None of the earths above mentioned interferes with the determination of the cerium.

Remarks on the Method.—In the earlier experiments made, larger quantities of sodium bismuthate were employed (3–5 g.) and no ammonium sulphate was added. This amount, however, gave a heavy precipitate of basic bismuth salt when the solution was heated to boiling, which invariably carried with it a small amount of ceric sulphate which could not be removed by subsequent washing. The ammonium sulphate prevents the precipitation of the basic bismuth salt, so that there is left only a small amount of undecomposed sodium bismuthate to be filtered off. The same Gooch crucible may be used for a large number of filtrations. The following determinations on solution "No. 3" above will illustrate the importance of the ammonium sulphate in the method.

	CeO_2 found.	
CeO_2 taken.	Without $(NH_4)_2SO_4$.	With $(NH_4)_2SO_4$.
0.2102	0.2067	0.2103
......	0.2062	0.2104

Delicacy of the Reaction.—Experiments show that the yellow color produced by oxidation of the cerium by means of the bismuthate affords a very sensitive test for minute quantities of cerium. A solution containing 0.2 mg. of CeO_2 in 100 cc. gives a distinct yellow coloration. The intensity of the color increases with increasing temperature. Experiments are now being made with the hopes of devising a colorimetric method for the determination of small quantities of cerium in the presence of other rare earths, such a mixture, for example, as obtains in incandescent mantles.

The titration method is being applied to the analysis of cerium minerals, monazite sand, and incandescent mantles.[1] The method of W. & M., however, involves oxidation in a strong nitric acid solution by means of bismuth tetroxide, the cerium being then reduced in nitric acid solution by a known excess of hydrogen peroxide and the excess of the latter titrated with permanganate. Three titrations were made on a cerium solution containing unknown amounts of lanthanum and didymium.

QUANTITATIVE LABORATORY.

[CONTRIBUTION FROM THE UNIVERSITY OF WASHINGTON.]

ANALYSIS OF MIXTURES OF HALOGEN ACIDS.

BY WILLIAM M. DEHN.

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In an alkaline sodium "hypobromite solution," prepared by adding bromine to an excess of caustic soda, the bromine is present in three

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[1] The above method had been worked out before a method by Waegner and Müller (*Ber.*, 36, 282 (1903)) had been noticed.

different forms, namely, sodium bromide, sodium hypobromite and sodium bromate. For a greater or less time after preparing such a mixture, the percentages of these three substances vary progressively, owing to the combined effects of the following reactions:

(*a*) $2NaOH + Br_2 = NaBr + NaOBr + H_2O$.

(*b*) $3NaOBr = 2NaBr + NaBrO_3$.

(*c*) $2NaOBr = 2NaBr + O_2$.

Whereas the main reaction (*a*) is immediate and quantitative, the other reactions proceed more or less slowly, owing to the varying influences[1] of heat, light, decrease of alkalinity, etc. A freshly and properly prepared[2] solution of hypobromite usually contains a little more than 50 per cent. of bromide, but this increases more or less rapidly and, ultimately, as the resultant of reactions (*a*) and (*b*), equals 83+ per cent. While the primary reaction of decomposition (*b*) is progressing, the secondary reaction[3] of decomposition (*c*) adds a further small per cent. of bromide. Various solutions of "hypobromite" may, therefore, have their bromine distributed within the following limits:

$NaBr = 50–83+$ per cent.; $NaOBr = 50–0$ per cent.; $NaBrO_3 = 16\frac{2}{3}–0$ per cent.

While engaged in other lines of research it became necessary to determine all of the halogen ions of such a mixture. On employing the methods of analysis then in use, it was found that they were either unreliable and inadequate or too laborious for our purposes. As the result of further investigation it was found that Volhard's method of titration, with modifications, could be employed for the rapid and accurate determination of all three components of such or any other homologous mixture of halogen acids.

Briefly considered the methods herewith given are based on: (I) the precipitation in *alkaline* solution of the bromide as AgBr; (II) the decomposition of the hypobromite by means of ammonia[4] or hydrogen peroxide[5] and the precipitation in *alkaline* solution of the resulting total halide; (III) the decomposition of the hypobromite with ammonia, the reduction of the bromate with iron and dilute sulphuric acid, and the titration in acid solution of the *total bromine.*

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[1] Gay Lussac, *Ann.*, 43, 153; *Compt. rend.*, 14, 927; Foerster and Jorre, *J. pr. Chem.*, 59, 53–101.; Skrabal, *Monatsh.*, 28, 319–382.

