stop-cocks, especially after the apparatus had stood unused for some time. That this trouble was not serious, is born out by the fact that more than one thousand determinations have been made with the first glass apparatus constructed, and it is in perfect condition at the present time. It does require some little skill to manipulate the apparatus. However, with a little experience, accurate determinations of oxygen may be easily and rapidly made.

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[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY.]

A VOLUMETRIC METHOD FOR THE DETERMINATION OF BARIUM.

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Introduction.—Volumetric methods for the determination of barium appear to be few in number and somewhat limited in application. Sutton enumerates five methods in all, of which the best known is probably the direct titration of the barium compound in alkaline solution with standardized potassium dichromate[1] until the supernatant liquid assumes a yellow color. The precipitate may also be filtered and washed, reduced by a measured excess of a ferrous salt, and the residual ferrous iron titrated with potassium permanganate.[2] Barium hydroxide or carbonate may be titrated directly with standardized acid,[3] while the neutral salts may either be titrated with sodium carbonate, using phenolphthalein as indicator,[3] or may be precipitated with ammonium hydroxide and carbonate and the washed barium carbonate titrated with standardized acid.[4] The new method here proposed depends upon the precipitation of barium as iodate and upon the oxidizing action of this compound upon an iodide solution, with subsequent titration of the free iodine with sodium thiosulphate.

Discussion of the Method.—The solubility of barium iodate in pure water is given[5] as 0.028 g. of salt, or about eight mg. of barium, per hundred cc. of solution at 25°, an amount too large to admit treatment of the compound as an insoluble salt. In accordance with the theory of electrolytic dissociation, however, it might be expected that the solubility could be reduced to a negligible amount by the presence of a sufficient excess of a soluble iodate, provided that the barium iodate approximates

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[1] Sutton, *Volumetric Analysis*, *London*, 1904, p. 161.

[2] *Ibid.*, p. 162. See also Mohr, *Titrirmethode*, Braunschweig, 1886, p. 346.

[3] *Ibid.*, p. 69.

[4] *Ibid.*, p. 70.

[5] Trantz and Anschütz, *Z. physik. Chem.*, **56**, 238 (1906).

complete dissociation when in saturated solution. A series of experiments showed that the desired condition is realized in neutral or alkaline solution when an excess of potassium iodate is used amounting to one-fiftieth formula weight per liter. Under these conditions the barium is so completely precipitated that 100 cc. of the filtrate show no turbidity upon being warmed with sulphuric acid. It was found that the solubility of the salt was increased slightly by the presence of other compounds, for which reason a concentration of iodate twice that stated above is recommended in carrying out the analysis.

The properties of the precipitated barium iodate are almost ideal for analytical work. It forms a white granular substance, settling quickly and leaving a perfectly clear liquid above; the precipitation is complete within five minutes, if the mixture is well stirred. The granules are of sufficient size to filter easily without choking the paper, and a second filtration is but very rarely necessary. In these respects the compound is in marked contrast with other barium salts, such as the sulphate, carbonate[1] and chromate, or with the insoluble salts of the alkaline-earth metals as a class, which almost without exception are difficult to handle, require special precautions during the precipitation, and usually necessitate repeated filtration for their complete removal from the filtrate.

The critical point in the analysis of the barium iodate is its treatment after filtration. The precipitate cannot, of course, be washed with water, in which its solubility is far too great. Experiments were therefore conducted to ascertain whether a more suitable liquid for the washing could be found. Samples of freshly precipitated barium iodate were rotated at room temperature for twelve hours with the ordinary concentrated ammonia (sp. gr. 0.90) and with 95 per cent. alcohol respectively, with the results which follow:

Solubility of $Ba(IO_3)_2$ in 85 per cent. alcohol,	3.1 mg. Ba per 100 cc.
Solubility of $Ba(IO_3)_2$ in conc. NH_4OH,	5.6 mg. Ba per 100 cc.
Solubility of $Ba(IO_3)_2$ in water,[2]	8.0 mg. Ba per 100 cc.

Either concentrated ammonia or alcohol would therefore be preferable to water for washing purposes. It proved impossible, however, to make direct use of alcohol since it precipitates even the water-soluble iodates, which choke the filter-paper and cannot be removed by a reasonable number of washings. A modified procedure has therefore been adopted; the precipitate is first washed a few times with concentrated ammonia, to remove the greater part of the excess iodate, and then finally subjected to several washings with alcohol. A series of test analyses was made to ascertain the extent to which this treatment might affect the accuracy of the results; constant quantities of barium chloride solution

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[1] Knöfler: *Ann.*, **230**, 345 (1885).

