tains other compounds. The solutions used in the analyses have been described previously.

No.	Compounds present.	Mgs. Ba taken.	Mgs. Ba found.	Error.
1	0.5 gm $NaNO_3$	85.84	85.96	+0.12
2	0.5 gm. $NaC_2H_3O_2$	85.84	86.41	+0.57
3	0.5 gm. KCl	85.84	85.95	+0.11
4	3.0 gms. KCl	85.84	85.92	+0.08
5	2.0 gms. NaCl	85.84	85.88	+0.04
6	3.0 gms. NaCl	85.84	86.06	+0.22
7	0.5 gm. NH_4Cl	85.84	85.44	—0.40
8	2.0 gms. NH_4Cl	85.84	85.49	—0.35
9	0.5 gm. $MgCl_2$	85.84	85.96	+0.12
10	2.0 gms. $MgCl_2$	85.84	85.40	—0.44

On the basis of a fairly large number of analyses, conducted under widely divergent conditions, it may be claimed that the method permits the determination of barium with an error not greater than a few tenths of a milligram in the hundred; when pure barium salts are analyzed, the error rarely amounts to more than a single tenth. The exceptional properties of the precipitate make the method of manipulation more convenient than any of the known volumetric methods. Two analyses can easily be conducted at the same time, and the average time required for their completion is about one hour and thirty minutes.

NEW YORK UNIVERSITY.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORIES OF CLARK UNIVERSITY.]

ON THE DETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS.

BY C. W. BACON.

Received October 28, 1908.

Introductory.—Halogens are at present determined in organic compounds almost exclusively by the method of Carius. While generally reliable, the method is quite laborious. First, it requires some hours of actual work, including, as it does, a gravimetric determination of silver halide. Besides, eight or nine hours' heating with fuming nitric acid involves a delay in getting the final result, which is at times extremely inconvenient.

About two years ago Stepanoff[1] published a method for the quantitative determination of halogens in organic compounds based on the reducing action of nascent hydrogen. He dissolves a weighed amount of the halogen compound in 20 to 40 cc. of 98 per cent. alcohol in an Erlenmeyer flask connected with a reflux condenser, places the flask on a water-bath and adds gradually through the condenser twenty-five times the amount of sodium corresponding to the reaction:

---

[1] Stepanow, *Ber.*, **39**, 4056 (1906).

$$R.Hlg + C_2H_5.OH + 2Na = Na.Hlg + C_2H_5.ONa + R.H.$$

When the action is over, he adds 20 to 40 cc. of water, distils off the alcohol, acidifies strongly with nitric acid, and determines the halogen in the resulting solution by Volhard's method.

Stepanoff's method was tried in these laboratories, exactly as described by its author, in connection with a study of the esterification of some refractory aromatic acids containing halogens. The results, however, were entirely unsatisfactory. The figures yielded by consecutive analyses of one and the same substance differed greatly from one another and were many per cent. removed from the truth.

At the request of Professor Rosanoff, I then undertook to reinvestigate the subject with a view to ascertaining under what conditions, if at all, nascent hydrogen can really be relied upon to reduce organic halogens quantitatively. The analytical conditions and procedure recommended below are the result of a large number of painstaking trials. If the simple directions are followed, success may be confidently expected in every case. A single determination requires about two hours; but if three or four determinations are carried on simultaneously, a considerable number of analyses can be conveniently performed in the course of a working day.

Analytical Directions.—Introduce about 0.2 gram of the halogen compound into a dry pear-shaped (Kjeldahl) flask.

If w is the number of grams of the compound taken, add $156w$ cc. of alcohol (*at least* 98 per cent.) if the compound contains chlorine, or $68w$ cc. if the compound contains bromine, or $44w$ cc. if the compound contains iodine. Connect the flask with a reflux condenser, clamp it over a square of wire gauze covered with a thin sheet of asbestos, and warm with a Bunsen burner until the substance is dissolved.

Introduce very gradually, through the condenser, a total of $19.5w$ grams of sodium if the compound contains chlorine, or $8.5w$ grams of sodium if the compound contains bromine, or $5.5w$ grams of sodium if the compound contains iodine.[1] *This operation should be extended over at least thirty minutes.* Toward the end of the operation maintain the solution at the boiling-point by means of a Bunsen burner, and when the introduction of the sodium is complete, boil the solution gently for one hour longer.

