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THE COLORIMETRIC METHOD OF DETERMINING HYDROGEN ION CONCENTRATION: SOME APPLICATIONS IN THE ANALYTICAL LABORATORY.

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(Read at the Meeting, June 1, 1921.)

HITHERTO in the literature of analytical chemistry the terms "acidity" and "alkalinity" have in general been very loosely employed. "Acidity" or "alkalinity" have usually been determined by titration, and expressed in one of two ways: (a) As the number of c.c. of standard acid or alkali required by a given weight of the substance in order to render it neutral to some indicator; (b) as the percentage of some acid or alkali to which the acidity or alkalinity is ascribed, in some cases quite arbitrarily. If we require to find the percentage of a single acid or alkali which we know to be present, there is no objection to the titration method, but in many cases the important point is not the total percentage of acid or alkali present, but the number of hydrogen or hydroxyl ions present.

Hydrogen ion concentration rather than the amount of acid present is the important factor in the curdling of milk, the precipitation of proteins, the hydrolysis of sugars, and processes of digestion or fermentation, to take only a few instances. The majority of bacteria, yeasts, etc., have a range of hydrogen ion concentration at which their growth is at a maximum, and for this reason this factor is of the greatest importance in the case of bacteriological media and in biological processes generally. The complete precipitation of metals as their sulphides in inorganic analysis is dependent on the hydrogen ion concentration of the solution.

If "acidity" or "alkalinity" were expressed in terms of the hydrogen ion concentration of a solution of known strength, this would merely involve the use of a number without reference to any particular indicator, acid or alkali.

Owing to the work carried out in recent years the accurate determination of hydrogen ion concentration is now a comparatively simple matter. If only reasonable accuracy is required determinations can be carried out as a routine test in any laboratory not involving any special apparatus or skill.

METHOD OF EXPRESSING HYDROGEN ION CONCENTRATION.—Dr. Monier Williams *ANALYST*, 1921, 315) has dealt with the theoretical considerations involved. The

symbol P_H , by which hydrogen ion concentration is expressed, indicates the logarithm of the reciprocal of the concentration of hydrogen ions in terms of normal—*e.g.*, when $P_H = 2$, the hydrogen ion concentration is $N \times 10^{-2}$, or one hundredth normal; when $P_H = 3$, one thousandth normal, and so on. At the point of absolute neutrality,—*i.e.*, for pure water— $P_H = 7$. When P_H is less than 7 the liquid is acid, and when P_H is greater than 7 the liquid is alkaline.

METHODS OF DETERMINATION—(a) *The Hydrogen Electrode or Electrometric Method*.—This is the most accurate method of determining hydrogen ion concentration. It has been described by Dr. Monier Williams (*loc. cit.*). Its disadvantages are the somewhat complicated apparatus required, and the fact that its use involves difficulties where a series of determinations is to be made.

(b) *The Colorimetric or Indicator Method*.—This method, though sufficiently accurate for ordinary purposes, is not capable of as great accuracy as the electrometric method. It requires, however, no special apparatus, and a large number of determinations can be carried out at the same time. It is inapplicable to very dark solutions, though it may be used for coloured solutions if the colour is not too deep. It may be used with success with turbid liquids such as milk.

The colorimetric method depends on the fact that with every indicator the colour change extends over a characteristic zone of hydrogen ion concentration; if, therefore, the hydrogen ion concentration of an unknown liquid lies within the range of a certain indicator, we can determine the factor with accuracy if we can find a solution of known hydrogen ion concentration which gives the same shade of colour with the indicator. The two essentials for this method are, therefore: (a) A complete series of indicators with well-marked colour changes which will cover a wide range of hydrogen ion concentration. (b) Solutions of known hydrogen ion concentration which are easily prepared and stable. By the use of some of the recently synthesised indicators of the phthalein series, together with methyl red, we can fulfil the first requirement. As the accompanying chart shows, these indicators show brilliant and permanent colour changes over a range of $P_H = 1$ to $P_H = 11$. If we have a solution of unknown hydrogen ion concentration, and we test it with various indicators until one is found to give a shade of colour intermediate between its extreme shades, we can then find a solution of known hydrogen ion concentration which gives the same shade of colour with the same amount of indicator.