[2] Trantz and Anschütz: *Loc. cit.*

were precipitated with excess of potassium iodate and the precipitates washed with varying quantities of ammonium hydroxide and alcohol, and finally analyzed according to the directions given later.

NH_4OH washings.	C_2H_5OH washings.	Mgs. Ba taken.	Mgs. Ba found.
2	3	84.40	84.40
3	3	84.40	84.42
4	6	84.40	84.49
5	3	84.40	84.24
8	3	84.40	83.81
3	8	84.40	84.03

The results indicate that the precipitate is not sensibly affected by being washed with ammonia from three to four times, or with alcohol from three to six times; when washed with ammonia five or more times, or with alcohol eight times, the precipitate loses slight but detectable amounts. In analyzing barium solutions by this method it is therefore recommended to wash the precipitate three times with concentrated ammonia and three to six times with 95 per cent. alcohol.

In order to test this point still further, the ammoniacal and alcoholic washings have been tested for barium in over one hundred and fifty analyses made in the course of this investigation. These washings averaged about 25 cc. of ammonia and 30 cc. of alcohol in each analysis, corresponding to about 8 cc. for each washing. The ammonia always contained slight traces of barium, which were estimated at from one-tenth to three-tenths of a milligram; the alcohol in many cases contained no barium that could be detected, and in a few cases traces that could hardly equal one-tenth of a milligram. That the quantity of dissolved barium is less than its full solubility value in the respective solvents would be expected—first, because the potassium iodate used as precipitant is still in contact with the barium iodate during the washings with ammonia, reducing the solubility of the precipitate, and secondly, because granular and crystalline precipitates such as the barium iodate are often slow in reaching their solubility equilibria.

The method may best be described by the following specific directions for its use.

Directions for Use of the Method.—The solutions required for the analysis are an approximately one-sixth normal solution of potassium iodate (about 36 grams per liter) and a one-tenth normal solution of sodium thiosulphate, standardized by any of the usual methods, preferably against a known iodate solution. The soluble barium compound to be analyzed is taken in an amount that will contain about 100 milligrams of barium, brought into solution in a small beaker, and rendered neutral or faintly alkaline by addition of ammonium hydroxide, which should be free from carbonates. Water is added to make up the volume to about

60 to 70 cc. After calculating approximately the quantity of sixth-normal iodate solution necessary to precipitate the barium, add this quantity together with an excess of 25 cc., stirring the mixture well and running in the iodate in a fine stream. Stir the mixture briskly for one minute and allow it to stand, with frequent stirring, for five minutes longer. Filter through a 7 cm. filter-paper, used either dry or filled in the usual manner with water to which a little potassium iodate has been added. During the filtration avoid spattering the liquid on the sides of the funnel, so that the subsequent washing may not be rendered more troublesome. Catch the filtrate in a clean beaker, and use portions of the clear liquid in transferring the precipitate to the paper; use of a rubber-capped stirring-rod facilitates the operation. Wash the precipitate three times with concentrated ammonium hydroxide, filling the paper to its upper edge, and continue the washings three or four times with 95 per cent. alcohol. Transfer the precipitate to a 500 cc. Erlenmeyer flask by perforating the paper and washing down the barium iodate with a stream of distilled water; finally add the washed filter-paper to the material in the flask. Add 50 cc. of a 10 per cent. solution of potassium iodide, which has previously been treated with sodium amalgam or whose iodate content has been determined by a blank test. Add 10 cc. of concentrated hydrochloric acid solution, cover the flask, and allow it to stand, with occasional shaking, for five minutes. Wash down the sides of the flask and titrate the free iodine with the standardized thiosulphate solution, using starch as indicator. Each molecule of thiosulphate used corresponds to one-twelfth atom of barium.

The method as given above may be applied to solutions of barium as hydroxide, chloride, bromide, iodide, nitrate, and acetate, or other soluble salt of an organic acid. Sodium salts may be present in any amount, and magnesium, ammonium, or potassium salts in amounts up to one-half gram, calculated as chlorides. The modifications necessary when the latter salts are present in larger amounts will be described in succeeding paragraphs.

The following analyses indicate the accuracy of the method when applied to pure barium compounds. They were made with a solution of barium chloride whose barium content was determined by gravimetric analysis, except in the case of No. 3, which was made with an analyzed solution of barium hydroxide. The thiosulphate solution was standardized against an analyzed potassium iodate solution. The potassium iodate (Kahlbaum's C. P. preparation) was analyzed by reduction to iodide by means of a slight excess of sulphurous acid, the iodide precipitated with a slight excess of silver nitrate solution, and the silver iodide filtered on a Gooch crucible and dried to constant weight at 120°.

