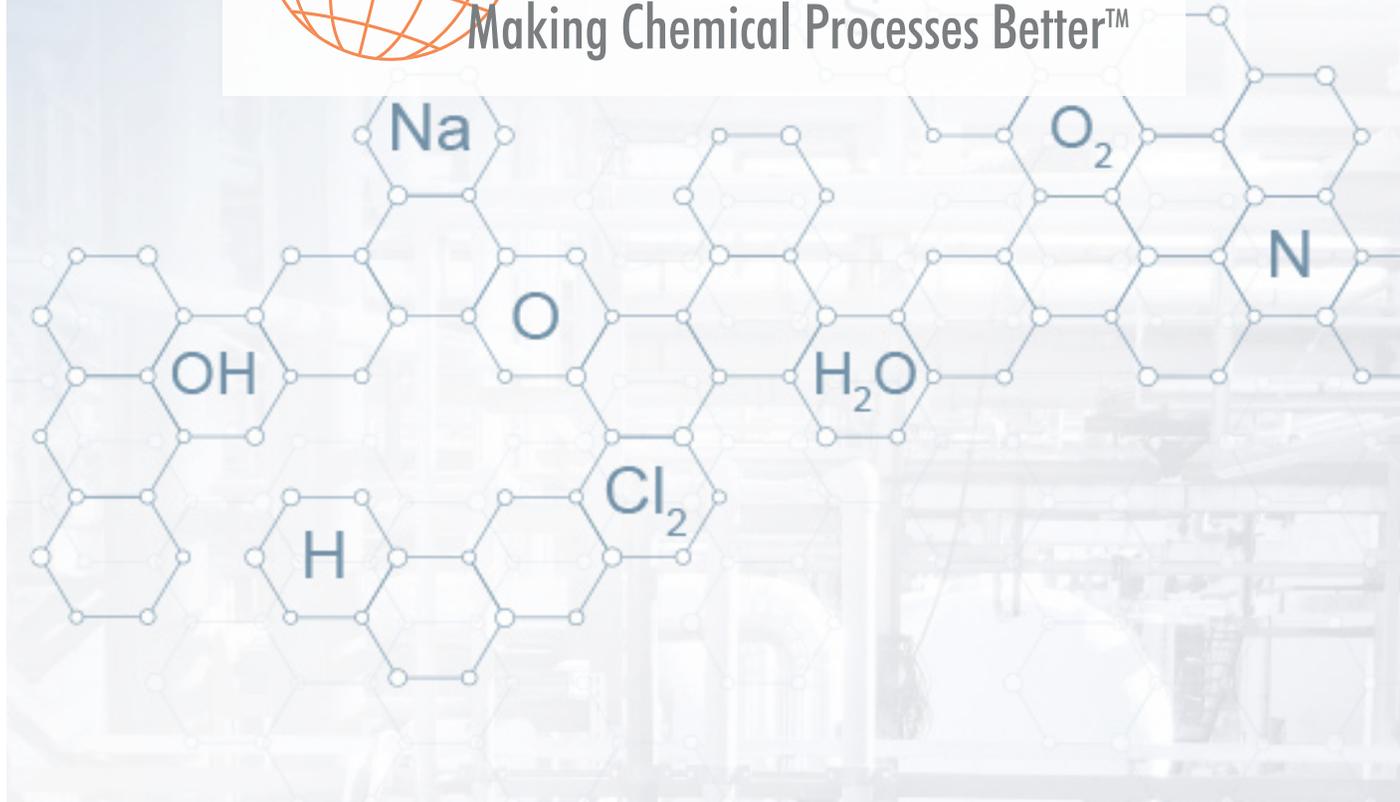




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BLEACH STRENGTH TEST

A CHEMICAL TEST METHOD TO
DETERMINE STRENGTH



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The liquid sodium hypochlorite made by our Sodium Hypochlorite System or by other methods is produced as sodium hypochlorite (NaOCl) in the presence of excess caustic. Because consumers require differing solution concentrations, bleach manufacturers need to measure specific components of the product. Sodium hypochlorite (NaOCl), excess caustic (NaOH), and excess alkalinity (Na₂CO₃) are components in bleach that are routinely tested. Although this test procedure does not address heavy metals and sodium chlorate (NaClO₃), a decomposition product, they should be tested at intermittent intervals and will require a qualified laboratory to perform these tests.