[2] Such a solution is best prepared by placing the NaOH solution in the lower part of an ordinary desiccator, the bromine in a dish in the upper part of the desiccator and letting stand at ordinary or lowered temperature until the bromine has evaporated spontaneously. Such a solution contains nearly 50 per cent. of its bromine as NaOBr, whereas solutions, prepared by adding bromine directly to alkali, usually contain less than 40 per cent. of its bromine as NaOBr.

[3] Bhaduri, *Z. anorg. Chem.*, 13, 385.

[4] $3NaOBr + 2NH_3 \longrightarrow N_2 + 3NaBr + 3H_2O$.

[5] THIS JOURNAL, 29, 1316. $NaOBr + H_2O_2 \longrightarrow O_2 + NaBr + H_2O$.

Analysis of Mixtures of Bromine Acids.

Method I. For Bromide.—A measured volume of the "hypobromite" solution in an Erlenmeyer flask is treated somewhat slowly with an excess of *N*/10 silver nitrate. During the addition of the latter, the mixture is shaken vigorously so that the formation of the silver bromide may be favored and the silver oxide, which is formed in alkaline solution after all of the bromide is precipitated, may be recognized by its dark brown or black color. If the solution is not already sufficiently alkaline, more sodium hydroxide is added before the silver nitrate is run in, for, in the absence of sufficient alkali, all of the *excess* of silver nitrate will not be precipitated as silver oxide, and the completion of precipitation of the silver halide will not be definitely indicated. Next, sufficient dry, acid sodium carbonate[1] is added to convert the sodium hydroxide into sodium carbonate and the silver oxide into silver carbonate, the color of the precipitate thereby being changed from brown or black to white or light yellow.

The well-shaken precipitate is freed from the solution containing the oxygen-halogen salts, by decanting, filtering and washing through a Gooch funnel,[2] no effort being made to transfer the precipitate to the funnel. The filter flask is emptied and washed, the Gooch funnel is readjusted, the precipitate in both the flask and the funnel is treated with dilute nitric acid, and the *excess of silver nitrate* is filtered and washed into the filter flask and titrated in the usual manner by the Volhard method. The difference between the *N*/10 silver nitrate and the *N*/10 potassium thiocyanate used is equal to the bromide in terms of *N*/10 silver nitrate.

Method II. For Hypobromite.—A measured volume of the solution in an Erlenmeyer flask is treated with a slight excess of ammonia or hydrogen peroxide[3] to decompose the hypohalite. Boiling is necessary to discharge the excess of ammonia since it dissolves silver halide. With hydrogen peroxide no boiling is necessary. The solution is next treated with an excess of *N*/10 silver nitrate, acid sodium carbonate,

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[1] This acid sodium carbonate is necessary only in the case of chlorine mixtures; it may be omitted in the case of bromide mixtures and must be omitted with iodine mixtures. It is necessary with chlorine for the reason that fixed alkalis but not alkali carbonates dissolve silver chloride. See also, THIS JOURNAL, 29, 269.

[2] Filter paper cannot be used unless approximate results only are desired, for the reason that hypohalous salts rapidly attack cellulose and yield by decomposition the corresponding halide. The latter then reacts with the silver oxide present and too high percentages of the halide in the sample analyzed are indicated.

[3] The hydrogen peroxide used must not precipitate with silver nitrate; if it does it should be treated with sufficient silver nitrate and filtered. When hydrogen peroxide is used the precipitate may remain dark colored.

etc., as in Method I. Filtering[1] here may be made through an ordinary paper filter instead of through a Gooch funnel. The difference between the $N/10$ silver nitrate and the $N/10$ potassium thiocyanate used is equal to the sum of the halide and the hypohalite, in terms of $N/10$ silver nitrate. The difference between the $N/10$ silver nitrate of this method and Method I is equal to the *hypohalite* in terms of $N/10$ silver nitrate.

