NOTE ON THE EXAMINATION OF WATER FOR TOWNS,

FOR ITS HARDNESS, AND FOR THE ENCRUSTATION IT DEPOSITS ON BOILING.

PRIVATE CIRCULAR.

PROFESSOR CLARK TO HIS CHEMICAL FRIENDS.

At various times during the last few years, I have been applied to for information respecting methods I had adopted for examining Waters for Towns; but ill health has almost always prevented me from returning a satisfactory answer. There has been recently somewhat more occasion for such inquiries, in consequence of the Commissioners of Woods and Forests having been pleased to require, as one of the indispensable conditions to a Bill for supplying Water to a Town being presented by them to Parliament, that there shall be given in reference to the waters already supplied to the town, as well as in reference to the Waters proposed to be supplied,—

"A statement of the quality of the Water as exhibited by chemical analysis, specifying its adaptation for Domestic and Manufacturing Purposes, and its degree of hardness with reference to the Tests and Scale of Dr. Clark."

I take the liberty to write out one answer to all inquirers; and, imperfect as I am aware the information must be, I hope my friends will receive it with such indulgence as is due to an effort at affording information to others by a person confined to bed by illness, and unfit for any considerable exertion of mind.

The processes alluded to for the examination of Waters are two—one for ascertaining the Hardness of Water; one for ascertaining the Alcalinity.

Each of these processes is fully described in the Specification of a Patent, printed in the Number of the Repertory of Patent Inventions for October, 1841. (Hodson, Publisher, 112 Fleet-Street, London.) Vol. 16, p. 225.

A water is, indeed, most materially affected in its fitness for domestic uses and manufacturing purposes, by the degree of its hardness. But many hard waters have the additional objection of depositing earthy matter on being boiled. This matter forms an encrustation on the boiler, and fills up tubes employed in giving passage to the heated water. In this land of steam-engines, it need not be told how annoying this quality is. Not only should the chemist be able to tell, ay or no, whether any such deposit will be formed; but, when one does occur, it is desirable to know how much altogether, and how much of each of the more important kinds of matter, will be deposited. Now, in the Specification alluded to, there is no express direction given for obtaining this important point of information; because this was not necessary to the invention there described; neither, indeed, had I then contrived a method for the purpose. But ever since September, 1845, I have been accustomed to derive this information from the hardness and the alcalinity of the water boiled and unboiled. To explain the method of deducing this information, is a principal object of the present Note.

Referring to the Specification, I begin by describing a few improvements that have been suggested by experience, since the Specification was enrolled.

PROCESS FOR ASCERTAINING THE HARDNESS OF WATER.

In June, 1843, having occasionally before met with some few specimens of waters, and more especially soft waters from springs, where the indications of the Soap Test, which in general are remarkably distinct, were obscure, I discovered the cause of this obscurity to be an excess of Carbonic Acid; that is, an excess over and above what is necessary to form alcaline or earthy Bicarbonates. This excess has the property of slowly decomposing a lather once formed.

For the purpose of guarding against an excess of Carbonic Acid in all cases, I recommend that before you measure out the water for trial, you shake it briskly in a stoppered glass bottle half filled with it, sucking out the air from the bottle at intervals by means of a glass tube, so as to change the atmosphere in the bottle.

In all trials of waters above 16° hardness, not only should such waters, and the distilled water to be used along with them in the trials, be treated in this manner, previous to their being measured out and mixed, but the measured mixtures themselves should be treated in like manner, before any Soap Test is added to them. The Soap Test itself should be occasionally so treated before it is measured out.

To obtain uniform results with the Soap Test, I recommend that as soon as you observe that a lather is formed, such as will remain all over the surface of the water for five minutes, you take a note, but only an *interim* one, of the quantity of the Soap Test that has been added. In about half an hour you should shake the bottle again, to see whether the lather will still remain for five minutes. If the water under trial do not exceed 4° or 5° of hardness, it is likely to require a little more Soap Test upon this renewed shaking; but in every case where more Soap Test is required, let more be added to the water. This latter quantity and the former will together make up the whole Soap Test that is to determine the hardness of the water under trial. For hours afterwards, unless perhaps the water do not exceed 1° or 2° of hardness, a lather lasting for five minutes may be restored by your shaking the phial. This mode of procedure, by producing a lather whose permanence we may repeatedly verify, will conduce much to the uniformity and accuracy of our trials.

TABLE FOR CONVERTING SOAP TEST MEASURES INTO DEGREES OF HARDNESS.

Ever since detecting the fallacy that might occur owing to an excess of Carbonic Acid, my health has prevented me from performing such a series of experiments as to afford materials for a table of this kind. Pressed, however, by the present occasion, and guided by my former experience, I have endeavoured to frame, as follows, a table worthy of confidence, by comparing together unpublished results obtained since then by others.

Table of the Soap Test Measures, corresponding to 100 Test Measures of each Standard Solution.