Comparative Sample Analysis

The test method will provide accurate and repeatable results by the producer and consumer to ensure the product is meeting the desired specification.

However, there are times when the strength of the sodium hypochlorite as tested by the manufacturer will differ from the consumer's results. Many times these differences can be accounted for by the losses in shipping due to decomposition. However, it is difficult to know when the differences in test results are decomposition losses and when they are errors in test methods or procedures.

In order for both the manufacturer and consumer to verify testing methods and decomposition losses, an easy procedure can be used to verify the accuracy and repeatability of each other's testing method and the decomposition losses that result due to shipping time and temperature.

At the time of loading, the manufacturer will take two retained 250 ml samples of the sodium hypochlorite loaded in the tank truck or shipping container. The manufacturer will place each sample in a separate insulated container with ice of sufficient quantity to keep the samples cold.

The manufacturer will retain one iced sample and send one iced sample with the shipment to be given to the consumer for testing. At the time of delivery, the consumer will take one more 250 ml retained sample of the sodium hypochlorite unloaded from the tank truck and place this third sample in another insulated container with ice.

Within a few hours of the arrival of the samples to the consumer's laboratory, the consumer will notify the manufacturer that the testing of the iced shipped samples will commence and both the manufacturer and the consumer will test each iced sample a total of three times. The consumer will also test the iced delivered sodium hypochlorite from the tank truck three times. By comparing results, both the manufacturer and the consumer will have data on the repeatability and accuracy of each other's results and the decomposition of the product during shipping will have been established for that given delivery time and temperature.

The differences in the results between the consumer and the manufacturer of the sodium hypochlorite should be a 0.5% or less. For example, if a test resulted in a strength of 13.70% by weight, a 0.5% error would mean the sample could have been from 13.63 to 13.77%. When comparing strength of bleach between the producer and consumer, this error can be significant. If these results are not achieved, a comparative review of laboratory methods and equipment may be required.

Analytical Method

The analytical methods described in this application note require that certain glassware and laboratory apparatus be available for use. The methods are easily performed using pipettes and volumetric glassware. The level of accuracy (and cost savings on chemicals) is directly related to the measurement. For example, higher degrees of accuracy will provide better quality control of the product and can potentially reduce manufacturing costs of the product. The following laboratory apparatus are to help you equip your facility with the minimum laboratory glassware and accessories needed to analyze your manufactured bleach.

Laboratory Apparatus	
Erlenmeyer flask (250 ml)	Burette support
Volumetric Pipette (5 ml)	Magnetic stirrer
Volumetric pipette (10 ml)	Magnetic stir bar
Volumetric pipette (25 ml)	Analytical balance (0.001 g)
Volumetric pipette (50 ml)	Reference weight (30 g)
Pipette bulb	Hydrometer (1.000 - 1.050)
Liquid Dispensers (optional) 5-30 ml	Hydrometer (1.050 - 1.100)
Weighing bottle	Hydrometer (1.100 - 1.150)
Volumetric flask (250 ml)	Hydrometer (1.150 - 1.200)
Graduated cylinder (10 ml)	Hydrometer (1.200 - 1.250)
Graduated cylinder (50 ml)	Hydrometer (1.250 - 1.300)
Burette (50 ml)	

Suggestions for Setting up Analytical Procedures

- Obtain a representative sample by flushing the sampling port so that the sample is fresh and free of foreign matter and then slowly take the sample over 30-60 seconds.
- Sample should be stored in a cool, dark place and analyzed as soon as possible. If the sample can not be tested immediately, the sample should be stored with ice or in a 40°F (5°C) refrigerator.
- Use good pipetting technique. Use a pipette bulb to draw solution into the pipette to a point above the level mark. Allow the bottom of the meniscus to reach the level mark. When dispensing the sample into a flask, touch the tip of the pipette to the side of the flask to remove only the “hanging drop”.
- Before titrating the sample, rinse the titration burette with acid, distilled water, and finally with the titrant. Fill the burette. Open the stopcock to allow the titrant to descend to the 0.00 ml mark. Make sure that the burette tip does not contain an air bubble.
- Make sure you swirl or thoroughly mix the titrant and sample in the flask during the titration.
- Refill the burette for the next titration.