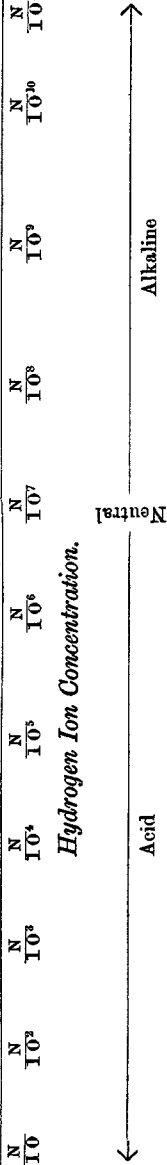
SOLUTIONS OF KNOWN HYDROGEN ION CONCENTRATION.—It is not possible for this purpose to use solutions of acids or alkali of known strength on account of the susceptibility of such solutions to changes of hydrogen ion concentration from accidental causes, such as the alkalinity of the glass, etc., but this difficulty may be overcome by introducing certain salts, such as phosphates, borates, etc., which have a "buffer" action—*i.e.*, which have the property, when in solution, of causing the hydrogen ion concentration to be only slightly affected by the addition of small amounts of acid or alkali. For ordinary purposes the following four solutions, together with $\frac{N}{10}$ hydrochloric acid and $\frac{N}{10}$ sodium hydroxide, are all that are required. By taking definite volumes of any of these solutions, with different volumes of $\frac{N}{10}$ hydrochloric acid or $\frac{N}{10}$ sodium hydroxide, solutions of practically any P_H required may be obtained.

INDICATORS.

P_H VALUES.

	1·0	2·0	3·0	4·0	5·0	6·0	7·0	8·0	9·0	10·0	11·0
Thymol blue ...	Pink	Orange	Yellow	—	—	—	—	Yellow	Greenish Blue	Blue	—
Brom-phenol blue	—	—	Yellow	Greenish Yellow	Blue Violet	—	—	—	—	—	—
Methyl red	—	—	—	Pink	Orange	Yellow	—	—	—	—	—
Brom-cresol purple	—	—	—	—	Yellow	Greenish	Purple	—	—	—	—
Brom-thymol blue	—	—	—	—	—	Yellow	Green	Blue	—	—	—
Phenol red	—	—	—	—	—	—	Yellow	Orange Red	—	—	—
Phenolphthalein ...	—	—	—	—	—	—	—	Colourless	—	Pink	—
Thymolphthalein ...	—	—	—	—	—	—	—	—	—	Colourless	Blue

Hydrogen Ion Concentration.



1. *Standard $\frac{N}{10}$ Sodium Citrate Solution.*—This is prepared by dissolving 21.008 grms. of pure citric acid in 200 c.c. of *N*-sodium hydroxide solution and diluting to 1,000 c.c. with water.

0.1 <i>N</i> -Citrate Solution.	0.1 <i>N</i> -HCl.	P _H .	0.1 <i>N</i> -Citrate Solution.	0.1 <i>N</i> -NaOH.	P _H .
C.c.	C.c.		C.c.	C.c.	
1.0	9.0	1.17	9.5	0.5	5.02
2.0	8.0	1.42	9.0	1.0	5.11
3.0	7.0	1.93	8.0	2.0	5.31
3.33	6.66	2.27	7.0	3.0	5.57
4.0	6.0	2.97	6.0	4.0	5.97
4.5	5.5	3.36			
4.75	5.25	3.53			
5.0	5.0	3.69			
5.5	4.5	3.95			
6.0	4.0	4.16			
7.0	3.0	4.45			
8.0	2.0	4.65			
9.0	1.0	4.83			
9.5	0.5	4.89			
10.0	0.0	4.96			

2. *Standard $\frac{N}{5}$ Sodium Borate Solution.*—This is prepared by dissolving 12.404 grms. of pure boric acid in 100 c.c. *N*-sodium hydroxide solution and diluting to 1,000 c.c. with water.