Degree of Hardness.	Soap Test Measures.	Differences for the next 1° of Hardness.
0° (Distilled Water)	1.4	1·8
1°	3·2	2·2
2	5·4	2·2
3	7·6	2·0
4	9·6	2·0
5	11·6	2·0
6	13·6	2·0
7	15·6	1·9
8	17·5	1·9
9	19·4	1·9
10	21·3	1·8
11	23·1	1·8
12	24·9	1·8
13	26·7	1·8
14	28·5	1·8
15	30·3	1·7
16	32·0	

When the measures of Soap Test necessary to form a lather, with 100 Test measures of a water, exactly correspond with a standard solution, then the degree of hardness will be the corresponding integral number found in the first column. Thus 24·9 of Soap Test will indicate 12° of hardness; 26·7 of Soap Test will indicate 13° of hardness.

But if the measures of Soap Test do not exactly correspond with a number in the first column, the hardness will be expressed partly by an integer, and partly by a fraction. The *integer* will be the hardness corresponding to the next lower number in the Soap Test column.

The *numerator* of the fraction will be the excess of the Soap Test measures in question above this number. The *denominator* of the fraction will be the corresponding difference, which follows the Soap Test in the next column.

Example.—Let 25·8 be the measures of Soap Test required by 100 Test measures of a given water.

24·9 is the next lower number in the Soap Test column. Therefore 12° of hardness, the corresponding degree, is *the integral part* of the required hardness.

The numerator of the fraction is $25{\cdot}8 - 24{\cdot}9 = {\cdot}9$. The denominator is the corresponding difference $= 1{\cdot}8$. *The fraction* itself is $\frac{\cdot 9}{1\cdot 8} = {\cdot}5$.

The whole hardness, therefore, is 12°·5.

PROCESS FOR ASCERTAINING THE ALCALINITY OF A WATER.

The tests employed are two—Test Paper and the Acid Test. Respecting these I have little to add to what is given in the specification.

Test Paper.—The colour should be first separated from the solid matter of the litmus, by boiling, subsidence, filtration, &c. The coloured solution thus obtained, being too weak for use, will require to be concentrated by evaporation. The colour will then have to be brought to a proper tint by means of dilute nitric acid, and afterwards applied to the paper by a flat camel hair brush. The only paper that I have found to be sufficiently free from acid or alcaline impurities, to be unexceptionable for test paper, is the drawing paper stamped with the name of Harding.

Acid Test.—In purifying Oxalic Acid, it is desirable to reject a very small crop, consisting of such of the crystals as fall first. These, I find, contain Quadroxalate of Potash. I find a little of this salt, even when the acid has been made by means of pure nitric acid and specimens of the best refined sugar of commerce—a circumstance well worthy of the attention of chemists engaged in the study of vegetation.

DEGREES OF HARDNESS AND DEGREES OF ALCALINITY EXPLAINED.

Degrees of Hardness.—Each degree of hardness indicates as much hardness as would be produced by one grain of chalk per gallon, held in solution in the form of Bicarbonate of Lime, free from any excess of Carbonic Acid. The degree of hardness caused by a lime salt depends, not on the state of combination of the Calcium it contains, but on the quantity of the Calcium. If, instead of being in the form of Bicarbonate of Lime, the Calcium this compound contains were in the form of Chloride of Calcium, or of Nitrate of Lime, or of Sulphate of Lime, or even of Lime Water, the Soap Test destroyed by it, and consequently the degree of hardness indicated, would be precisely the same.

A quantity of a soluble magnesian salt equivalent to one grain of Chalk, destroys a like quantity of Soap Test, and consequently indicates one degree of hardness. The same is the case with Salts of Iron, and Salts of Alumina. Salts of the Alcalies do not produce hardness.

Degrees of Alcalinity.—For each degree of Alcalinity that a water possesses, a gallon of it will require as much acid to neutralise it as one grain of Chalk would require. Hence a solution of Lime Water, or of Bicarbonate of Lime, in distilled water, should be of the same degree of Hardness as of Alcalinity. The most usual cause of Alcalinity in water is Bicarbonate of Lime; but Bicarbonate of Magnesia, which causes hardness, likewise causes Alcalinity, and Bicarbonate either of Soda or of Potash, which does not cause hardness, causes Alcalinity. *

TO INFER THE DEGREES OF HARDNESS AND THE DEGREES OF ALCALINITY FROM AN ORDINARY ANALYSIS.

For Hardness.—Compute the grains of Lime, Magnesia, oxides of Iron, Alumina, in a gallon of the water, each into its equivalent of Chalk. The sum of those equivalents will be the Hardness of the water.

For Alcalinity.—Compute in like manner, the grains of Bicarbonates of Lime, Magnesia, Soda, Potash, in a gallon of the water, each into its equivalent of Chalk. The sum of those equivalents will be the Alcalinity of the water. But the results thus obtained have much less chance to be accurate than the Hardness and the Alcalinity ascertained directly by means of the Soap Test and the Acid Test.

* When a Phosphate of Lime is present, as happens rarely and in small quantities, it is probable that for every two degrees of hardness the Phosphate occasions, it will produce only one degree of Alcalinity; that is, all the Lime in the Phosphate will cause hardness; but one half of it will be neutralised, and only the remaining half alcaline.

