no use quantitatively, are by far the best on the large scale, since the various stages can be carried out with great rapidity. The resulting beryllium product is entirely soluble in sodium bicarbonate, a test which Parsons has shown to be very delicate. The separation of aluminium from beryllium will be described in a later paper.

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[CONTRIBUTION FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

## A STUDY OF INDICATORS FOR THE DETERMINATION OF TEMPORARY HARDNESS IN WATER.

BY JOHN F. NORTON AND H. I. KNOWLES.

Temporary hardness in water is due largely to the presence of calcium and magnesium bicarbonates. On heating, these decompose according to the equation

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + CO_2 + H_2O.$$

The bicarbonates, being salts of a weak acid and a relatively strong base, are hydrolyzed in solution, imparting alkaline properties to the water.

$$Ca(HCO_3)_2 + 2H_2O \rightleftharpoons Ca(OH)_2 + 2H_2CO_3.$$
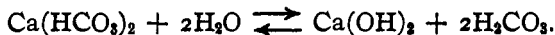
The most rapid and satisfactory method for determining temporary hardness is by titration of the alkali with standard acid in the presence of a suitable indicator. For this latter purpose, methyl orange is in quite general use, although the committee on Standard Methods[1] of Water Analysis recommends lacmoid, crythrosine or phenacetolin.[2] Peters[3] suggests alizarine, while Blacker[4] claims that dimethylamidoazobenzene gives good results. Howard[5] and Pope recommend methyl red and certain of its derivatives. Reichard[6] offers an inorganic indicator—bismuth oxyiodide.

Indicators are weak tautomeric acids or bases. According to Noyes[7] the fundamental equations upon which the theory of indicators is based are:

$$(H^+) = \frac{1-\alpha}{\alpha}\frac{K_{IA}}{\gamma}$$

for acid indicators and

[1] "Standard Methods of Water Analysis," *Am. Pub. Health Assn.*, 1912, p. 37.

[2] We are informed that the next report on Standard Methods will give preference to methyl orange.

[3] *Apoth. Ztg.*, 18, 25 (1903).

[4] *Chem. Ztg.*, 37, 56 (1912).

[5] *J. Chem. Soc.*, 99, 1333 (1911).

[6] *Pharm. Zentr.*, 53, 1033 (1912).

[7] THIS JOURNAL, 32, 815 (1910).

$$(OH^-) = \frac{\alpha}{1 - \alpha} \cdot \frac{K_{IB}}{\gamma}$$

or

$$(H^+) = \frac{1 - \alpha}{\alpha} \cdot \frac{K_w \gamma}{K_{IB}}$$

where α = fraction of indicator transformed; γ = ionization of indicator salt formed; K_{IA} and K_{IB} = ionization constants of acid and basic indicators, respectively; H^+ and OH^- = concentration of these ions in mols per liter; K_w = ionization constant of water. "These equations express the principle that in any titration with a given indicator the end point (determined by color change) is reached when the H^+ concentration in the titrated solution attains a definite value. This value varies with the ionization constant of the indicator and the fraction transformed."[1]

It can be shown mathematically that α should always be a relatively small value, usually not greater than 25% if accurate results are to be obtained.

The use of indicators in water analysis differs from their use in ordinary volumetric work on account of the presence of a variety of salts, and of weak acids, both organic and inorganic, which may have a very decided effect on the results obtained.

Walker and Kay[2] have suggested that the alkalinity or acidity of a water be expressed in terms of the hydroxyl or hydrogen-ion concentration. It will be seen at once that this will have little relation to the temporary hardness, which should also include the "reserve"[3] alkalinity or acidity.

The problem before us is to determine the range of hydrogen-ion concentrations corresponding to a complete neutralization of the bicarbonates by an acid, including the effect of the presence of other salts and of carbonic acid. Knowing this, we will then choose a series of indicators having the proper constants. This series will then be subjected to a practical test on waters of known composition, after first ascertaining the best end point for each indicator.

Since sulfate of alum is in common use for the purification of water supplies, it seems desirable to have an indicator which will be sensitive to the acidity produced by this salt. Comparative tests will therefore be made to determine this property.

Experimental Part.

Hydrogen-Ion Concentration in Titrated Waters.—To determine this a series of four waters was conceived, analogous in composition to neutral waters so far as concerns those constituents which might affect indi-

[1] THIS JOURNAL, 32, 821 (1910).
[2] J. Soc. Chem. Ind., 31, 1013 (1912).
[3] Washburn, Proc. Ill. Water Supply Assn., 93, 101 (1910).

cator end points (Table I). Solutions were then made up to represent
the composition of these waters after the bicarbonates had been neu-
tralized with hydrochloric acid (Table II).