High Accuracy Analytical Methods

- Tare a weighing bottle on the analytical balance. Pipette 25 ml of the bleach sample into the weighing bottle and weigh to the nearest 1.0 mg (0.001g). This is the weight of the original sample:

$$\text{Specific gravity of the bleach} = \frac{\text{sample weight}}{25 \text{ ml}}$$

- Transfer the sample to a 250 ml volumetric flask, washing all of the sample out of the weighing bottle into the volumetric flask with distilled water. Dilute to the mark with distilled water and mix thoroughly. Aliquots of this sample will be used for the sodium hypochlorite, excess caustic, and excess sodium carbonate titrations. Typical size aliquot solutions are 5 or 10 ml for the bleach test and 50 ml for the excess caustic and excess sodium carbonate test.

Grams per liter Available Chlorine

Reagents	
Glacial acetic acid (50% by weight) - 1:1 (1 L)	Sodium thiosulfate - 0.1N (1 L)
Starch solution indicator (1 L)	KI crystals (500 g)

Procedure

- Add 50 ml of distilled water to an Erlenmeyer flask.
- Pipette a 5 ml aliquot of the bleach sample into the Erlenmeyer flask with stirring. Suggested aliquot of stock solution (25/250):
 - 3-10% sodium hypochlorite: 10 ml ... using 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$... ~15 ml titrant
 - 10-16% sodium hypochlorite: 5 ml ... using 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$... ~20-25 ml titrant
- Add 2 or 3 grams (1/2 teaspoon) of KI crystals and 10 ml of 1:1 acetic acid (in this order) to the Erlenmeyer flask.
- Titrate the solution with standardized sodium thiosulfate (0.1N) ($\text{Na}_2\text{S}_2\text{O}_3$) until the mixture is straw yellow in color. A white sheet of paper should be placed under the flask with a small high intensity light pointing at the flask. This will help see the color change and achieve accurate, repeatable results. The sodium thiosulfate must be added by drops and not a steady stream. If this slow addition of sodium thiosulfate is not done, the final results will not be accurate or repeatable.
- Add 5 ml of starch indicator and continue to very slowly, drop by drop, titrate the mixture until the blue color disappears.

Calculation of Grams per Liter Available Chlorine

Based on the following titration information:

Original Dilution:	25/250 (25 ml of original bleach to 250 ml of aliquot solution)
Sample Size:	Assume 5 ml for example
Titrant (Sodium Thiosulfate):	Variable (In actual calculations use the molarity number provided by the supplier. Assume titrant = 0.1009 M = 100.9 mM for this example.)
Titrant Consumed ($\text{Na}_2\text{S}_2\text{O}_3$):	Variable (For this example assume 21.9 ml used during titration)
Stoichiometry:	1/2 = 0.5
Molecular weight of Chlorine:	70.91 grams/mole

The addition of acid to the titration flask changes the original chemical form of bleach from NaOCl to HOCl to Cl_2 . Under these conditions, sodium thiosulfate is used to reduce the valence of the chlorine atom from +1 to -1 (to the chloride ion - Cl), a change of 2 electrons. The two electron change is accounted for in the calculation by the stoichiometry of 1 to 2 or 0.5.

$$\text{g/L of available chlorine} = \frac{(\text{ml of titrant}) \times (\text{mM of titrant}) \times \text{stoichiometry} \times \frac{(1 \text{ mole})}{(1000\text{mM})} \times \frac{(70.91 \text{ grams})}{(\text{mole})}}{(\text{sample size} \times \text{original dilution})}$$

