ARE CHEMISTS GENERALLY PREPARED TO ABANDON CLARK'S METHOD FOR ESTIMATION OF HARDNESS IN WATERS?

By Dr. Albert R. Leeds.

At the present time, when many chemists retain and others have laid aside Clark's method, it is difficult to discover what is signfied by the figures repórted under hardness in a reported analysis, and it is most desirable that this obscurity should be done away with, and a uniformity of practice secured.

The objects in view, in the ordinary course of analysis, when hardness is determined, are as follows :

1st. Simply to place the water in the category of hard or soft waters. Usually private individuals desiring water analyses wish to know merely of their fitness for domestic use, and the estimation of the hardness by soap solution is adequate to supply the information needed on this point. But inasmuch as the analyst starts with an unknown water, which often turns out to be magnesian in character, or to owe part of its hardness to other constituents than lime and magnesia salts, the time expended in estimating its hardness, temporary and permanent, by soap, is greater oftentimes than that demanded by other methods.

2d. Soap destroying power. The analyst in his laboratory uses as nearly pure potassium oleate as he can prepare, and dissolves this soap in a mixture of two volumes of alcohol and one of water. His object is to so adjust his manipulation as to effect a combination of the lime and magnesia with the oleic acid, and to obtain from a table of hardness as near an approach to the actual quantities of these bodies, estimated as calcium carbonate, as possible.

To achieve this result, he frequently has occasion to dilute with distilled water and to manipulate with various refinements having no relation to the actual use of soap. For factory use the soad destroying power can best be determined by trial with the particular water and soap used ; for general purposes it can be sufficiently well estimated from the calcium carbonate equivalent deduced from titration with sodium carbonate.

Very frequently soap is used with water as hot as the hand can bear, and the valuable suggestion has been made by Mr. Herbert Jackson that on heating to 70° C * the soap test gives the same figures as are obtained by means of dilution. Even with this device, the results vary widely in many cases from the true calcium carbonate equivalent, while they do not necessarily give soap-destroying power.

3d. Boiler incrusting solids—"scale." Hardness, however determined, should not be used in judging of the scale-forming properties, but if chemists will persist in guessing, as they do at present, the Hehner figures allow of safer guess work than those obtained by soap.

4th. Character and amount of chemicals to be added before precipitation and filtration of hardening and scale-forming substances. Ordinarily this is effected by the addition of lime, soda or soda-ash, singly or combined. Now the Hehner method in its direct determination of alkalinity before and after evaporation with sodium carbonate bears a certain analogy with the process of softening. In practice a trial should always be made using the calculated amounts of reagents, for such is the effect of the condition and relative proportions of the salts present in water, that agreement between the theoretical and actual results after treatment is frequently lacking. Still it is obtained in a fair number of cases, and much more with the soda than with the soap titration. Moreover, when soda is employed, the softening as judged by the soap test, may be apparent (so far as scale is concerned) rather than real.

What is needed, both as to scale and its prevention, is a specia

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technical study having these two objects solely in view. A method followed will be indicated in a subsequent paper.

Having stated the objections which led me several years ago to abandon the soap test, I desire to give some experiments made at that time which appeared desirable before taking this step.

In the first place are minute variations in the conduct of the test, or of the temperature, etc., sufficient to originate discrepancies between the actual amounts of calcium carbonate equivalent and those given in the table of hardness, when the test solution of calcium chloride is employed and the test is performed in the usual manner. The experiments were made with potassium oleate dissolved in 2:1 dilute alcohol and of such strength that 14.25 c.c. produced a permanent lather with 50 c.c. CaCl solution = 20 pts. $CaCO_3$ per 100 c.c.

COMPARISON WITH ORDINARY TABLE OF HARDNESS. (By $CaCl_2$.)

Mgrms. $CaCO_3$ taken.	c. c. by Ordinary Table.	c. c. by Experiment.	Differences in c. c.	Mgrms. $CaCO_3$ by Experiment.	Differences Mgrms. $CaCO_3$.
0.0	0.70	1.05	0.35	0.55	0.55 +
2.0	2.05	2.15	0.10	2.21	0.21 +
4.0	3.60	3.90	0.30	4.43	0.43 +
4.0	3.60	3.80	0.20	4.29	0.29 +
6.0	5.00	5.58	0.58	6.80	0.80 +
8.0	6.40	6.41	0.01	8.01	0.01 +
10.0	7.80	7.90	0.10	10.15	0.15 +
12.0	9.15	9.30	0.15	12.26	0.26 +
16.0	11.75	11.78	0.03	16.10	0.10 +
20.0	14.25	14.25	0.00	20.00	0.00

The comparison shows that these discrepancies are practically of no importance.