0.2 <i>N</i> -Borate Solution.	0.1 <i>N</i> -HCl.	P _H .	0.2 <i>N</i> -Borate Solution.	0.1 <i>N</i> -NaOH.	P _H .
C.c.	C.c.		C.c.	C.c.	
5.5	4.5	7.94	9.0	1.0	9.36
5.75	4.25	8.14	8.0	2.0	9.50
6.0	4.0	8.29	7.0	3.0	9.68
6.5	3.5	8.51	6.0	4.0	9.97
7.0	3.0	8.68	5.0	5.0	11.08
7.5	2.5	8.80			
8.0	2.0	8.91			
8.5	1.5	9.01			
9.0	1.0	9.09			
9.5	0.5	9.17			
10.0	0.0	9.24			

3. *Standard (M/15) Potassium Dihydrogen Phosphate Solution* is prepared by dissolving 9.078 grms. pure potassium dihydrogen phosphate (KH_2PO_4) in 1,000 c.c. water.

4. *Standard (M/15) Sodium Phosphate Solution* is prepared by dissolving 23.87 grms. pure sodium phosphate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$) in 1,000 c.c. water.

The two last solutions are used in combination.

DETERMINING HYDROGEN ION CONCENTRATION

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PHOSPHATE STANDARDS.

M/15 Na_2HPO_4 Solution.	M/15 KH_2PO_4 Solution.	P_H .	M/15 Na_2HPO_4 Solution.	M/15 KH_2PO_4 Solution.	P_H .
C.c.	C.c.		C.c.	C.c.	
0.0	10.0	4.49	6.0	4.0	6.98
0.1	9.9	4.94	7.0	3.0	7.17
0.25	9.75	5.29	8.0	2.0	7.38
0.5	9.5	5.59	9.0	1.0	7.73
1.0	9.0	5.91	9.5	0.5	8.04
2.0	8.0	6.24	9.75	0.25	8.34
3.0	7.0	6.47	9.9	0.1	8.68
4.0	6.0	6.64	10.0	0.0	9.18
5.0	5.0	6.81			

The following solutions are also required :

$\frac{N}{10}$ Sodium Hydroxide Solution (Free from Carbonate).—One hundred grms. of pure sodium hydroxide are dissolved in 100 c.c. water in a flask covered with tin-foil, and allowed to stand overnight for the carbonate to settle. The solution is then filtered quickly with the aid of the pump through a hardened filter. Ten c.c. are diluted to about $\frac{N}{5}$ strength with distilled water free from carbon dioxide, standardised against potassium hydrogen phthalate to phenolphthalein, and diluted to $\frac{N}{10}$ strength. This solution is stored in a bottle coated with paraffin wax and connected by a glass tube with a burette. The bottle and the burette have side-tubes joined to soda-lime tubes to prevent the entrance of carbon dioxide.

$\frac{N}{10}$ Hydrochloric Acid.—The ordinary laboratory solution may be used. The above solutions, with the exception of the $\frac{N}{10}$ sodium hydroxide, are kept in well-stoppered resistant glass reagent bottles. The only other apparatus required consists of burettes, graduated pipettes, suitable dropping bottles for the indicators, and racks for the test-tubes.

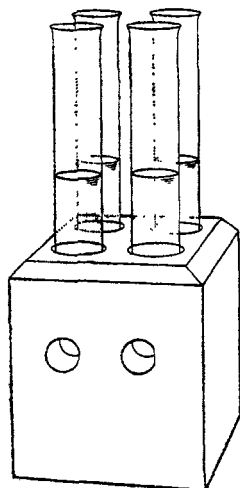
INDICATOR SOLUTIONS.—The following table shows a complete series of indicators which may be used for solutions from $P_H=1$ to $P_H=11$. These indicators are now readily obtainable on the market.

			Strength of Solution.	Range of P_H .
			Per Cent.	
Thymol blue	0.04 in water	{ 1.2 to 2.8 8.0 to 9.6
Brom-phenol blue	0.04 "	2.8 to 4.66
Methyl red	0.02 in 50 per cent. alcohol	4.4 to 6.0
Brom-cresol purple	0.04 in water	5.2 to 6.8
Brom-thymol blue	0.04 "	6.0 to 7.6
Phenol red	0.02 "	6.8 to 8.4
Thymolphthalein	0.04 in alcohol	10.0 to 11.0

METHOD OF DETERMINATION—1. For Clear or Turbid Liquids Free from Colour.

