LV1.—*On a Volumetrical Process for the Analysis of Waters.*

BY EDWARD NICHOLSON, F.C.S., Staff Assistant-Surgeon.

THE want of a process by which surgeons and other scientific men interested in hygienic matters, could easily make an analysis of water, has long been felt; and attempts have several times been made to supply the deficiency.

Professor Clark, of Aberdeen, indicated the tincture of soap as a test for the presence of earthy salts in water; he adapted a burette, with a special graduation, to the determination of the hardness of water by the tincture of soap, and drew up a table for calculating the amount of the different earthy salts corresponding to the quantity of soap decomposed by the water.

The beautiful experiments of Professor Clark, after some examination and criticism by Professor Playfair, Mr. Campbell, and others, was adopted by MM. Boutron-Chalard and F. Boudet, as the basis of the so-called "Hydrotimétrie," for which a prize of 2,000 francs was awarded them by the Academy of Sciences. These chemists adapted the soap solution of Professor Clark to a more complete determination of the earthy bases, and as their very useful method has been used to some extent in France, and is employed in the Hygienic Laboratory of the Army Medical School at Fort Pitt, I will give a brief outline of the process they employ.

The solution of soap employed by MM. Boutron-Chalard and Boudet, is of such a strength, that 23 degrees of their burette (equal to 2.4 c.c.) form a permanent lather on agitation with 40 c.c. of a solution of chloride of calcium, containing 0.25 grm. per litre. One degree is deducted for the excess of soap-solution requisite to form the lather significative of the termination of the reaction. These 22 degrees correspond then to .01 grm. of chloride of calcium, or to a quantity of any other soap-decomposing substance, varying according to the relation of its equivalent to that of chloride of calcium. The number of degrees of soap-solution decomposed by 40 c.c. of a water, when multiplied by certain factors, given in a table, gives the amount of chloride of calcium, or of any other salt, *ad libitum*, contained in the water.

The operations for the analysis of water by this method, comprise the following determinations:—

1. The hardness of 40 c.c. of water; this hardness is caused by carbonic acid gas, lime, magnesia, and whatever iron and alumina may be present.

2. The hardness of 40 c.c. of water from which the lime has been precipitated by oxalate of ammonia; this gives the hardness caused by magnesia and by carbonic acid gas.

3. The hardness of 40 c.c. of the water from which carbonate of lime and carbonic acid gas have been expelled by boiling; this *permanent* hardness, after a deduction of 3 degrees for carbonate

of lime still remaining in solution, is owing to salts of lime other than carbonate, and to salts of magnesia.

4. The hardness of 40 c.c. of the boiled water from which the *permanent* lime has been precipitated by oxalate of ammonia; this gives the magnesian hardness.

5. The sulphuric acid is estimated by adding to 40 c.c. of water, a measured quantity of solution of nitrate of baryta, of known hardness; the hardness of the mixture is determined, and the loss of hardness indicates the hardness of the sulphuric acid contained in the precipitated sulphate of baryta.

The distinguishing features in this improvement of Clark's process, are the estimation of the permanent lime and magnesia salts, and of the sulphuric acid.

This easy method of estimating the more important constituents of water render this process most valuable in the economical analysis of waters, as a means of determining the effect of a water on steam boilers and in domestic operations, and also as a method for calculating the exact amount of lime that must be added to water, to eliminate the carbonic acid and carbonate of lime. But, apart from its economical value, considering the process in the point of view of chemical analysis, it is liable to some objections, and appears susceptible of certain improvements.

Two of the determinations are made after the addition of oxalate of ammonia; and I find that this introduces a possibility of error, since the oxalate of ammonia, when added even in small excess, either gives a peculiar hardness of its own, or else deranges the production of a lather, so as to render the result uncertain. It is also impossible to express the exact constitution of the solid ingredients of the water, or give any precise idea of their composition. No account is taken of the alkaline salts, and thus the advantages of the method are not fully brought out.

Impressed with the delicacy of the reaction given by the solution of soap, with the minutest quantity of earthy base, or of carbonic acid gas (·00002 grm. of lime will cause a detectable hardness of 1-7th of a degree), I have endeavoured to adapt this delicate test to a more complete and reliable method of volumetrical analysis; and I believe I have succeeded in bringing the process of MM. Boutron and Boudet, by several modifications and additions, to an exactitude which leaves little to be desired. I have also simplified the calculations, so as to render them even easier than those necessary in ordinary gravimetrical analysis.