Calculation examples from example numbers above

$$\frac{21.9 \times 100.9 \times (0.5 \times 0.001 \times 70.91)}{5 \times (25/250)} = 156.71 \text{ g/L of available chlorine}$$

$$\frac{21.9 \times 100.9 \times 0.03546}{5 \times (25/250)} = 156.71 \text{ g/L of available chlorine}$$

*If 10 ml aliquot of the bleach sample is used to test strong bleach, change to sample size to 10 ml. Conversion of grams per liter available chlorine to weight percent sodium hypochlorite or weight percent available chlorine requires an accurate measurement of the specific gravity using sample weight divided by 25 ml. Therefore, only grams per liter available chlorine should be used for specifications, comparison testing, and to price the value of the product.

When grams per liter available chlorine is used, there is a direct proportional relationship between the raw materials used. For example, the raw materials used to produce 120 g/L available chlorine versus 160 g/L available chlorine is a ratio of 1.333. Therefore, the value of the product has direct proportional relationship to the g/L available chlorine with the exception of delivery cost. If the weight percent of sodium hypochlorite or available chlorine is used for final results, much greater errors in measurement will exist and the value of the product will not be directly proportional to the weight percent.

- Weight percent of sodium hypochlorite (NaOCl) = $\frac{\text{g/L available chlorine} \times 1.05}{10 \times \text{specific gravity of sample}}$
- Weight percent of available chlorine = $\frac{\text{weight percent sodium hypochlorite}}{1.05}$
- Trade percent available chlorine = $\frac{\text{g/L available chlorine}}{10}$

Weight Percent Sodium Hydroxide & Sodium Carbonate

A variety of methods are currently being used by bleach manufacturers to measure excess caustic and alkalinity. These methods include the use of barium to precipitate carbonate species or the use of various pH indicators during the titration steps. We recommend the analytical methods below that does not include a barium precipitation step. Phenolphthalein and methyl orange are used as pH indicators.

Barium precipitation is used by some laboratories in the weight percent sodium hydroxide and sodium carbonate titrations. Our experience has been that some type of chemical problem exists with the method and does not produce accurate results. Reagents: Hydrochloric acid 0.1 N (1 L), Phenolphthalein indicator 1% (500 ml), Neutral hydrogen peroxide solution 30% (500 ml), Methyl orange indicator 0.1% (500 ml).

Procedure

- Add 50 ml of distilled water to an Erlenmeyer flask.
- Pipette a 50 ml of the aliquot bleach sample into the flask while stirring. This sample is from the same 25/250 dilution used in the available chlorine test.
- Slowly add 3 ml of neutral 30% H₂O₂ solution to the flask. The addition of 30% of H₂O₂ solution must be done carefully. The hydrogen peroxide is added to remove all of the sodium hypochlorite from the solution by converting it to salt and oxygen. Higher bleach concentrations give a more vigorous reaction. This means the neutralization of 15% requires more care than adding H₂O₂ to a 5% bleach solution and precautions are necessary. Stir the solution while adding the H₂O₂ to prevent a sudden, vigorous reaction.
- To determine if enough hydrogen peroxide has been added, after the solution is carefully stirred and has then stopped to settle for 30 seconds, add one more drop of hydrogen peroxide to the solution. If no bubbles of oxygen are noted, no further addition of hydrogen peroxide is required. If oxygen bubbles appear, continue adding drops of hydrogen peroxide until no oxygen is generated. Do not use 3% H₂O₂ since it may have free acid in the solution and will neutralize the excess caustic. Many times this will greatly reduce the measured strength of excess caustic. Only use 30% H₂O₂.
- Add 5 drops of the phenolphthalein indicator and stir.
- Continue to stir and titrate the solution with standardized 0.1 N HCl until the pink color disappears. A white sheet of paper should be placed under the flask with a small high intensity light pointing at the flask. This will help see the color change and achieve accurate, repeatable results. The 0.1 HCl must be added by drops and not a steady stream. If this slow addition of 0.1 HCl is not done, the final results will not be accurate or repeatable. Record the ml of acid used. N = normality of standardized acid; A = ml acid used to titrate to the phenolphthalein endpoint.
- Add 10 drops of the methyl orange indicator and stir.
- Continue to stir and titrate the solution very slowly, drop by drop, with standardized 0.1 N HCl until the yellow color changes to the first appearance of a “rust/red” color. This endpoint is not instantaneous. Stirring the titration, notice the “rust” color that appears as you drop HCl into the solution before it turns back to yellow. The first stable appearance of this color is what you are titrating to. Record the ml of acid used. B = total ml acid used to titrate to the methyl orange endpoint.