Number.	Mgs. Ba taken.	Mgs. Ba found.	Error.
1	34.24	34.22	—0.02
2	34.24	34.20	—0.04
3	61.14	61.20	+0.06
4	85.84	85.83	—0.01
5	85.84	85.72	—0.12
6	120.08	120.25	+0.17

Effect of Foreign Bodies. Sodium Salts.—Analyses of a barium chloride solution to which were added quantities of a sodium chloride solution varying from one-half gram to three grams showed that no modification of the method is made necessary by the presence of sodium salts. When the sodium salt amounts to as much as two or three grams special care should be taken to stir the solution vigorously and continuously during the precipitation of the barium iodate, which will otherwise carry down small quantities of sodium iodate, giving rise to high values for the barium.

Potassium Salts.—When present in amounts up to one-half gram, potassium chloride does not noticeably affect the accuracy of the barium determination. When present in larger amounts, however, it gives rise to values for the barium which may be one to two milligrams high. The high values are probably due to the occlusion of potassium iodate. This salt can of course only be occluded from the undissociated portion of the compound, which is probably very small in quantity in the dilute solution from which the barium iodate is precipitated; when additional potassium salts are added, however, the dissociation is reduced and there is greater opportunity for the occlusion to occur. This occlusion can be prevented by carrying out the precipitation in hot solution. The faintly alkaline barium solution is heated nearly to boiling and the calculated excess of potassium iodate added in a thin stream, with constant stirring. The stirring should be continuous during the first one or two minutes, while the greater part of the precipitate is forming, after which the solution may be allowed to come slowly to room temperature or may even be cooled more quickly by immersion of the beaker in cold water. Frequent stirring is essential, whichever method of cooling be adopted, as small amounts of barium iodate will remain unprecipitated even after long standing, if the solution is left in quiet. When fully cooled, the mixture is filtered and the precipitate analyzed as usual. Under the above conditions of precipitation the barium iodate forms a mass of gritty, glass-like crystals, whose rate of solution in hydrochloric acid is much slower than that of the softer and finer material formed by precipitation in the cold. In order to avoid error from this source, the washed precipitate should be transferred to the Erlenmeyer flask with a rather small quantity of water, so as to avoid excessive dilution of the acid, and after addition of the potassium iodide and the hydrochloric acid the mixture should be shaken thoroughly until no particles of undissolved precipitate can be seen upon the bottom of the flask. Titration with thiosulphate before the oxidation of the iodide is complete is generally believed to give erroneous results. With the above modifications, the method may be applied to any mixture of barium and potassium salts. Analysis No. 4 in the following table was conducted in this way, while No. 3, in which only one-half gram of potassium chloride was present, was carried out without this modification.

Ammonium Compounds.—Ammonium salts exert a slight solvent action upon the barium iodate, even when the acidity due to their hydrolysis has been overcome by addition of ammonium hydroxide, while the latter compound decreases the solubility of the barium salt, as solubility determinations have shown. Neither of these factors is of sufficient importance to affect the precipitation of the barium iodate measurably under the conditions of the method. It was found, however, that high results are obtained in the presence of large amounts of ammonium salts, just as with potassium salts, the compound occluded being presumably ammonium iodate. Precipitation from a hot solution, conducted as described in the preceding paragraph, reduces the occlusion below the limits of analytical detection, as shown by analysis No. 8. When the amount of ammonium salt is less than one-half gram, calculated as chloride, the precipitation may be carried out in the cold; analysis No. 7 was performed under these conditions.

Magnesium Salts.—Magnesium salts affect the method in the same way as potassium and ammonium salts. The precipitation may be carried out in the cold when the magnesium salt amounts to less than one-half gram, calculated as chloride; when the amount is larger, precipitation from hot solution is necessary. A small quantity of ammonium chloride should always be added to the solution to prevent precipitation of magnesium hydroxide when the solution is rendered alkaline, and more particularly to prevent formation of this compound and consequent choking of the filter when the precipitate is washed with concentrated ammonia. Analyses Nos. 9 and 10 illustrate the two methods of procedure.

Other Compounds.—Calcium and strontium must not be present in the solution except in traces, since their iodates are also precipitated in part under the conditions of the analysis. Tests in the presence of other metals were not conducted, since the iodates of nearly all the heavy metals are insoluble in alkaline solution. The method works without error in the presence of the various acid radicals mentioned previously.

The following table contains the results of specimen analyses conducted under the various conditions mentioned in the preceding text; they represent the average errors which occur when the barium solution contains 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.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORIES OF CLARK UNIVERSITY.]

ON THE DETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS.

BY C. W. BACON.

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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:

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