The burettes employed are divided into tenths of cubic centimetres or degrees, each $0.1 \text{ c.c.} = 1^\circ$. These, with two pipettes of 10 c.c. and 50 c.c. respectively, a few basins and beakers, a few three-ounce stoppered bottles, and a graduated litre-measure, form all the apparatus required.

The following solutions are employed as test-fluids :—

1. *An Alcoholic Solution of Soap*.—The solution employed by MM. Boutron and Boudet is made with hard Marseilles soap, and in consequence it is solid at ordinary temperatures. This is a great inconvenience, from the necessity of heating the test-fluid ; but, after experimenting on a considerable number of soaps, Dr. Parkes has found that the soft potash-soap of the London Pharmacopœia is the best ; and this has accordingly been used by me. The solution is made by dissolving the soap, without heat, in a mixture of equal weights of alcohol and water.

The soap-solution is made of such a strength, that 20 degrees (2 c.c.) are exactly equivalent to 50 c.c. of a water containing 0.1 grm. per litre (or 7 grains per gallon) of carbonate of lime, and on adding to 50 c.c. of such a water 22 degrees, a permanent lather is produced by agitation. This requisite excess of 2 degrees per 50 c.c. is to be deducted from all determinations of hardness.

2. A solution of *nitrate of baryta*, containing 0.26 grm. per litre and equivalent in point of hardness to the aforesaid standard water containing 0.1 grm. per litre of carbonate of lime. 50 c.c. of this solution mark 20 degrees.

3. A stronger solution of *nitrate of baryta* is usually employed ; it contains 1.300 grm. per litre ; 50 c.c. of it mark 100 degrees.

4. A solution of *nitrate of silver* containing 8.500 grm. ($\frac{1}{20}$ of the equivalent of the salt) per litre.

5. A solution of *oxalate of ammonia*, containing 0.355 grms. ($\frac{1}{20}$ of the equivalent of the salt) per litre.

6. A solution of *permanganate of potash* containing 0.159 grm. ($\frac{1}{1000}$ of the equivalent of the salt) per litre.

The above graduation of the solutions has been adopted, as the important advantage is thereby obtained, of being able to calculate the quantity of any substance per litre of water, by multiplying the number of degrees obtained by the atomic weights of the substance.

Thus—

20 degrees $\times 50$	(eq. of CaO.CO^2)	= $.1000 \text{ grm.}$ per litre, of carbonate of lime.
20 degrees $\times 28$	(eq. of CaO)	= $.0560 \text{ grm.}$ per litre, of lime.
20 degrees $\times 35.5$	(eq. of Cl)	= $.0710 \text{ grm.}$ per litre, of chlorine.

The quantities thus obtained, when multiplied by 70, show the number of grains per gallon of water.

The Analytical Process.

1. 50 c.c. of the water to be analysed are measured by the pipette into a stoppered bottle of about three-ounce capacity. The soap-solution is gradually dropped in from the burette, the bottle being strongly shaken at intervals, until a lather begins to form on the surface. The soap-solution is then added more cautiously, and enough has been added, when the water, on agitation, presents an iridescent, large-bubbled lather, breaking down very slowly, and, after a few minutes, leaving the surface perfectly covered with a beady film, reconvertible into a lather on again agitating. After a little practice, the exact point where the lather becomes permanent is attained by the addition of one small drop, about one-sixth degree, of soap-solution. The process thus indicates the presence of .0005 grm. per litre of lime.

Two degrees are deducted for the excess necessary to produce a lather. The number of degrees found represents the hardness due to lime, magnesia, iron, and carbonic acid gas. The alkaline salts usually found in water, have no effect on the soap-solution.*

2. The amount of *lime* and *magnesia*, and, by difference, of free *carbonic acid gas*, is found by taking the hardness of the water after expulsion of the carbonic acid gas. To this effect 50 c.c. of the water are evaporated to dryness with one or two drops of sulphuric acid, and the residue is ignited to expel excess of acid; if the vapours be offensive, the residue may be neutralized by a few drops of ammonia, before ignition. The residue is dissolved in 50 c.c. of distilled water, and the hardness is ascertained. Oxide of iron will remain insoluble; its amount is to be deducted from the carbonic acid.