Calculations

Percent NaOH by weight:

$$\frac{\{B-[2(B-A)]\} \times N \times 0.040}{50/250 \times \text{wt of original sample}} \times 100$$

The addition of acid to the titration flask directly titrates the NaOH with HCl. Thus, the value 0.040 is the formula weight of NaOH (40) divided 1,000 because we are working in milliliters. The indicator, phenolphthalein, in base is red. After the base is titrated, the additional acid starts to change the mixture pH. When the pH changes from pH 10 to 8.2, the indicator changes from red to colorless indicating that all the base is titrated.

Percent Na₂CO₃ by weight:

$$\frac{[2(B-A)] \times N \times 0.053}{50/250 \times \text{wt of original sample}} \times 100$$

After the caustic titration is complete, the addition of more acid will titrate the carbonate ion (CO₃²⁻) to carbon dioxide (CO₂) a 2 electron change. Thus, the value 0.053 is the formula weight of Na₂CO₃ (106) divided by the electron change divide by 1,000 because we are working in milliliters. After the carbonate ion is titrated, the additional acid starts to change the mixture pH. When the pH changes for pH 4.4 to 3.1, the indicator changes from yellow to red indicating that all the carbonate ion is titrated.

Calculation of Liquid Bleach pH

The pH of liquid bleach can be calculated using the data from the weight percent sodium hypochlorite titration.

- Measure the liquid bleach specific gravity.
- Calculate the trade percent NaOH: Trade percent NaOH = weight percent NaOH x specific gravity
- Calculate the g/L NaOH: g/L NaOH = trade percent x 10
- Calculate the moles/liter (M) of NaOH: $M \text{ NaOH} = \frac{\text{g/L NaOH}}{40}$
- Calculate the pH: $\text{pH} = 14 + \log (M \text{ NaOH})$

Liquid Bleach pH Calculation Based on the Weight Percent NaOH Titration

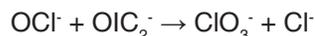
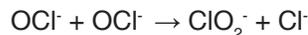
Trade % NaOH	g/L NaOH	M NaOH	pH
0.001	0.01	0.00025	10.40
0.002	0.02	0.00050	10.70
0.003	0.03	0.00075	10.88
0.004	0.04	0.00100	11.00
0.005	0.05	0.00125	11.10
0.010	0.10	0.00250	11.40
0.015	0.15	0.00375	11.57
0.020	0.20	0.00500	11.70
0.025	0.25	0.00625	11.80
0.030	0.30	0.00750	11.88
0.035	0.35	0.00875	11.94
0.040	0.40	0.01000	12.00
0.045	0.45	0.01125	12.05
0.050	0.50	0.01250	12.10
0.055	0.55	0.01375	12.14
0.060	0.60	0.01500	12.18
0.065	0.65	0.01625	12.21
0.070	0.70	0.01750	12.24
0.075	0.75	0.01875	12.27
0.080	0.80	0.02000	12.30
0.085	0.85	0.02125	12.33
0.090	0.90	0.02250	12.35
0.095	0.95	0.02375	12.38
0.100	1.00	0.02500	12.40
0.105	1.05	0.02625	12.42
0.110	1.10	0.02750	12.44
0.115	1.15	0.02875	12.46
0.120	1.20	0.03000	12.48
0.125	1.25	0.03125	12.49
0.130	1.30	0.03250	12.51
0.135	1.35	0.03375	12.53
0.140	1.40	0.03500	12.54
0.145	1.45	0.03625	12.56
0.150	1.50	0.03750	12.57
0.155	1.55	0.03875	12.59
0.160	1.60	0.04000	12.60
0.165	1.65	0.04125	12.62
0.170	1.70	0.04250	12.63
0.175	1.75	0.04375	12.64
0.180	1.80	0.04500	12.65
0.185	1.85	0.04625	12.67
0.190	1.90	0.04750	12.68
0.195	1.95	0.04875	12.69
0.200	2.00	0.05000	12.70
0.205	2.05	0.05125	12.71
0.210	2.10	0.05250	12.72
0.215	2.15	0.05375	12.73
0.220	2.20	0.05500	12.74
0.225	2.25	0.05625	12.75
0.230	2.30	0.05750	12.76
0.235	2.35	0.05875	12.77
0.240	2.40	0.06000	12.78