In the second place, is it desirable to abandon the use of the ordinary table, calculated from Clark's Table of Hardness, and, following a suggestion of Mr. Wanklyn, to take the equivalent of calcium carbonate directly from the soap titre minus a certain correction. For the purpose of this inquiry, I took 1.6 grms. oleic acid, exactly neutralized with decinormal soda made up to 300 c.c., and finding solution stronger than theory required, diluted until 50 c. c. water, containing the equivalent in $CaCl_2$ of 10 mgrms. $CaCO_3$ was exactly equivalent to 11.4 c. c. soap 50 c. c. distilled water alone was equivalent to 1.4 c. c. soap. The results were :

$CaCl_2$ sol. c. c.	$CaCO_3$ Mgrms.	Oleate Calculated.	Oleate Used.
10.0	4.0	5.4	5.40
15.0	6.0	7.4	7.40
20.0	8.0	9.4	9.45
25.0	10.0	11.4	11.40
50.0	20.0	21.4	21.50

By deducting 1.4 from the c. c. oleate used, the amount of $CaCO_3$ equivalent is obtained directly. Were the continuance of the soap best desirable on other grounds, the testing of this method with calcium and magnesia salts, singly and combined, would have been further prosecuted.

Thirdly, Would another salt of calcium give the same results taken from the Hardness Table, as $CaCl_2$?

A solution of standard $CaSO_4$ = 0.200 grm. per titre $CaCO_3$ was made up by adding 20 c. c. $\frac{N}{10}$ H_2SO_4 to 56 c. c. CaO solution containing 1 mgrm. per c.c. Different volumes of this solution were made up to 50 c. c. and titrated with a soap solution of 14.25 c. c. = 20 mgrm. $CaCO_3$ as determined with standard solution of $CaCl_2$.

TABLE OF HARDNESS. (By Ca SO_4.)

$CaSO_4$= $CaCO_3$mgrms used.	c. c. by ordinary Table.	c. c. by experiment.	differences in c c.	mgrms$CaCO_3$ by experiment.	differences mgrms $CaCO_3$.
0.0	0.70	1.05	0.35	0.55	0.55+
2.0	2.05	2.10	0.05	2.08	0.03+
4.0	3.60	3.60	0.00	4.00	0.00
6.0	5.00	5.00	0.00	6.00	0.00
8.0	6.40	6.40	0.00	8.00	0.00
10.0	7.80	7.80	0.00	10.00	0.00
16.0	11.72	11.70	0.02	15.95	0.05—
20.0	14.25	14.10	0.15	19.76	0.24—

A solution of $CaCO_3$ in CO_2 water was made with the view of holding as little free CO_2 as posssble. *50 c. c. = 20 mgms.* Ca CO_3=13.6 c. c. soap solution=18.97 mgrms. of $CaCO_3$ per table. Further experiments showed that distilled water containing increasing amounts of dissolved CO_2 give corresponding differences from the titre obtained with Carbonic acid free water.

Fourth. Could a magnesium salt be made to give results corresponding to the equivalent $CaCO_3$ as taken from the table?

50 c.c. $MgSO_4$ sol. =20 mgrms. $CaCO_3$ was titrated with soap run in 1 c. c. at a time and with much shaking. It gave no satisfactory end reaction but an apparent permanent lather at about 12 c. c. instead of 14.25 c. c.

Repeated with intervals of three minutes between each c. c., an unsatisfactory end reaction was obtained with 10 to 12 c. c.

25 c. c. $MgSO_4$+25 c. c. water was titred as follows:

First: 6 c. c. with 1 c. c. at 2 minute intervals.
6.7 c. c. at 5 minute intervals.
7.1 to 7.5 c.c. at 5 minute intervals.
7.5 not normal lather : 7.6 nearly normal.
7.6 to 7.8 c. c. at three 5 min. intervals.

The whole operation required an hour and the final result with a normal lather yielded 7.8 c. c.=10 pts. per 100,000. In another experiment with less time and shaking 8.4 c. c. were used, and the final outcome shows that with sufficient care and patience an agreement can be obtained in the case of magnesium salt (1 mol. CaO=1 mol. MgO) with theoretical figures up to the equivalent of 10 parts $CaCO_3$ per 100,000. But a method which necessitates so great an expenditure of time, labor and care to obtain results that only in certain cases are approximately correct, should, it appears to me, be abandoned.

The results were as follows :

TABLE OF HARDNESS. (By $MgSO_4$.)

$MgSO_4$ = $CaCO_3$ mgrms.	c. c. by Table.	c. c. by experiment.	differences in c. c.	mgrms. $CaCO_3$ by experiment.	differences mgrms.
2.00	2.00	2.10	0.10	2.08	0.08+
4.00	3.60	3.60	0.00	0.00	0.00
6.00	5.00	5.03	0.03	6.03	0.03+
8.00	6.40	6.65	0.25	8.35	0.35+
10.00	7.80	7.80	0.00	0.00	0.00
10.00	7.80	8.40	0.60	10.90	0.90+
20.00	14.25	12.00?			
20.00	14.25	10 to 12 ?			

In conclusion, I would ask whether the members are prepared to take formal action, and to recommend a rule of practice in estimating and reporting upon what shall be conventionally styled the "Temporary" and "Permanent" Hardness.