Then allow the temperature of the solution to fall to about 50 or 60°, dilute through the condenser with cold water, acidify with nitric acid, add an excess of silver nitrate, and on complete cooling determine the excess of silver titrimetrically by Volhard's method. If the halogen involved is chlorine, filter out the precipitated silver halide before titrating with

---

[1] These quantities represent about 15 times the amount of sodium corresponding to the chemical equation given in the preceding section, assuming the substance analyzed to contain 100 per cent. halogen.

sulphocyanate. If the halogen is bromine or iodine, filtration is unnecessary.[1]

A few additional remarks may not be superfluous. The statement that the liquid should be boiled for an hour after the solution of the sodium is complete, may seem surprising, for sodium ethylate is believed by some to have no action upon halogen compounds of the aromatic series. While the additional boiling is probably unnecessary in the case of aliphatic compounds, the following experiment will show that the operation is not useless in the case of refractory aromatic compounds. An alcoholic solution of hexachlorbenzene was boiled for one hour with the amount of sodium ethylate required by the above directions. The solution, diluted with water and acidified, was found to contain no less than 25 per cent. of the amount of sodium chloride corresponding to the hexachlorbenzene used. While in similar experiments I was unable to transform monobrombenzene into phenetol, there is no doubt but that the alcoholates of sodium attack halogens in a benzene ring quite vigorously. In fact, if the action were not somewhat too slow for analytical purposes, it might be employed, independently of any other method, for the quantitative estimation of halogens in organic compounds.

Special experiments showed that distilling off the alcohol (as Stepanoff does) before titrating with sulphocyanate is unnecessary. In the solution copiously diluted with water, the alcohol has no effect upon the end-point.

Finally, Kahlbaum's sodium was found to be sufficiently pure for use in connection with the method here proposed.

Some Test Results.—The following results were obtained by the method proposed:

1. A sample of 1-2-4-6-trichlorbenzoic acid prepared in this laboratory was found to contain 47.29 per cent. of chlorine. Calculated, 47.19 per cent.

2. Two samples of ethyl 1-2-4-6-tribrombenzoate, containing theoretically 61.99 per cent. of bromine, gave 61.32 per cent. and 61.25 per cent., respectively. The substance was probably not quite dry, but the agreement of the two results is satisfactory.

3. A sample of pure benzene hexachloride was found to contain 73.23 per cent. of chlorine. The theoretical percentage for $C_6H_6Cl_6$ is 73.15.

4. *Ten consecutive analyses* of carefully dried hexachlorbenzene (Kahlbaum's), with theoretically 74.71 per cent. chlorine, gave the following results: 74.78, 74.71, 74.78, 74.76, 74.62, 74.64, 74.69, 74.78, 74.71, 74.75 per cent.

Taking into account the fact that the four substances used are among the most stable organic halogen compounds, these results may be con-

---

[1] See Rosanoff and Hill, THIS JOURNAL, **29**, 269 (1907).

sidered as sufficient proof of the general applicability and accuracy of the method.

The investigation was carried out under the guidance of the Director of these laboratories, Professor M. A. Rosanoff, whom the writer wishes to thank again for his friendly interest and assistance in the work. Acknowledgment is also due to Dr. W. L. Prager for his assistance in the early part of the work.

WORCESTER, MASS., June, 1908.

[FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, DEPARTMENT OF ANIMAL HUSBANDRY, UNIVERSITY OF ILLINOIS.]

THE DETERMINATION OF TOTAL SULPHUR IN URINE.

BY F. W. GILL AND H. S. GRINDLEY.

Received October 28, 1908.

In connection with the nutrition investigations of this laboratory, it became necessary to make a large number of total sulphur determinations in human urine. The sodium peroxide method as devised and described in detail by Folin[1] for the determination of total sulphur in urine was selected for this work. Some time after this method had been in use, it was noticed that more or less frequently the fusion resulting evolved hydrogen sulphide gas upon being acidified with the hydrochloric acid. The discovery of this fact was a great surprise and at the same time very discouraging since this method had already been used in determining the total sulphur in several hundred samples of urine.

This being the case much time and labor were devoted to studying the Folin method with the hope that by finding the proper method of procedure and observing the proper precautions the method could still be used in the investigation undertaken. The details of the method as described by Folin were closely and carefully followed in all respects, and repeated attempts were also made to modify the Folin method by increasing the time of fusion and by the addition of a greater quantity of sodium peroxide so as to insure the complete conversion of the sulphur of the urine into sulphuric acid. However as a result, the method still gave fusions which upon acidifying with the hydrochloric acid evolved hydrogen sulphide gas. It was found in this connection that the addition of two or three grams of sodium peroxide to the hot fused mass during the oxidation gave fusions which did not liberate hydrogen sulphide upon acidifying. It should be noted here that the Folin sodium peroxide method as applied to urine does not, like the Osborne[2] sodium peroxide method as used for the determination of sulphur in air-dried foods and other dry substances, specifically state to add sodium peroxide to the hot fusion

---

[1] *J. Biol. Chem.*, 1, 157 (1906).

[2] This Journal, **24,** 142 (1902). *Ibid.*, **26,** 111 (1904).