3. The *lime* is determined by the well-known application of permanganate of potash to the oxidation of oxalic acid.

To 50 c.c. of the water, add 50 c.c. (or, if the hardness exceeds 50 degrees, 100 c.c.) of the standard solution of oxalate of ammonia, let the mixture stand in a warm place for an hour, and filter. The filtrate and washings are heated in a basin to about 70° C.,

* If the hardness exceed 80 degrees, or if much magnesia be present, the earthy soap often assumes a curdy form, deranging the production of a lather; in this case only 25 c.c. should be taken for experiment, the 50 c.c. being made up with distilled water.

with a few drops of hydrochloric acid, and the standard solution of permanganate of potash is added from a burette. Subtract the number of cubic centimetres of permanganate required for oxidation of the excess of oxalic acid, from the number of cubic centimetres of oxalate of ammonia added to the water: the difference gives the number of degrees of lime.

50 c.c. of the permanganate-solution ought exactly to oxidise 50 c.c. of the oxalate of ammonia-solution.

4. *Determination of the Alkalies.*—The amount of lime and magnesia once obtained by the processes described, the ordinary process of estimating the alkaline salts by evaporating a certain quantity of the water with sulphuric acid, and weighing the resulting sulphates, is much facilitated. The lime and magnesian hardness have merely to be multiplied by the equivalents of sulphate of lime and of sulphate of magnesia, and the numbers thus obtained to be deducted from the amount of mixed sulphates per litre of water. I have however devised the following method for the volumetrical determination of the alkaline salts:—

To 50 c.c. of the water, ignited with sulphuric acid, as before described (2),* add 20 c.c., or more, of the stronger solution of nitrate of baryta, taking care that the hardness of the quantity added (2 degrees per 1 c.c.) be much greater than that of the water, as previously ascertained. If no alkaline sulphates are present, the amount of sulphate of baryta precipitated will be exactly equivalent in hardness to the amount of earthy sulphates; and the hardness, when ascertained by the soap-solution, will be exactly that of the baryta-solution added. If, for example, 20 c.c. = 40 degrees of baryta-solution have been added to 50 c.c. of water containing 35 degrees of sulphate of lime and of magnesia (total 40 + 35), 35 degrees of sulphates of baryta will be precipitated and the hardness will be reduced to 40 degrees, exactly the hardness of the baryta added. But, on the other hand, if sulphate of soda be present in the water, in addition to the earthy sulphates, a greater quantity of sulphate of baryta will be precipitated, and the hardness will be reduced to less than 40 degrees. Should it be reduced to 36 degrees, that will show that 4 degrees of alkaline sulphate were present.†

* It may be as well, at process No. 2, to evaporate 200 c.c. of water with sulphuric acid, dissolve the ignited residue in 200 c.c. of distilled water, and take 50 c.c. for analysis.

† If 20 c.c. of baryta solution have been added, the excess of soap-solution, to form

5. The *chlorine* is determined in 50 c.c. of the water by the solution of nitrate of silver. If the quantity be very small, it is best to evaporate 500 c.c. of water to a small bulk, and count cubic centimetres as degrees.

6. The *sulphuric acid* is determined by adding to 50 c.c. of the water, 10 c.c., or more if necessary, of the stronger baryta-solution, and ascertaining by the soap-solution the hardness of the mixture. The loss of hardness from the precipitation of sulphate of baryta, gives the number of degrees of sulphuric acid.

7. *Iron* is determined in the usual manner by the permanganate of potash solution. 500 c.c. of the water are evaporated to a small bulk with hydrochloric acid; the iron is reduced by sulphurous acid, and estimated by the permanganate of potash solution. Ten cubic centimetres are counted as one degree of Fe^2O^3 .

If silica be present, it will remain on redissolving the ignited sulphates, and if 200 c.c. of the water have been evaporated with sulphuric acid, it may be estimated by weighing.

In process 2, the oxide of iron becomes insoluble, and increases the amount of carbonic acid gas, from which it must be deducted.

All the processes here described are of very easy execution. The method of estimating carbonic gas is unequalled in exactness and facility of execution by any method I know, and the process for estimating the total capacity of saturation of the alkalies is extremely exact and satisfactory. The estimation of sulphuric acid, devised by M.M. Boutron and Boudet, is likewise of great precision.

I append examples of the calculation of an analysis performed by this process, to show the advantage obtained by the method of graduation I propose, in establishing an empirical formula for the salts contained in waters.