TABLE I. Composition of Synthetic Waters.					TABLE II. Composition of Synthetic Waters. "After Titration."				
	Parts per million.					Parts per million.			
	I.	II.	III.	IV.		I.	II.	III.	IV.
Ca(HCO₃)₂.....	61	122	202	243	CaCl₂.........	42	83	140	194
Mg(HCO₃)₂.....	30	60	60	90	MgCl₂.........	20	39	39	59
MgSO₄.........	..	..	25	25	MgSO₄.........	..	..	25	25
CaCl₂.........	..	..	..	28	H₂CO₃[1].......	92	184	287	409
H₂CO₃.........	20	40	80	100					

The hydrogen-ion concentration of each of these waters was then de-
termined by the method suggested by Walker and Kay,[2] and the follow-
ing results obtained:

Water.	I.	II.	III.	IV.
H^+ conc.	5×10^{-6}	10^{-5}	2×10^{-5}	3×10^{-5}

On the basis of these results it was decided to test only those indicators
which change color between H^+ ion concentrations of 10^{-4} and 10^{-6}.
The three recommended by Standard Methods were also included. Table
III gives a list of those chosen, together with the H^+ ion concentration
at the color change, and the composition of the indicator solutions.

TABLE III.—INDICATORS.

Indicator.	H^+ conc. at color change.[3]	Soln. g. per 100 cc.
Dimethylamidoazobenzene (butter-yellow)	10^{-4}	0.2 95% alcohol
Sodium alizarine sulfonate...............	10^{-6}	0.1 water
Methyl red...........................	10^{-5}	0.1 95% alcohol
Gallein..............................	10^{-6}	0.1 water
Methyl orange........................	10^{-5}	0.1 10% alcohol
Lacmoid.............................	....	0.1 95% alcohol
Erythrosine..........................	....	0.01 water
Phenacetolin.........................	....	0.2 50% alcohol

An inorganic indicator, bismuth oxyiodide, was also made up accord-
ing to directions given by its discoverer, Reichard.[4] A light yellow
solution resulted, of color intensity equal to that given by a few drops
of methyl orange in 100 cc. of water. In the presence of alkali this indi-
cator became colorless, but a subsequent addition of acid failed to re-
produce but a part of the original yellow. Because of this fact, and of
its small coloring power, this indicator appeared to be impracticable.

[1] It has been assumed that H₂CO₃ has not escaped in titrating.
[2] *J. Soc. Chem. Ind.*, **31**, 1013 (1912).
[3] Salm., *Z. physik. Chem.*, **57**, 471 (1906).
[4] *Pharm. Zentralblat*, **33**, 1033 (1912).

Determination of Color for End Point.—The determination of a practical working end point for each indicator was next considered. To accomplish this, 1 to 2 cc. of the indicator (according to its color strength), were added to 100 cc. of water. To half of this were added 1 to 2 cc. of strong acid and to the other 1 to 2 cc. of strong alkali. This gave the two color forms of the indicator corresponding to 100% transformation. Thus in the case of butter-yellow or methyl orange, a yellow- and a red-colored solution were obtained. The solution containing the alkali was then poured into a "Petri" dish. Portions of the acid colored solution, say 5 cc., 7$^{1}/_{2}$ cc., and 10 cc., were taken and diluted to 50 cc. with distilled water. The solutions thus obtained were poured into "Petri" dishes. By placing these dishes successively over that containing the alkali-colored solution, the color at end points corresponding in this case to 10%, 15% and 20% change from alkaline to acid reaction of the indicator was approximately obtained. To get the true color at the end point, which by trial in this way proved to be a good one, a portion of the alkali-colored solution equal to that of the acid-colored solution used to give this suitable end point color, was taken out and replaced by distilled water. Thus if a good end point for butter-yellow was given by a 15% transformation, 7$^{1}/_{2}$ cc. of the yellow alkali solution would be replaced by water, giving, when the two colors were combined (85% yellow and 15% red), the true color at an end point corresponding to 15% transformation of the indicator.

By such a knowledge of the fraction of the indicator transformed from the color in alkaline solution to that in acid solution, an end point to which that indicator could always be titrated was definitely fixed; and the need, therefore, of endeavoring to remember the color at this suitable end point was eliminated. The indicators studied in this way, and their fractions transformed from alkaline solution to acid at a suitable end point are given in Table IV.

TABLE IV.

Indicator.	Fraction transformed. Per cent.	Indicator.	Fraction transformed. Per cent.
Butter-yellow[1]............	12	Lacmoid.............	25
Sodium alizarine sulfonate.	30	Phenacetolin..........	25
Methyl red..............	10	Methyl orange........	15
Gallein...........(about)	100		

Gallein was discarded because of its very indefinite end point.