—The solution to be tested is tried with various indicators until one is found which gives a tint lying between its extremes of colour. Ten c.c. of the solution are then run into a clean test-tube, washed with neutral distilled water, and 5 or more drops of the indicator solution are added. With a little practice it is easy to judge from the shade of colour roughly what the P_H value is. Ten c.c. of a solution of this P_H value are then prepared in another test-tube from the standard solutions by consulting the tables—e.g., if the solution gives a neutral colour with brom-phenol blue, the P_H may be judged to be about 3.5. From the tables we see that a mixture of 4.75 c.c. of $\frac{N}{10}$ citrate solution and 5.25 c.c. of $\frac{N}{10}$ hydrochloric acid has a P_H value of 3.53. This mixture is therefore prepared by running in the solutions from burettes or graduated pipettes. Five drops of the indicator are added and the colours compared. If the shades of colour do not match, another tube of a different P_H value is prepared until an exact match is obtained.

2. *For Coloured Liquids.*—For this purpose the piece of apparatus known as a comparator is used (see diagram). It consists of a cubical block of wood of $3\frac{1}{2}$ inches



side, with four holes bored vertically to hold four test-tubes. Two holes are also bored horizontally completely through the block, so that it is possible to look through two pairs of test-tubes simultaneously. In hole No. 1 is placed the tube containing 10 c.c. of the solution to be tested and 5 drops of indicator. Hole No. 2, behind this, holds a tube containing 10 c.c. of distilled water. In No. 3 we have the tube containing 10 c.c. of the standard solution with 5 drops of indicator, and, behind this, in No. 4 is a tube containing 10 c.c. of the coloured solution. In this way the colour is compensated, and we can compare the shades of colour without interference from the colour of the solution. If the colour of the solution is very dark, it may not be possible to distinguish the colour of the indicator, and recourse must be had to the electro-metric method. Where a large number of determinations has to be made it is convenient to have racks holding test-tubes containing a series of standard solutions with the indi-

cator, so that the tubes can be easily picked out for comparison and replaced. In this way a large number of solutions can be dealt with in a very short time. With practice it is quite easy to get a rough idea of the P_H value of a solution by merely adding the indicator without the use of standard solutions, and in many cases this may be all that is required.

THE DETERMINATION OF ACIDITY OR ALKALINITY OF COMMERCIAL ARTICLES.

—The method is very useful where a large number of samples have to be compared for acidity, such as gelatin, flour, starches, milk, sulphur, and many others. For merely comparative purposes all that may be necessary is to add the indicator to a suspension or solution of known strength and compare the colours without determining the actual P_H value.

Fine Chemicals.—Every pure salt when in a solution of definite concentration

should give a solution of definite P_H value. The method may therefore be used as an indication of the purity of salts and of the presence of an excess of the free acid or base. Where a strong acid is combined with a strong base the P_H of the solution should be about 7. If the base is stronger than the acid the P_H of the solution will be greater than 7, and if *vice versa*, the P_H will be less than 7.

The following are a few of the more interesting results obtained with commercial chemicals.

Sodium Salicylate.—Pure sodium salicylate prepared by dissolving pure salicylic acid in the calculated amount of pure sodium hydroxide solution was found experimentally to have in 2 per cent. solution $P_H=9.1$. A large number of commercial samples, on the other hand, were found in 2 per cent. solution to lie between $P_H=4.4$ and $P_H=5.8$. The reason appears to be that manufacturers are careful to keep an excess of salicylic acid present in order to avoid the discoloration which occurs if the salt is allowed to become alkaline. The excess of salicylic acid is found on titration to average about 0.1 per cent.

Morphine Hydrochloride.—The P_H of a 1 per cent. solution of morphine hydrochloride was found by experiment to be 3.65. Several commercial samples varied from 4.5 to 4.8, evidently containing a very slight excess of morphine. One sample, however, had a P_H of 6.5. It was not so readily soluble as usual, and was shown to contain free morphine.

