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Suspended Solids Quality Test for Bleach Using Vacuum Filtration

(Revised 11/17/03)

Background

The suspended solids quality test for bleach using vacuum filtration is a general procedure for assessing bleach quality and clarity. In the manufacture of bleach, off-color and turbidity are frequent problems in unfiltered bleach due to the presence of transition metal ion complexes in solution and as precipitates.

This procedure is based on the time it takes to filter 1 liter of bleach at constant vacuum. A laboratory water aspirator will typically pull a vacuum equal to 20 inches of Hg on a filtration flask. When 1 liter of bleach is filtered under vacuum (20 in. Hg), high clarity bleach will take <3 minutes to filter. In contrast, low clarity bleach will take at least twice this amount. This large difference between low clarity and high clarity bleach can be used as a quality assessment of bleach.

Utilities that specify the use of the Suspended Solids Quality Test for Bleach Using Vacuum Filtration as an acceptance criterion for delivered bleach have found that high clarity bleach results in increased customer satisfaction by preventing floccing problems, oxygen gassing, as well as pipe, chemical feed equipment and instrumentation coating and clogging.

Analytical Method

Because it is difficult to standardize water aspirator vacuum, the Alltech Benchtop Vacuum Station (Deerfield, IL) was used to establish the vacuum guidelines for the bleach suspended solids test.

Apparatus	***Catalog Number***
Alltech Vacuum Station, 115 V	6417
Millipore 1 Liter glass flask, 1 Liter	XX1504705
Millipore base and tube cap, 47mm	XX1504702
Millipore 300 ml funnel, 47mm	XX1004704
Millipore spring clamp, 47mm	XX1004703
Millipore Filter Paper, Type AA, 0.8 µm	AAWP 047 00

Procedure

A. Assembling the Filtration Apparatus

The filtration apparatus is comprised of the vacuum station, flask, a base and tube cap, funnel, clamp, tygon tubing, and filter paper.

1. Attach the main cable to the Vacuum Station and plug the unit into a 115 V outlet.
2. Place the base and tube cap onto the ground glass flask.

3. Connect the tygon tubing to the vacuum station by pushing the tygon tubing over an appropriate luer lock barb and screwing one barb into the Vacuum Station and the other onto the base and tube cap.
4. Place a single 0.8 µm filter paper onto the glass filter evenly spacing around the center of the sintered glass filter.
5. Secure the filter paper by attaching the filter funnel to the base and tube cap using the spring clamp.

   Note: The position of the spring clamp is very important. Some leaking has been Observed when the spring clamp applies uneven pressure. Determine the Proper positioning of the spring clamp by filtering water and looking for leaks. When a position is found that is leak-free, proceed with the bleach filtration.

6. To prevent unintended bumping of the filter flask, it is a good idea to secure the filter flask to a ring stand.
7. Turn the Vacuum Station on by pressing the power switch to the on position.
8. Input the Vacuum Station set point.

B. Setting the Vacuum Station Set Point

Calculating the set point - At sea level, atmospheric pressure equals 762 mm Hg (or 30 inches). A typical laboratory water aspirator vacuum will "pull" 20 to 25 inches of mercury. This pull is what draws the liquid through the filtration system at a faster rate compared to gravity filtration. In the literature, it is common to describe vacuum pressure as either inches of mercury or millimeters of mercury. The conversion is

$$1 \text{ inch Hg} = 25.4 \text{ mm Hg}$$

Thus, when a water aspirator pulls 20" of mercury it is equivalent to 508 mm Hg (20 x 25.4 = 508).

To set the vacuum on the Alltech Vacuum Station to match a water aspirator, the atmospheric pressure in mm Hg needs to be calculated. This is accomplished by subtracting the vacuum to be pulled (in mm Hg) from the atmospheric pressure at sea level (762 mm Hg). For example, to pull 20 inches Hg, we need to pull 508 mm Hg. This means that 10 inches or 254 mm Hg (762 - 508 mm Hg) remain. This value is the set point on the Alltech Vacuum Station. For example, what is the set point for pulling 12 inches of mercury?

1. 12 inches Hg X 25.4 mm Hg per inch = 305 mm Hg
2. 762 mm Hg - 305 mm Hg = 454 mm Hg = set point

C. Setting the Vacuum Pump Cycle Time

The pump in the Vacuum Station operates on a cycle to maintain the desired vacuum. For the clarity application, a fast cycle is preferred. The vacuum pump cycle time is referred to as "Hysteresis" in the Alltech literature.

