

SOME EXPERIMENTS WITH THE SOAP SOLUTION.

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SOME little time since I had occasion to examine some samples of water, with a view to determining their comparative value for boiler and manufacturing purposes. With one of the samples especially, which was very hard, the soap test gave such unsatisfactory results that the method described by O. Hehner (ANALYST VIII. 77) was tried upon it, and in order to make the results comparable among themselves, the same method was applied to the other samples.*

The results on the two hardest samples were as follows (sample A being the one especially referred to):—

HARDNESS (=CaCO₃) IN PARTS PER 100,000.

Sample.	BY SOAP TEST.			BY HEHNER'S METHOD.		
	Permanent 20 c.c.	Total 20 c.c.	Total 10 c.c.	Temporary.	Permanent.	Total.
A	41·915	45·955	51·050	21·14	39·65	60·79
C	31·31	33·30	34·845	19·20	19·93	39·13

Of course in the above, the 20 c.c. and 10 c.c. lots were diluted up to 100 c.c. with distilled water before applying the soap test.

Some of the other analytical results on these waters were as follows:—

PARTS PER 100,000.

	Analyst.	Cl.	SO ₃	CaO.	MgO.	Total Solids.	Loss on Ign.
Water A.	Waller ..	1·633	28·10	26·85	4·829	86·5	8·0
„	Chemist C.	3·00	28·76	26·74	..	88·1	6·0
„	„ H.	81·3	17·6
Water C.	Waller ..	1·100	12·02	15·31	3·280	49·0	8 0
„	Chemist C.	60·7	5·0

* *Lakmoid* was found to be more satisfactory as indicator in this case, than the phenacetolin indicator, recommended in Mr. Hehner's article.

I did not learn until some time afterwards that other chemists had also made examinations of samples of these waters a month or six weeks before mine was made.

The results which they obtained for hardness by the soap test were as follows:—

PARTS PER 100,000.

		Temporary.	Permanent.	Total.
Water A ..	Chemist C.	18·8	29·7	48·5
"	Chemist H.	32·
Water C ..	Chemist C.	14·7	19·	33·7

As I had reported the results obtained by the Hehner method the discrepancy was very marked, especially in the case of water A.

Having noted that with different amounts of the water different results were obtained by the soap test, the idea naturally suggested itself to try the action of soap with different amounts of lime and magnesia. Accordingly a solution of pure double refracting spar was made after the regular method (solution of 1 grm. in hydrochloric acid, evaporating until neutral, and dilution to 1 litre). (This will be called "Ca solution.") A solution containing 2·46 grms. crystallised magnesium sulphate in 1 litre was also made (called "Mg solution"). A third solution, made by mixing 150 c.c. of each of the other solutions, was also prepared (called "mixed solution"). Different proportions of these solutions, diluted in every case to 100 c.c. with distilled water, were then tested with the soap solution.

The results were as follows:—

c.c. of Solution diluted to 100 c.c.	Cubic centimeters of Soap Solution to Produce Permanent Lather after Standing.							
	Ca Solution.		Mg Solution.			Mixed Solution.		
5	10·7	10·8	12·15	12·35	12·20	10·2	10·2	10·2
10	19·7	19·9	23·5	23·3	..	18·3	..	19·7
20	37·7	37·8	(35 to 40 uncertain.)			(27·5 uncertain.)		
30	54·	55·
40	(74 uncertain.)	

100 c.c. of distilled water required 1·3 and 1·4 c.c. soap solution to form a lather.

The figures in the last column for "mixed solution," were obtained by first adding 70 or 80 per cent. of whole amount of soap solution, which was finally used, mixing in without violent shaking, allowing to stand for 30 minutes, and then finishing the titration as usual. Where magnesium was present, care was taken to carry the test beyond the point where a temporary lather forms, mentioned by Wanklyn, and probably noticed by every chemist who has made much use of the soap test.

My usual practice has been to take the standard of the soap solution from the results obtained on 10 c.c. of the Ca solution, making no allowance for the action on the soap of the water used for dilution. That mode of calculating has seemed to give the

most accurate results that the soap test appeared capable of. Calculating the standard in this way, the value of 1 c.c. of the soap solution would be $0.01 \div 19.8 = 0.000505$ CaCO_3 , but it is evident that a variety of different standards could be obtained from the above results on the Ca solution. Two different sets of standards would be obtained according as we deduct 1.35 c.c. for the influence of the water of dilution or not.

In the following tables, the columns headed "Ded't" give the results obtained by calculation, where this deduction is made :—

Ca SOLUTION.