Calcium Chloride.—A sample of crystalline calcium chloride was found to have a P_H in 2 per cent. solution of over 11. Calcium chloride, if pure, should give a practically neutral solution. The result was found to be due to the presence of free lime in the sample.

Potassium Iodide.—The reaction of this salt is of considerable importance from the pharmacist's point of view, as there must be no possibility of iodine being set free in the various combinations in which it is likely to occur. For this reason a salt with a slight alkaline reaction is to be preferred. If the P_H of a 2 per cent. solution is not less than 7 nor more than 9, the salt will be satisfactory from this point of view.

As other instances in which the method may be useful the determination of the alkalinity of natural waters and of soap solutions may be mentioned. For the standardisation of the reaction of bacteriological media it has to a very large extent replaced the old method of titration to phenolphthalein.

In the author's experience, in a commercial laboratory dealing with a large variety of materials, this method is finding fresh uses almost daily. There are probably many other analytical problems, besides those mentioned above, to which this method might be applied. The aim of this paper, for which but little novelty is claimed, is mainly to illustrate to those analysts who have not yet had experience of it what is, in the author's opinion, a valuable addition to analytical methods.

My thanks are due to Messrs. Allen and Hanburys, Ltd., in whose laboratories this work was carried out.

DISCUSSION.

Mr. W. PARTRIDGE said that the National Health Insurance Committee had given attention to the question of hydrogen ion concentration in so far as it was

applicable to bacteriological media, and the results of their investigation could now be obtained in pamphlet form. Referring to the personal element, which was so important in colour matching, he pointed out that the matching apparatus was independent of the original colour of the solution.

Mr. C. L. L. CLAREMONT questioned the method of expressing the results on the ground that it was a purely conventional way of expressing something we did not understand at all. In his opinion such methods as these did not mark any advance in general laboratory work, and he did not consider the method really useful. Many years ago, when other indicators were used, the results were quite as accurate and good as now.

Mr. B. S. EVANS said that there was considerable conventionality in the use of indicators, and that different indicators did give different results with different acids, and he considered it all to the good that some attempt should be made to express acidity, independently of the indicator. He would be glad to know if Mr. Evers knew of any apparatus for balancing extraneous colours in ordinary colorimetric work, as, for instance, in the colorimetric estimation of manganese in copper, where the colour of the iron present interferes with the matching of the permanganate. He cited the case of acid phosphates as one in which ordinary titration with indicators was useless.

Mr. HAWKINS said the chief difficulty was the question of carbon dioxide. Small quantities of carbon dioxide were liable to creep in, and everybody knew that in the case of the Kjeldahl process such small quantities made a distinct difference. He would be glad to have a little information as to an indicator sufficiently insensitive to carbon dioxide and yet acting as a sharp indicator in artificial light.

Mr. BOLTON asked if Mr. Hawkins had tried cochineal for Kjeldahl estimations, as he had found it sensitive both by day and night, and he thought it would be difficult to find a better indicator for that purpose.

Mr. CHAPMAN, after thanking the author for having brought the matter before the meeting in such a clear manner, remarked that everyone knew how unsatisfactory itmus, methyl orange, etc., were, on occasions, as indicators, and alluded, as an example, to the adjustment of the hydrogen ion concentration of soluble starch used in Lintner's method of determining diastatic activity. With these new indicators one could, at any rate, get definite results.

Mr. EVERS, in reply, stated that he had had considerable experience with this method and the methods in general use, and had obtained far more uniform results in this way than by the ordinary method of standardisation. Hydrogen ion concentration could be determined rapidly—rapidity was its great point, and the trouble of titration was eliminated. It was a means of getting something absolutely definite; you did understand what you were determining. So far as he knew, there was no previously described apparatus suitable for Mr. Evans's purpose, but probably the apparatus he had demonstrated would be suitable. He had always used brom-phenol blue for ammonia titrations, as he had found that it was not interfered with by carbon dioxide. He did not consider that cochineal had any advantages over these indicators, and it was not so effective for determining hydrogen ion concentration.