Reading water. Besides determining the manganese in the water, determinations were made with the water containing varying amounts of added manganese.

(a) BOSTON WATER

No.	cc. taken	Grams of Manganese Added	Grams of Manganese Recovered
1	100	0.00000	0.00000
2	100	0.00010	0.00009
3	100	0.00010	0.00010
4	100	0.00010	0.00009

(b) READING WATER

No.	cc. taken	Grams of Manganese Added	Grams of Manganese Recovered
1	100	0.00000	0.000065
2	100	0.00000	0.000070
3	100	0.00000	0.000075
4	100	0.00010	0.000170
5	100	0.00010	0.000170
6	100	0.00010	0.000165

E. The following experiment shows the effect upon the determination of large amounts of chlorine.

No.	cc. Boston City Water	mgs. Chlorine added to a liter	Grams Manganese Added	Grams Manganese Recovered
1	1000	50	0.00010	0.000085
2	1000	500	0.00010	0.000075
3	100	50	0.00010	0.000079
4	100	500	0.00010	0.000080
5	100[1]	500	0.00010	0.000080

The writer finds this method rapid, convenient, serviceable, and reasonably accurate. He recommends it to other analysts with the hope that more data regarding the manganese content of ground waters may be placed on record.

He also wishes to thank his friend, Professor Henry Fay, for fundamental suggestions, and to acknowledge the services of his assistant, Miss Grace Ide Fairchild, who has made most of the determinations.

14 BEACON ST., BOSTON, April 15, 1907.

A RAPID METHOD FOR THE DETERMINATION OF CALCIUM IN WATER, AND ITS SIGNIFICANCE IN CONNECTION WITH THE ANALYSIS OF WATER FOR BOILER PURPOSES.

BY F. E. HALE.

In the examination of water for boiler purposes it is extremely important to be able to determine the relative amounts of calcium and magnesium salts present. The determination of the total hardness by the

[1] Boston water contains about 2.5 parts of chlorine per million.

soap method furnishes a rapid and fairly accurate means of finding the total calcium and magnesium content. With the development of a rapid and accurate method of determining the total calcium there is at hand the means of knowing the total magnesium, since the latter is the difference between the total hardness and the total calcium. Again the determination of the alkalinity by titration with N/50 sulphuric acid in the presence of methyl orange as an indicator gives us a rapid and accurate means of ascertaining the amount of carbonates. By these three methods combined the characteristics of a boiler water become at once apparent.

The method[1] here described is an adaptation to water of an old and standard method for calcium. The results are very accurate and a complete analysis may be made in thirty minutes. The order of procedure is as follows:

Method of Determination. To 100 cc. of the water to be examined add 10 cc. of a saturated solution of ammonium chloride and 1 cc. of ammonium hydroxide (1:1). Precipitate the calcium by adding oxalic acid in solution (5 cc. of a saturated solution made from the recrystallized acid) until a faintly acid reaction is obtained, as determined by a few drops of azolitmin solution or by the absence of the odor of ammonia. Any iron or aluminum precipitated by the ammonia will redissolve. It is better to add one-half of the oxalic acid first and rotate vigorously before bringing to acid reaction. Add an excess of ammonium oxalate (5 cc. of a saturated solution), boil vigorously for fifteen minutes and filter on asbestos in a platinum Gooch crucible, previously ignited, but not weighed. Wash the beaker four or five times with hot water beginning at the top and covering every portion of the sides of the beaker to the bottom, decanting into the crucible each time. Wash the crucible down once or twice, remove and wash down the outside. The total wash water is usually between 35 cc. and 50 cc. Do not clean the beaker with a policeman but place the crucible in the beaker. Add boiling water sufficient in amount to cover the crucible, pour 10 cc. of sulphuric acid (1-1) into the liquid and titrate the oxalic acid of the precipitate with N/50 permangate. From the total number of cubic centimeters of permangate used substract 0.3 cc. for a blank and each 0.1 cc. remaining equals one part per million of calcium, calculated as calcium carbonate.