Titration with Indicators.—With the indicators thus chosen and their suitable end points known, a series of waters was made up and titrated. In titrating, 100 cc. Nessler tubes were used in place of the "Petri" dishes, the shade given by these two tubes when held one before the other, and

[1] Dimethylamidoazobenzene: For convenience this will be hereafter designated by its trade name, Butter-yellow.

viewed by transmitted light, gave the color at the determined satisfactory end point. Table V gives the composition of the artificial waters used, while Table VI shows the results obtained in titrating 100 cc. of the water with hydrochloric acid (about 0.008 N).

TABLE V.

Composition of Artificial Waters, Series No. 1.

	Parts per million.			
	I.	II.	III.	IV.
$Ca(HCO_3)_2$...................	14.8	29.6	49.2	59.1
$Mg(HCO_3)_2$...................	30.0	60.0	60.0	90.0
$MgSO_4$........................	....	....	25.0	25.0
$CaCl_2$........................	....	....	....	28.0
H_2CO_3[1].....................	9.0	22.0	22.0	28.0

TABLE VI.

Titration of Artificial Waters, Series No. 1.

	I.	II.	III.	IV.
Hardness (calculated)[2]............	29.6	59.4	71.4	98.0
Indicator.		Hardness found.		
Methyl red (1 mg.)................	12.8	30.2	36.1	48.6
Sodium alizarine sulfonate (2 mg.)..	5.7	7.8	7.4	8.6
Methyl orange (1 mg.).............	25.9	54.0	64.5	87.4
Lacmoid[3] (2 mg.).................	24.8	52.3	63.0	85.5
Phenacetolin[3] (4 mg.).............	23.6	52.4	63.1	86.5
Butter-yellow (0.5 mg.)............	29.6	59.6	71.5	98.6

These results show clearly that butter-yellow is the best indicator to use in titrating bicarbonates in the presence of carbonic acid. Methyl orange, methyl red and sodium alizarine sulfonate give low results, while lacmoid and phenacetolin not only give low figures, but it was found that a series of end points could be obtained by varying the heating of the solution before final titration. To determine the end point to which methyl orange would have to be titrated in order to give accurate results in the case of water No. IV, 100 cc. were taken, 1 mg. of indicator added and the required amount of acid for neutralization run in. The color of this solution was a deep orange and corresponded to over 50% trans- formation of the indicator. Such an end point is hardly practicable.

Butter-yellow was next compared with erythrosine. The latter was used both in the presence of ether and of chloroform, the titration in both cases being done in glass-stoppered bottles. The ether solution was made by dissolving 0.025 g. of indicator in 100 cc. of ether which had been washed with weak alkali and then with distilled water until it was neutral to rosolic acid. 10 cc. of this ether solution were added to the water to be titrated. Using erythrosine in conjunction with chloroform,

[1] Approximate.

[2] Hardness expressed as parts of $CaCO_3$ per million.

[3] Solution brought to boiling before finishing titration.

2.5 cc. of a water solution of indicator (1 : 10000) and 5 cc. of neutral chloroform were added. As this amount of indicator was found to give low results, the amount was increased to 5 cc. Table VII gives the composition of the waters used and Table VIII the results obtained.

TABLE VII.

Composition of Waters I to III, Series No. 2.

Salt.	Parts per million.		
	I.	II.	III.
Ca(HCO₃)₂	30.0	70.0	100.0
Mg(HCO₃)₂	10.0	30.0	40.0
CaCl₂	10.0	20.0	30.0
MgSO₄	5.0	10.0	20.0
H₂CO₃[1]	1.0	2.0	2.0

TABLE VIII.

Titration of Waters I to III, Series No. 2.

	I.	II.	III.
Hardness (calculated)	25.4	63.8	89.2
Indicator.		Hardness found.	
Butter-yellow (¹/₄ mg.)	26.3	64.5	88.8
Erythrosine (in ether)	26.0	62.7	83.1
Erythrosine[2] (2.5 cc.)	24.7	61.1	82.9
Erythrosine[2] (5 cc.)	25.6	63.0	83.6

Erythrosine also gives slightly lower results than butter-yellow, the discrepancy increasing with the hardness. Ether solution is slightly better than chloroform, but not sufficiently so to overcome the disadvantage of the ether due to the escape of small amounts when the stopper is removed from the bottle. Butter-yellow has again been shown to give excellent results.

In order to still more rigidly test the effect of the presence of carbonic acid, waters containing excessive amounts were analyzed with the results as shown in Table IX.

TABLE IX.

Analysis of Waters I and II, Series No. 3.

	Parts per million.		
	I.	II.	III.
Hardness (calculated)	22.0	66.9	95.9
H₂CO₃	1110.0	1150.0	117.0
		Hardness found.	
Lacmoid (100 % trans.)	22.4	64.3	90.9
Erythrosine (5 cc.)	16.8	51.6	80.0
Butter-yellow (¹/₄ mg.)	22.6	63.1	95.6

Sensitiveness of Indicators to Alum.—It is sometimes necessary to use an indicator which is sensitive to small amounts of acid such as exist in waters which have been overdosed with alum. The indicators used

[1] Approximate.