I. *Analysis of the Water supplied by the Chatham Water Company to Fort Pitt.*

	Degrees.	
1. Hardness	53°·7	{ Carbonic acid gas* Calcium Magnesium Iron
2. Hardness after ignition with sulphuric acid ..	49°·7	{ Calcium Magnesium
3. Calcium ascertained by permanganate	48°·3	Calcium

a lather, will be greater; 2·8 degrees must be deducted. But it is perhaps better always to add 50 c.c. (100 degrees) of baryta. The deduction is then 4 degrees, and the loss of hardness on 100 degrees is the amount of alkali.

* The iron is to be deducted from the gross carbonic acid, 4 degrees.

	Degrees.	
4. Hardness after ignition with sulphuric acid, } solution, and 60 degrees of baryta added }	53°·6	(Sodium loss 6°·4)
5. Chlorine	5°·5	
6. No sulphuric acid		
7. Iron	0°·2	

Deduction of an Empirical Formula for the Salts contained in the above Water.

This calculation, so tedious by the ordinary method, becomes here of extreme simplicity. I combine the 5·5 degrees of chlorine with an equal number of degrees of sodium, a balance of ·9 degrees of sodium is left. This with the calcium and magnesium is calculated as carbonate.

	Deg.	Equiva.	Grm.	per litre.	Grs. per gal.
Carbonate of lime ..	48·3	× 50	= ·2415	× 70	= 16·905
Carbonate of magnesia	1·4	× 42	= ·0058	× 70	= ·406
Carbonate of soda....	·9	× 53	= ·0047	× 70	= ·329
Chloride of sodium ..	5·5	× 58·5	= ·0321	× 70	= 2·247
Oxide of iron.....	·2	× 80	= ·0016	× 70	= ·112
Silica			= ·0020	× 70	= ·140
			·2877		20·139
Carbonic acid gas	3·8	× 44	= ·0167	=	= 2·52 c.
		(2CO ²)	8·93c.c.		in per gal.
Residue on ignition.....			·2810		= 19·68.

II. *Water from a pump at Fort Pitt.*

	Degrees.	
Total hardness	36·8	
Calcium and magnesium	21·0	
Calcium	16·9	
Sodium	5·0	
Iron (Fe ² O ³)	1·2	
Sulphuric acid	4·8	
Chlorine	3·6	
	Degrees.	Grm. per litre. Grains per gal.
Carbonate of lime	16·9 × 50	= ·0845 × 70 = 5·915
Carbonate of magnesia	·7 × 42	= ·0029 × 70 = ·203
Carbonate of iron	1·2 × 116 2(FeO,CO ²)	= ·0139 × 70 = ·973
Sulphate of magnesia.....	3·4 × 60	= ·0204 × 70 = 1·428
Sulphate of soda.....	1·4 × 71	= ·0099 × 70 = ·693
Chloride of sodium.....	3·6 × 58·5	= ·0210 × 70 = 1·470
		·1526 10·682.
Carbonic acid gas	14·6 × 44	= ·0642 = 31·3c.c. pr. lit.
		(× ·537) (31·3 c.c. × 4·54 × ·061)
Solids by evaporation ·1500 per litre.		= 8·67c. in. per gallon.

I may mention that the solution of permanganate of potash, of the standard here employed, answers admirably for the estimation of organic matter in water. 500 c.c. of water are heated to $70^{\circ}\text{C}.$, with a few drops of pure sulphuric acid, and the standard solution is added, 1 c.c. at a time, until a colour, lasting for 10 minutes, is obtained. Every 10 c.c. of test-solution thus decolorised is equal to one degree of organic matter requiring one equivalent of oxygen for complete oxidation (corresponding to $\text{C}^2\text{O}^3, \text{HO}$, for example).

I may say a few words as to the best manner of attaining the rapidity which forms one merit of this process. I first set 200 c.c. of water to evaporate with a few drops of sulphuric acid for processes 2 and 4; I also precipitate the lime in 50 c.c. for process 3. By the time I have taken the total hardness, and estimated the chlorine, sulphuric acid and iron, the evaporation is finished and the residue ready to be taken in hand. Two or three analyses can thus be easily performed in a day. One point must be carefully observed: that the distilled water contain no carbonic acid gas. The delicacy of the soap-test for this gas is so great that the distilled water will speedily acquire one or two degrees of hardness, if left exposed to the air. If it has acquired any hardness from this cause, it should be boiled previously to use.

In conclusion I must beg to acknowledge my obligations to Dr. Parkes, who, by his discovery of the fact, that, contrary to expectation, potash-soap might be employed to make a soap solution perfectly fluid at ordinary temperatures, removed what would have been an insuperable bar to any perfection of the method of analysis.