Trade % NaOH	g/L NaOH	M NaOH	pH
0.245	2.45	0.06125	12.79
0.250	2.50	0.06250	12.80
0.255	2.55	0.06375	12.80
0.260	2.60	0.06500	12.81
0.265	2.65	0.06625	12.82
0.270	2.70	0.06750	12.83
0.275	2.75	0.06875	12.84
0.280	2.80	0.07000	12.85
0.285	2.85	0.07125	12.85
0.290	2.90	0.07250	12.86
0.295	2.95	0.07375	12.87
0.300	3.00	0.07500	12.88
0.305	3.05	0.07625	12.88
0.310	3.10	0.07750	12.89
0.315	3.15	0.07875	12.90
0.320	3.20	0.08000	12.90
0.325	3.25	0.08125	12.91
0.330	3.30	0.08250	12.92
0.335	3.35	0.08375	12.92
0.340	3.40	0.08500	12.93
0.345	3.45	0.08625	12.94
0.350	3.50	0.08750	12.94
0.355	3.55	0.08875	12.95
0.360	3.60	0.09000	12.95
0.365	3.65	0.09125	12.96
0.370	3.70	0.09250	12.97
0.375	3.75	0.09375	12.97
0.380	3.80	0.09500	12.98
0.385	3.85	0.09625	12.98
0.390	3.90	0.09750	12.99
0.395	3.95	0.09875	12.99
0.400	4.00	0.10000	13.00
0.405	4.05	0.10125	13.01
0.410	4.10	0.10250	13.01
0.415	4.15	0.10375	13.02
0.420	4.20	0.10500	13.02
0.425	4.25	0.10625	13.03
0.430	4.30	0.10750	13.03
0.435	4.35	0.10875	13.04
0.440	4.40	0.11000	13.04
0.445	4.45	0.11125	13.05
0.450	4.50	0.11250	13.05
0.455	4.55	0.11375	13.06
0.460	4.60	0.11500	13.06
0.465	4.65	0.11625	13.07
0.470	4.70	0.11750	13.07
0.475	4.75	0.11875	13.07
0.480	4.80	0.12000	13.08
0.485	4.85	0.12125	13.08
0.490	4.90	0.12250	13.09
0.495	4.95	0.12375	13.09
0.500	5.00	0.12500	13.10

Weight Percent Sodium Chlorate

In basic solution, OCl^- decomposition to form chlorate ion has been shown to be a second order process¹ $\text{Rate} = k_2 [\text{OCl}^-]^2$ with the following stoichiometry: $3\text{OCl}^- \rightarrow \text{ClO}_3^- + 2\text{Cl}^-$.

The decomposition of OCl^- involves chlorite ion (ClO_2^-) as an intermediate in the following generally accepted mechanism².



The most reliable ClO_3^- measurement is by ion chromatography (IC). The titration method for ClO_3^- suffers from many interferences and thus is not very accurate. We have an arrangement with an analytical laboratory to measure the various components in liquid bleach. Contact Dr. Bernard Bubnis at the address below.

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Bleach Strength
Weight percent Bleach
Weight percent Caustic
Weight percent Alkalinity
Clarity/Suspended Solids

Inorganics
Chlorate Ion
Bromate Ion

Transition Metal Ions
Iron
Copper
Nickel

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