Method III. For Total Halogen and Bromate.—A measured volume of the solution in an Erlenmeyer flask is treated with sufficient hydrogen peroxide or ammonia to decompose the hypohalite. The solution is freely diluted with water and then treated with a sufficient quantity of finely divided iron.[2] While shaking vigorously, the solution is next acidulated with very dilute sulphuric acid. After corking the flask and letting stand for 10–60 minutes, the solution is filtered and treated with an excess of $N/10$ silver nitrate. Nitric acid is next added and the solution is boiled to oxidize the ferrous iron. After cooling, the excess of $N/10$ silver nitrate is determined with $N/10$ potassium thiocyanate, the iron already present being the indicator. The difference between the $N/10$ silver nitrate and the $N/10$ thiocyanate is equal to the *total halogen* present in terms of $N/10$ silver nitrate. The difference between the $N/10$ silver nitrate of this method and Method II is equal to the *bromate* in terms of $N/10$ silver nitrate.

Analysis of Mixtures of Chlorine Acids.

Solutions of ions containing chlorine are analyzed as above; bleaching powder involves certain modifications of weighing, of breaking up of the insoluble particles, of first adding sodium hydroxide, then acid sodium carbonate, etc., that are sufficiently obvious.

Analysis of Mixtures of Iodine Acids.

For the reason that silver iodate is insoluble in neutral solution but soluble in alkaline solution, whereas silver iodide is insoluble in both, a generous quantity of sodium hydroxide must be added in Method I to keep the former in solution. The precipitate must be distinctly dark colored and no acid sodium carbonate can be used. In Method II sufficient ammonia is used to decompose the sodium hypoiodate and keep the silver iodate in solution.

The advantages of these methods are: (1) employment of volumetric solutions that are not only easily prepared but easily preserved; (2) the determination of the different halogen acids with the same volumetric

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[1] Filtering is necessary to remove the bromate and other trioxygen halides, since, when treated with nitric acid, they oxidize the thiocyanate used in the Volhard method.

[2] Hendrixson, *Am. Chem. J.*, **32**, 242; Tschernobéeff, *Chem. Ztg.*, **29**, 442. Other reducing reagents have been employed with less success.

solutions, thus eliminating errors and rendering the calculations easy; and (3) the methods are not only rapid but accurate.

In the following table, 1 g. of bleaching powder (calculated) or 10 cc. of solutions were used in each analysis; the results are given in terms of $N/10$ $AgNO_3$:

Method.	"Hypobromite" solution.	"Bromate" solution.	"Hypochlorite" solution.	Bleaching powder.	"Hypoiodite" solution.
I	76.74	62.04	12.77	78.43	100.30
I	76.72	62.12	12.68	78.49	100.42
II	138.44	62.15	23.79	92.57	101.45
II	138.30	62.04	23.65	92.51	101.43
III	142.34	73.28	24.02	96.90	121.36
III	142.27	73.20	24.01	96.96	121.25
$N/10$ Na_3AsO_3	123.01	.....	22.04	28.20	......
Calculated per cent. of total halogen					
HX	53.91	84.76	52.96	80.91	82.73
HOX	43.32	0.02	45.62	14.61	0.91
HXO_3	2.77	15.22	1.42	4.48	16.36

It will be observed that the arsenite method of direct titration of hypohalous acids gives results in close agreement with the above methods. Though the three halogen ions of the above homologous mixtures may be estimated by combination of Method III above, the arsenite method, and the iodometric method, three additional volumetric solutions are required, *viz.*, $N/10$ sodium arsenite, $N/10$ sodium thiosulphate, and $N/10$ iodine and potassium iodide. For the reason that these solutions are unstable, the superiority of the above-described methods is evident.

SEATTLE, WASH., February 22, 1909.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF CHROMIUM.

FIRST PAPER.—THE ANALYSIS OF SILVER CHROMATE.

BY GREGORY PAUL BAXTER, EDWARD MUELLER AND MURRAY ARNOLD HINES.

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Introduction.

The following table[1] gives the results of investigations upon the atomic weight of chromium from the time of Berzelius, recalculated with the use of recent atomic weight ratios upon the basis of silver (107.88) and oxygen (16.000).[2]

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[1] Clarke, A Recalculation of the Atomic Weights, Smith Misc. Coll., 1897.

[2] The following atomic weights are used in the recalculation of the older values: Ag = 107.88; Cl = 35.457; Pb = 207.09; N = 14.01; Ba = 137.37; S = 32.07; H = 1.008; K = 39.095; As = 74.96; I = 126.92. The values of Rawson and Meineke are reduced to the vacuum standard; the others are not so corrected.