Soap required by 10 c.c.			Standard 1 c.c. Soap = CaCO_3 .	
Test made on		Ded't.		Ded't.
5 c.c.	21.5	18.8	0.000465	0.000532
10 c.c.	19.8	18.45	0.000505	0.000542
20 c.c.	18.825	18.2	0.000530	0.000549
30 c.c.	18.17	17.71	0.000550	0.000564

The hardness of the Mg solution and mixed solution, expressed in terms of CaCO_3 , would be as follows :—

Test made on.	Mg Solution.				Mixed Solution.			
	10 c.c. = Soap.		Hardness = CaCO_3 per c.c.		10 c.c. = Soap.		Hardness = CaCO_3 per c.c.	
	c.c.	c.c.	Standard 0.000505.	Standard 0.000542.	c.c.	c.c.	Standard 0.000505.	Standard 0.000542.
		Ded't.		Ded't.		Ded't.		Ded't.
5 c.c.	24.46	21.76	0.0012352	0.0011794	20.4	19.7	0.00103	0.0010677
10 c.c.	23.4	22.05	0.0011817	0.0011951	18.3	16.95	0.000924	0.0009187
10 c.c. st'dg.	19.7	18.35	0.000995	0.0009946

These results confirm the observations of Mr. A. H. Allen (December Meeting of the Society of Chemical Industry, vol. VII., p. 795), that the ratio of lime hardness to magnesia hardness by the soap test is not 2 to 3, or 42 to 75, as asserted by Wanklyn (*Water Analysis*, 7th Ed., p. 100); also that a mixture of calcium and magnesium salts shows a lower degree of hardness than either of them separate.

What remained of the sample of water A was then taken up after it had been standing $3\frac{1}{2}$ months. It was again tested for total solids, hardness by *Hehner's* method, etc. The results were :—

	Total Solids.	Loss on ign.	Temp. Hard's.	Perm. Hard's.	Total Hard's.
When first received	86.5	8.	21.14	39.65	60.79
After standing $3\frac{1}{2}$ months ..	77.	9.	8.2	36.2	44.4

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Some of this water was placed in a bottle, and tests were applied, as with the Ca and Mg solutions, diluting whatever amount was taken, up to 100 c.c., with distilled water before applying the soap test.

EXPERIMENTS ON SAMPLE A (after standing $3\frac{1}{2}$ months).

cc. of a taken.	c.c. of Soap required.		100 c.c. of a = c.c. Soap		Hardness per 100000.	
		Ded't.		Ded't.	Standard = 0.000505.	Ded't. Standard = 0.000542.
1	1.6	0.25	16.	2.5	80.800	13.550
2	2.6	1.25	13.	2.25	65.650	33.875
5	5.1	3.85	10.2	7.7	51.510	41.734
10	8.75	7.45	8.75	7.45	44.187	40.379
20	14.4	13.05	7.2	6.525	36.360	35.365
30	19.8	18.45	6.6	6.15	33.30	33.333
40	26.2	24.85	6.55	6.2125	33.077	33.672
50	31.4	30.05	6.28	6.01	31.714	32.574
60	37.4	36.05	6.23	6.008	31.478	32.573

Which figure should be taken as representing the total hardness of this water?

The soap solution was entirely used up in making these tests, or they would have been carried farther. A small amount of another soap solution happened to be available, which like the first had deposited a slight sediment, which as before was filtered off, affording a clear, bright solution. With this tests were also made on the Ca solution. The results were:—

Ca Solution used.	Soap Solution Used.			10 c.c. = c.c. Soap.	
					Ded't.
5	10.85	10.85	10.9	21.73	21.23
10	20.5	20.6	21.	20.3	19.45
20	37.	38.1	38.	18.85	18.21
30	56.	18.67	18.25

100 c.c. of distilled water took 1.2 and 1.3 c.c. soap solution.

The value of the soap solution was a little different from the first one, but the results show essentially the same as before.

The results by the soap test are apparently altogether unreliable, for very hard waters especially, and even with waters comparatively soft the results for permanent hardness are still more untrustworthy. This last point is alluded to by Mr. Wanklyn (*Water Analysis*, 7th Ed., p. 98) where he expresses disapproval of any attempt to determine the different kinds of hardness (temporary or permanent) by means of the soap test.

It would seem advisable to abandon the use of the soap test entirely, for although

all *chemists* are well aware of the roughly approximate character of the results, their clients usually are not, and attribute as much importance to the figure for “hardness by soap test” as to any other figure on the report of a chemist whom they may employ.