The above strength of permanganate is the proper strength to use for 100 cc. of water up to 500 parts per million of calcium calculated as calcium carbonate. For quantities of calcium above that amount the quantity of water taken for analysis should be reduced to 50 cc., or other convenient volume, and diluted with distilled water. For

[1] Sutton, Volumetric Analysis, page 161 ; Peters, Am. Jour. Sci., Vol. X, page 362.

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quantities of calcium below 20 parts per million it is advisable to use 200 cc. of the water to be analyzed.

Complete precipitation of the calcium may also be obtained by heating on a steam bath, but requires one to two hours. This manner of heating does not lengthen the time of attention required from the chemist, which in any case is but 10-15 minutes, and is preferable in routine work. The bath used by the author was of such construction that the beakers rested on the top of an inside drying oven and were surrounded by live steam.

So many chemists experience difficulty in using a Gooch crucible that it may be well to mention the simple manner in which the asbestos is prepared. Long fiber asbestos[1] is pulled apart into shorter lengths, about one-half inch, and each clump gently squeezed together from the ends to separate the fibers, which are then vigorously shaken out in distilled water in a stoppered Erlenmeyer flask. No further preparation, such as washing with acid, is needed. This material furnishes a silky mat which allows of rapid filtration and retains the finest precipitate. A single filtration is usually sufficient, although the filtrate should always be carefully watched and occasionally it is necessary to pass the liquid through a second time. In preparing an asbestos felt suction should be released gradually to avoid injuring the continuity of the felt, and in igniting it care should be taken that the crucible be fanned with the flame until it is dry, to avoid blowing any fine holes in the felt by steam.

Examination of the Method.

The solutions employed were as follows:

Calcium chloride solutions, carefully standardized gravimetrically.

Aluminum sulphate solution, neutral.

Ferric sulphate solution, slightly acid, containing ammonium chloride and nitrate.

Magnesium sulphate solution.

$N/100$ *permanganate solution,* made from the $N/10$ solution and carefully standardized against $N/10$ oxalic acid.

In testing the accuracy of this method under all possible conditions several hundred experiments have been made including more than a hundred analyses of natural waters. The examples given in the accompanying table will suffice to show the accuracy of the results under extreme artificial conditions. Purposely absurd conditions were chosen in the first two experiments, and, since such amounts of aluminum and iron do not interfere, smaller amounts certainly will not. Corroborative experiments have shown this to be true. Magnesium in large amounts does not interfere even with small amounts of calcium when precipitated as described in this article. Simple precipitation by ammonium oxalate in

1 Procured from Eimer & Amend, N. Y. City.

neutral solution has been shown by experiment to be incomplete with small amounts of calcium in the presence of large amounts of magnesium[1], hence the adoption of the above method of precipitation. A good excess of ammonium oxalate is necessary to the success of this method and much excess of oxalic acid is to be avoided. Washing the precipitate of calcium oxalate with hot or with cold water, or with hot ammonium chloride solution produces no difference in the results. Soluble organic matter, such as produces color in water, is without effect. Insoluble organic matter will produce a slight affect; for example, microscopic organisms in very large amounts (10,000 to 25,000 units per cubic centimeter) may produce an error of a few parts per million, but, in such rare instances, or in case of sewage analysis, the sample should be filtered before precipitation of the calcium. It is essential to recrystallize the oxalic acid, as it was found that grave errors may arise from failure to do so. Several parts per million of calcium may be precipitated from impure oxalic acid, which in saturated solution readily holds calcium in solution.

It has been stated by Richards, McCaffrey and Bisbee[2] that one liter of water at 95° dissolves 14 mgrms. of calcium oxalate and at 25° dissolves 6.8 mgrms. The amount of wash water used in the analysis is approximately 30 cc. Consequently, when using boiling water in washing, there should result an absolute error of about 3.5 parts per million of calcium carbonate, and, when using cold water, of about 1.5 parts per million. No such negative error has appeared as a constant in this work. It appears that, while many substances may exert a slight effect in preventing complete precipitation of calcium, the oxalate once precipitated in proper crystalline condition does not readily redissolve.