DELICACY OF THE TESTS.

For Hardness.—Suppose the Thames to yield a mean of 14° of Hardness. Carefully conducted experiments should then range between 14°·1 and 13°·9 of Hardness. That is to say, the mean result of more experiments than one should be within 0°·1 of the extremes; and it is to be remembered, that the Hardness of a water may be ascertained repeatedly within an hour. But 0°·1 of hardness is equivalent to one-tenth of a grain of Chalk per gallon; that is, 1 of Chalk in 700 thousand times its weight of water. But as the operation is performed on only the 70th of a gallon, (1000 grains,) the whole weight of hardening matter that we actually operate upon in this experiment, is a 70th of 14 grains, that is, one-fifth of a grain; and the smallest weight we actually measure to, is the 70th of the 10th of a grain, that is, the 700th of a grain. I do not remember any process of equal quantitative delicacy, in the whole range of chemical analysis; and this one is the more remarkable as it is performed with Soap Test, previously known as almost the rudest and least determinate of chemical reagents.

For Alcalinity.—If the Thames be at 14° of Hardness, it would probably yield 13°·1 of Alcalinity. Such a water, if tried according to the directions of the Specification, should give 13°·1 of Alcalinity each time. The difference between the experiments, if carefully performed, should appear not on the first, but only on the second place of decimals. Now, since 1° of Alcalinity corresponds to one grain of Chalk per gallon, and since the Acid Test indicates less than 0°·1 of Alcalinity, or one of Chalk in 700 thousand of water, we may safely infer that the Acid Test will measure one of Chalk in 1 million of water. Thus we obtain, for record, even more accurate results by the Acid Test than we do by the Soap Test. Nevertheless, the Soap Test is, in the abstract, the most delicate; for, although we use nearly the same quantity of each test, yet, in the case of the Acid Test, we act on the eighth of a gallon; whereas, in the case of the Soap Test, we act on only the 70th of a gallon.

HOW TO MAKE THE FOREGOING PROCESSES AVAILABLE FOR ASCERTAINING THE QUANTITY OF ENCRUSTATION THE WATER DEPOSITS ON BOILING.

For this purpose, the points to be ascertained are,—

1. The Hardness and the Alcalinity of a given water, unboiled.

2. The like particulars of the same water, after being boiled, without loss of steam for at least $2\frac{1}{2}$ hours, and then cooled, and (if necessary) filtered.

From these indications, the weight per gallon of earthy deposit formed by boiling, if there be any, is deduced as follows.—

Let $\begin{cases} h = \text{hardness of unboiled.} \\ h' = \quad \text{"} \quad \text{" boiled.} \\ h - h' = H, \text{ that is, degrees of Hardness lost by boiling, occasioned by the precipitation of earthy salts, which may be either alcaline or neutral, or partly both.} \end{cases}$

Let $\begin{cases} a = \text{alcalinity of unboiled.} \\ a' = \quad \text{"} \quad \text{" boiled.} \\ a - a' = A, \text{ that is, degrees of Alcalinity lost by boiling, occasioned by the precipitation of alcaline earthy salts.} \end{cases}$

NOTE.—Observe that H is equal to A only in the case where *all* the precipitate is Chalk and Carbonate of Magnesia, which is but seldom the case.

$H - A =$ So much of the hardness lost by boiling, as is produced by the precipitation of neutral earthy salts.

$(H - A) \times 1{\cdot}36 = B$, that is, the above neutral earthy salts, calculated as dried Sulphate of Lime, in grains per gallon.

Collected and represented in a Report, thus—

Hardness of the Water	Unboiled, ...	
	Boiled, ...	
Deposit by boiling, in grains, per gallon,—		
Alcaline earthy salts, calculated as Chalk, . .		A
Neutral earthy salts, calculated as dried Sulphate of Lime, ...		B
Total, ...		$A + B$
Alcalinity of the water	Unboiled	
	Boiled	

When the alcalinity is only 1° or 2°, it is not worth while boiling the water, as hardly any precipitation will take place.

If you cannot conveniently arrange so as to boil the water without loss of steam, I recommend that you boil it with as little loss as possible, and, when the water has cooled, that you make up the loss in weight of the vessel and its contents, by adding distilled water. Mere boiling causes one change on the saline contents of the water. Boiling with evaporation causes an additional change.

I recommend that the Alcalinity of a water be always stated by itself in a Report; that is, not mixed up with the Hardness: perhaps, indeed, it should be given in the Appendix to the Report; for persons not familiar with Chemistry are apt to be puzzled about the Alcalinity, whereas the degree of Hardness and weight of deposit per gallon, almost never give them any difficulty. But the Alcalinity should not be altogether omitted from the Report, as the statement of it is necessary for a comparison of the results obtained by different Chemists.

It will be for others to decide whether the ascertaining of the quantity of the deposit that a water forms on boiling, should or should not form a part of the Chemical Analysis serving to specify "its adaptation for domestic and manufacturing purposes," as required by the Commissioners of Woods and Forests.

T. C.

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