[2] In chloroform.

above were therefore tested to determine their sensitiveness to alum by adding a known alum solution to 100 cc. of distilled water containing the indicator, until the color change was obtained. The color was then duplicated by using standard acid. The results are given in Table X.

TABLE X.

Sensitiveness of Indicators to $Al_2(SO_4)_3$.

Indicator.	$Al_2(SO_4)_3$ added (in parts per million).	Cc. HCl corresponding.
Butter-yellow............................	25	0.3
Methyl orange...........................	15	0.3
Phenacetolin[1]...........................	3	0.1
Lacmoid[1]...............................	2	0.1
Butter-yellow[1]..........................	10	0.3

Sodium alizarine sulfonate, erythrosine and congo red were tried, but found impracticable on account of color lake formation. When phenacetolin and lacmoid were used, the solution was previously heated in order to have conditions the same as in the determination of alkalinity with these indicators. It is evident from the above values that lacmoid and phenacetolin are the most sensitive indicators, while butter-yellow is in about the same class with methyl orange.

Since lacmoid possessed the admirable quality of being highly sensitive to alum, an effort was made to increase the accuracy of this indicator in the determination of alkalinity. The end point of the indicator was, therefore, extended from a 25% transformation to nearly 100%, or total transformation; that is, to a red. This end point, it may be observed, is one which approaches more closely that obtained by using lacmoid according to the procedure given by Standard Methods for the determination of alkalinity. Table IX gives the data and it is evident that but little better results were obtained.

Accurate End Point for Butter-Yellow.—In order to always titrate to the same end point, and still avoid the rather long method for obtaining it as described above, the following directions were worked out, which give the proper color with a minimum of effort. To 100 cc. of distilled water add 0.1 cc. of an alcoholic solution of butter-yellow (2 : 1000) and 0.40 cc. of 0.02 N sulfuric acid. Titrate the unknown solution, containing the same amount of indicator, until the color matches that of the standard.

Summary.

(1) Butter yellow (dimethylamidoazobenzene) is the best indicator to use in titrating the bicarbonate alkalinity (temporary hardness) of natural waters.

(2) Lacmoid gives the best results in the presence of alum, but low results are obtained in determining bicarbonates. For low alkalinities

[1] Temperature of solution 90–95°.

the difference is negligible, but its use is not to be recommended where the alkalinity is over 100.

(3) A standard color is recommended for titrations with butter-yellow.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF VIRGINIA.]

A RAPID METHOD FOR THE ESTIMATION OF COPPER AND IRON.

BY GRAHAM EDGAR.

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The insolubility of cuprous thiocyanate in dilute acid solutions has formed the basis for a number of methods for the estimation of copper. Without attempting to give complete references to the literature on this subject it may be pointed out that Rivot[1] and Van Name[2] have shown that the gravimetric estimation of copper as cuprous thiocyanate is accurate under properly regulated conditions, while Volhard,[3] Guess,[4] Jamieson,[5] and others, have based volumetric processes upon the same precipitation. The accuracy of the volumetric processes seems to be questioned by many reference books on analytical chemistry. Thus Low[6] states that cuprous thiocyanate is sufficiently soluble to necessitate the use of empirical tables in calculating the results of Guess's method, while Sutton[7] states that Volhard's method is inapplicable in the presence of iron. These statements seem to be contradicted by the results obtained by Van Name, Volhard, and by the results given in the present paper.

While engaged in the investigation of certain reactions of cuprous thiocyanate the writer was impressed by the simplicity and accuracy of the Volhard method, and carried out preliminary experiments which resulted in a modification of the Volhard procedure by which not only copper, but iron associated with it, may be rapidly and accurately estimated. The principles involved are as follows: (1) the copper is precipitated as cuprous thiocyanate and iron reduced to the ferrous state by the action of sulfur dioxide and standard NH_4CNS solution; (2) the excess of sulfur dioxide is removed by boiling, a current of carbon dioxide being passed into the solution meanwhile. The solution is then cooled and filtered; (3) the filtrate is treated with an excess of standard $AgNO_3$ solution, and is then titrated for iron with standard $KMnO_4$ solution; (4) the

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[1] Compt. rend., 38, 868 (1889).

[2] Z. anorg. Chem., 26, 230 (1901).

[3] Z. anal. Chem., 18, 285 (1879).

[4] Low, "Techn. Meth. of Ore Analysis," 7th ed.

[5] THIS JOURNAL, 30, 760 (1909).

[6] Loc. cit.

[7] "Vol. Meth. of Anal.," 10th ed., p. 200.