This method for calcium has been tried and used very successfully by a fellow chemist. The following is an interesting proof of its accuracy. One liter of a mineral water was evaporated and the calcium determined in the usual way to be 117 parts per million. The method of this paper gave 118 parts per million. There were also present 119 parts of magnesium calculated as calcium carbonate.

Calculation and Interpretation of Mineral Analyses.

Various schemes are followed in combining the elements present in a water into salts. Almost all of them follow, more or less, the solubility of the salts, beginning with sodium chloride and ending with the carbonates. On account of the difficulty of obtaining proper figures for sodium and potassium, and the ease with which the carbonates, sulphates, chlorides, calcium and magnesium may be determined, as well as the fact that it is these latter salts which concern us in the question as to whether a water is good or bad for boiler use, it would seem far more advantageous to com-

[1] Fresenius, Quant. Chem. Anal., p 73, c., page 145.
[2] Proc. Am. Acad., **36**, 377-393.

bine the elements according to the degree of insolubility of their salts, beginning with the carbonates and sulphates and ending with the nitrates

Number of Experiment	Quantity of water Analyzed	Ammonium chloride (saturated solution)	Ammonium oxalate (saturated solution)	Ammonium hydroxide (solution 1:1)	Oxalic acid (saturated solution)	Azolitmin used as indicator	Heated on steam bath	Aluminum	Ferric iron	Magnesium sulphate, calculated as CaCO₃	Calcium chloride introduced, calculated as CaCO₃	Calcium found, calculated as CaCO₃	N/100 Permanganate solution required
	cc.	cc.	cc.	cc.	cc.		hrs.	(In parts per million.)					cc.
1	100	10	10	moderate (+)	(—)	(—)	3	100	100	...	248	249.0	49.8
2	"	"	"	"	"	"	2	100	100	...	24.8	24.5	4.9
3	"	"	"	"	"	(+)	3	...	...	...	140	140.0	28.0
4	"	"	"	5	"	"	1.5	...	...	...	140	140.0	28.0
5	"	"	"	"	"	"	1	...	...	...	140	141.5	28.3
6	"	"	"	"	"	"	1.5	...	...	100	140	140.5	28.1
7	"	"	"	"	25	"	2	...	...	100	140	141.0	28.2
8	"	"	"	"	(—)	"	1.5	...	...	100	70	70.5	14.1
9	"	"	"	"	25	"	2	...	...	100	70	71.0	14.2
10	"	"	"	"	"	(—)	"	...	...	100	35	37.5	7.5
11	"	"	"	"	"	(—)	"	...	...	100	35	37.5	7.5
12	200	"	"	"	(—)	"	1.5	...	...	100	7	8.0	3.2
13	"	"	"	"	25	(—)	2	...	...	100	7	7.0	2.8
14	"	"	"	"	"	"	"	...	...	100	3.5	2.3	0.9
15	100	"	"	"	"	"	"	...	...	100	0	0.0	0.0
16	"	"	5	1	5	(+)	"	...	...	100	280	280.0	56.0
17	"	"	"	"	"	"	"	...	...	100	140	140.0	28.0
18	"	"	"	"	"	"	"	...	...	100	70	71.0	14.2
19	"	"	"	"	"	"	"	...	...	100	35	37.0	7.4
20	200	"	"	"	"	"	"	...	...	100	7	7.0	2.8
21	"	"	"	"	"	"	"	...	...	100	3.5	1.8	0.7

(+) and (—) mean that the solutions heading the column were or were not used.

