydroxylamine hydrochloride solution (1/2%) drop for drop against the excess chromate. After standing for a few minutes the titration may proceed.

[9] When the percentage of sulfur in the compound is not known, the acidification noted above is omitted. Barium solution is added a few cc. at a time, the solution being set aside for about two minutes after each addition and a thorough stirring. When an excess of barium solution has been added the indicator will give no color. The solution is now acidified and the analysis completed in the usual way.

The solution is gently boiled for five minutes, cooled to 70–80° and neutralized with sodium hydroxide as before. Chromate solution is added until the end-point secured will match the standard end-point. After five minutes the solution is again tested. Ordinarily another small addition of chromate will be needed. After standing for another five minutes the end-point is usually unchanged. The solution is now acidified with 2 drops of 1:1 hydrochloric acid, held for five minutes at 80–90° and again neutralized with sodium hydroxide solution. In most cases the end-point will be unchanged by this treatment but in an analysis requiring a large amount of barium solution a little more chromate may be needed. With practice it will become unnecessary to cool the solution; the temperatures have been so chosen that with several analyses on hand the solutions will cool to the proper point during the various manipulations without extra attention. The complete analysis takes about one and one-half hours.

Preliminary Tests of the Method.—The $N/20$ barium chloride solution was standardized by weighing as barium sulfate. Expressed as mg. of sulfur per cc. of solution the average of five concordant results was 1.6360. The $N/20$ potassium chromate solution was standardized by weighing as barium chromate. Expressed as mg. of sulfur per cc. of solution the average of four concordant results was 1.602.

The ratio of the two solutions above was taken in 200 cc. of water, using the same technique as described above for analysis. The following ratios of potassium chromate-barium chloride were secured: 1.0228, 1.0214, 1.0223, 1.0207, 1.0226, 1.0254; average, 1.0226. Making use of the above ratio and the measured value of the chromate solution, calculation assigns to the barium chloride solution 1.6383 mg. sulfur per cc. The value actually found was 1.6360.

Lastly a sample of C. P. potassium sulfate was analyzed for sulfur by the precipitation and weighing of barium sulfate, giving the following values: 18.19, 18.19%. Analysis by the volumetric method gave: 18.22, 18.28%.

Results

The following table presents the results obtained in the analysis of several organic compounds by the volumetric method. As a check these compounds were also analyzed by the ordinary gravimetric procedure

TABLE I

ANALYSIS OF ORGANIC SULFUR COMPOUNDS

		Percentage of sulfur		
Compound	Calcd.	Volumetric method	Gravimetric check	Gravimetric method
o-Chlorobenzenesulfonamide	16.74	16.64, 16.73	16.40, 16.73	16.71
n-Butyl sulfone	17.99	18.11, 18.03	17.46, 17.48[a]	17.46, 17.80
Diphenyl sulfone	14.69	14.62, 14.52	15.05	14.54
Benzyl sulfide	14.98	14.98, 14.82	14.89[a]	14.83
Diphenyl sulfoxide	15.86	15.60, 15.66	16.10 (av.), 15.69[a]	15.73
Sulfonal	28.10	28.02, 27.90	27.96[a]	27.78
Di-*p*-tolyl sulfone	13.01	12.95, 12.89 12.98, 12.96	13.30	12.97
o-Benzoic sulfinide	17.52	17.47, 17.80		17.45
Allyl thiourea (crude)	27.63	26.43, 26.20	26.27[a]	26.53
N-Benzoylbenzenesulfonamide	12.28	12.26, 12.22 12.07	12.04[b]	12.22

[a] Precipitate digested with dilute nitric acid.

[b] Precipitate digested with oxalic acid.

following their oxidation in the Parr bomb. The gravimetric results are shown in Col. 5. Column 4 marked "Gravimetric check" presents results obtained as follows: immediately at the close of the volumetric analysis the solution was treated with 2 cc. of 1:1 hydrochloric acid and heated to boiling. Twenty-five cc. of hydrogen peroxide (3%) was added to the boiling solution. After the customary period allowed for digestion, the precipitate of barium sulfate was collected and weighed in the usual manner. Not all of the barium chromate is removed by this procedure; enough usually remains to give the precipitate an *extremely faint* yellow tint. However, the results show a fair agreement with those of the direct analysis and in some cases may prove of value as a check.

Summary

The Wildenstein volumetric method of analysis for sulfate has been modified by the use of ferrous thiocyanate as an external indicator and adapted to the analysis of organic compounds following their oxidation in the Parr bomb. Provision has been made for a gravimetric check upon the volumetric procedure.

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O-ALKYL SUBSTITUTED HYDROXYLAMINO ACIDS, ESTERS AND ALCOHOLS[1]

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N-Hydroxylamino acids of the type, $HONHC_nH_{2n}COOH$, have been prepared,[2] as have also O-hydroxylamino acids of the type, $H_2NOC_nH_{2n}COOH$,[3] but no O-alkyl substituted hydroxylamino acids or esters with the general formula, $RONR'C_nH_{2n}COOR''$, in which R′ and R″ may either be alkyl groups or hydrogen, are described in the chemical literature. As a part of a general study of O-alkyl substituted hydroxylamines, it was thought that it would be of interest to synthesize a few substances of this type and to investigate their properties, especially since they would be derivatives of that very important class of chemical compounds, the amino acids.

When ethyl bromo-acetate was treated with two molecular equivalents of O,N-dimethylhydroxylamine, there was formed ethyl methylmethoxy-

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[1] Presented in part at the Fall Meeting of the American Chemical Society at Swampscott, Massachusetts, September, 1928.

[2] Traube, *Ber.*, **28**, 2298 (1895); Gomberg, *Ann.*, **300**, 75 (1898); Hantzsch and Wild, *ibid.*, **289**, 309 (1896).

[3] Werner, *Ber.*, **26**, 1567 (1893); Werner and Sonnenfeld, *ibid.*, **27**, 3350 (1894); Werner and Bial, *ibid.*, **28**, 1378 (1895); Werner and Falck, *ibid.*, **29**, 2658 (1896).