and chlorides. We have, then, sufficient data at hand for a judgment, whether we have a complete analysis or not. Furthermore, it is best to combine according to the solubilities at ordinary temperatures, because little is known with certainty as to what changes take place under the different conditions in the boiler. Cecil H. Cribb[1] has published a very instructive article on the Influence of Temperature and of Concentration on the Saline Constituents of Boiler Water. Proper reactions, as these are determined, may be written from the combinations at ordinary temperatures to show what will happen in the boiler at high temperatures and pressures. For example, at boiling temperature solutions of magnesium sulphate and calcium carbonate react to form basic magnesium carbonate and calcium sulphate with loss of carbon dioxide, and in the boiler this

[1] Analyst, July, 1900, p. 169.

basic carbonate undoubtedly is deposited practically as the oxide, or hydroxide of magnesium, allowing the free carbon dioxide to act corrosively upon the boiler. In this reaction there are two insoluble bodies to help along the reaction, calcium sulphate and magnesium oxide. There is no reason to doubt that magnesium chloride and calcium carbonate under like conditions would react to form calcium chloride and the very insoluble magnesium oxide with loss of carbon dioxide.

Not much deposition of hard scale can take place in a boiler until considerable concentration has been reached, unless the water is very hard, since calcium sulphate is soluble to the extent of 270 parts per million at a pressure of 132 pounds per square inch, and to 180 parts at a pressure of 513.5 pounds per square inch[1].

To return to the insolubility at ordinary temperatures of the salts under consideration. Watt's Chemical Dictionary furnishes the following data:

	Grams dissolved in 100 grms. of water.	Parts per million.	Temperature.
Calcium sulphate,	0.19	1,900	0° C.
	0.206	2,060	20° C.
	0.214	2,140	40° C.
Calcium carbonate neutral,	0.0094	94	cold.
Calcium carbonate, in water	0.07	700	0° C.
saturated with carbon dioxide,	0.088	880	10° C.

From this table it is seen that, even in the presence of carbon dioxide, calcium carbonate, at ordinary temperatures is more insoluble than calcium sulphate.

Again, C. H. Bothamley[2] found that solid calcium carbonate in contact with magnesium sulphate solution, or solid magnesium carbonate in contact with a solution of calcium sulphate, resulted always in a solution of magnesium sulphate and a deposit of calcium carbonate. Hence calcium carbonate is more insoluble than magnesium carbonate. The sulphate of magnesium is, of course, very soluble, as are the chlorides and nitrates of calcium and magnesium.

The procedure would then be to calculate the alkalinity to calcium first, unless the alkalinity exceeds the total hardness, which rarely occurs, and then only when carbonates of sodium and of potassium are present. If the carbonates exceed the necessary amount of calcium, the rest of the alkalinity may be calculated to magnesium carbonate, and sulphates, chlorides, etc., combined with magnesium until the latter is exhausted. But if the calcium exceed the amount necessary to take care of the alkalinity, there is no magnesium carbonate, and the excess of calcium may then be calculated to sulphate first, then chloride or nitrate until exhausted, and the magnesium is combined with the remaining acid radi-

[1] Tilden and Shenstone, Phil. Trans., part 1, 1884. p. 23.
[2] J. Chem. Soc., 1893, 698.

cals until exhausted. Any remaining chloride, nitrate, and sulphate may be calculated to sodium and potassium salts.

Many analyses of mineral waters have been made in which this method for calcium has been profitably employed. Among them are the following:

1. A well-known mineral water gave a hardness of 162 by the soap method and an alkalinity of 160. The total calcium was found by this method to be 155. The magnesium was precipitated in the filtrate from the calcium oxalate and found to be 3 parts per million,—all results expressed, as usual, in terms of calcium carbonate.

2. A water from North Carolina contained the following:

$SiO_2 = 0$. Fe = 3, Total hardness = 1363, Alkalinity = 260, Cl = 8,200. $SO_3 = 250$, N as nitrate = 0. The total calcium, determined by this method, was 483. The magnesium, precipitated in the filtrate, was found to be equivalent to 872 of calcium carbonate. The total calcium and magnesium was then 1355, as against a hardness of 1363. The hardness was determined in 2 cc. portions diluted to 50 cc. with distilled water. Four determinations required 4.7, 4.4, 4.6, 4.6 cc. of soap solution, an average of 4.6 cc. A difference of one quarter of a tenth of a cubic centimeter would account for the discrepancy in the hardness.

Let us examine into the nature of the salts present. The alkalinity all belongs to the calcium, since the total calcium exceeds it. There was then *260* parts per million of *calcium carbonate*. The total calcium less the alkalinity ($483-260=223$) equals the calcium present in some other form and calculated to sulphate equals *303* parts *calcium sulphate*. Of the SO_3 125 parts are therefor combined with calcium. The total SO_3 250 minus 125 leaves 125 parts SO_3 to be calculated to magnesium sulphate and equals *188* parts *magnesium sulphate*. Of this 63 parts are magnesium oxide and equals 157 in terms of calcium carbonate. The hardness less the total calcium gives the total magnesium in terms of calcium carbonate ($1363-483=880$). But as the magnesium was actually determined by gravimetric analysis to be equivalent to 872 of calcium carbonate, we will use that figure. The total magnesium minus that in the form of sulphate ($872-157=715$) equals the amount of magnesium to be calculated to chloride, since the chlorine will more than cover it, and equals *679* parts *magnesium chloride*. Of this 508 parts are chlorine. The total chlorine less that in the form of magnesium chloride is calculated to sodium chloride ($8,200-508=7,692$) and equals *12,747* parts *sodium chloride*. The result is:

$CaCO_3$ 260, $CaSO_4$ 303, $MgSO_4$ 188, $MgCl_2$ 679, NaCl 12,747.

The sulphate in this analysis was determined by precipitation with barium chloride and Jackson's[1] turbidimetric method, using the candle

[1] This Journal, **23**, 801.

turbidimeter. Hence the complete mineral analysis was accomplished by rapid methods.

3. A well water from Western New York.

Data. Hardness 485, Alkalinity 186. Cl 48, SO_3 213, N as nitrate 7.5. Fixed solids 682. Total calcium 348. Hence total magnesium is equivalent to 137 of calcium carbonate, (485-348).

Calculating in practically the same manner as before, as it happens. we arrive at the result:

$$CaCO_3\ 186,\ CaSO_4\ 224,\ MgSO_4\ 125,\ Mg(NO_3)_2\ 39,\ NaCl\ 80,\ SiO_2\ and$$
$$Al_2O_3\ 28\ (by\ difference).$$

Conclusion.

In resumé it may be said that the method is admirably suited for the routine analysis of large numbers of samples, may be considered accurate to two parts per million, is applicable to all quantities of calcium including that of sea water, is equally accurate with large and small quantities of calcium, furnishes, in combination with the soap method, a rapid method of determining the total magnesium, and hence is extremely valuable in the rapid analysis of mineral and boiler waters.

MT. PROSPECT LABORATORY.
    DEPT. WATER SUPPLY, GAS AND
        ELECTRICITY, N.Y. City, Dec. 27, '06.

THE RECOVERY OF ALBUMINOID AMMONIA FROM DISTILLATES CONTAMINATED WITH PERMANGANATE.

BY F. E. HALE.

In the distillation of albuminoid ammonia in sanitary water analysis it frequently happens that bumping occurs and permanganate is washed over into the distillate. Usually this happens with a hard water, or is occasioned by the use of alkaline permanganate the alkali of which contains considerable carbonate. Consequently it may usually be prevented by care in selecting for the permanganate solution only alkali containing less than five percent of carbonate and by taking care in the preparation of the alkaline permanganate solution to pour it into the retaining bottle as soon as sufficiently cool after boiling off the ammonia. The easiest remedy, when bumping has occurred, is to distill a second portion of the water which is being analyzed, but occasionally this is impossible from lack of sufficient water and a method of recovery from the distillate seems to be worthy of description.

The method, which is entirely of a chemical nature, consists in reducing the permanganate by an alkaline sulphite solution, oxidizing the manganous salt to the hydrated peroxide, filtering off the manganese on