1. When the Vacuum Station is turned on it is in the Set Point Mode.
2. Enter the set point by scrolling either the ↑ or ↓ buttons on the membrane key pad.
3. Press and hold the mode button until the Hysteresis screen appears.
4. Scroll the ↑ or ↓ buttons on the membrane keypad until a Hysteresis value of 5 is established.
5. Touch the hold button 2 times to return to the Set Point Mode. After the set point and the hysteresis value have been set, the system is ready for bleach filtering.

D. Bleach Filtration

1. Set the Vacuum Station set point for 20 inches of mercury (set point = 254).
2. Set the Hysteresis to 5.

   Note: The keypad screen will show the set point and the actual pressure:

   SET = 254 ACT = 760

   This screen tells you that a set point of 254 has been entered and that the actual vacuum is 760 mm Hg (i.e. no vacuum is being pulled). Once the values are inputted, the pump will begin to cycle and the ACT value will begin to decrease (vacuum is being pulled). The ACT value will decrease until the set point is reached. When the ACT = SET the pump will begin to cycle to maintain the set point pressure. Because a cycling time (hysteresis) of 5 was entered, the pump will turn on/off when the ACT $\pm$5 units of the set point value.

3. Vigorously mix the sample to be tested and carefully fill a 1 liter volumetric flask to the mark with bleach.

   Note: Proper safety procedures must be observed during the clarity test including ensuring proper ventilation, the use of safety shields and glasses, and other generally established practices for handling liquid bleach.

4. Prepare a stopwatch for timing the filtration.
5. Wet the filter paper (otherwise you cannot pull a vacuum).
6. Turn the Vacuum Station on by pressing the power switch to the “ON” position and when the SET and ACT pressure readings are about equal, begin the filtration (and start the filtration stopwatch) by carefully filling the filtration funnel with bleach until the volumetric flask is empty.

   Note: Carefully watch the bleach pour through the filter paper. Typically the bleach running through the filter starts to slow down as suspended solids build up on the filter paper. If the bleach suddenly speeds up, this indicates that the filter paper has torn from the high level of suspended solids in the bleach. If the sample bleach consistently tears the filter paper, double the filter paper as previously discussed.

7. After the bleach has passed through the filter, turn off the stopwatch and record the time.

Important: Because bleach is corrosive, the system must be ventilated between filtration runs.

- a. After completing a bleach filtration, touch the mode keypad 1X -- you are now in the Continuous Vent Mode.
- b. Allow the system to vent for at least 5 minutes prior to filtering a second bleach sample.
- c. Touch the mode keypad 2X to return to the filtration mode.
- d. Replace the filter(s) and wet the surface with water. A vacuum will start to build as indicated on the keypad screen (ACT begins to decrease).
- e. Place 1,000 ml of bleach into the filter funnel and start the filtration stopwatch

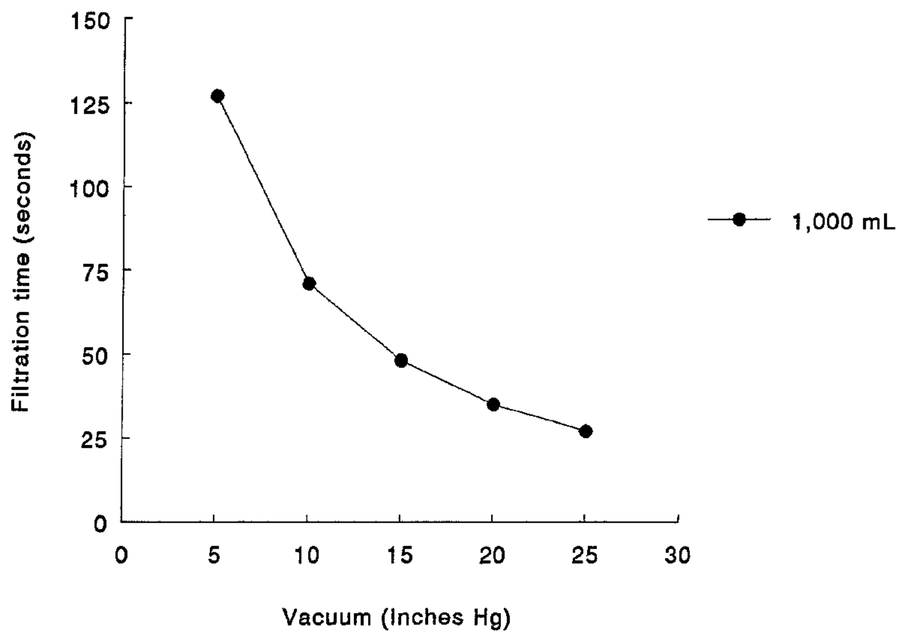
E. Filtration Times

Bleach filtration times for 1-liter volumes were recorded for tap water, filtered bleach and non-filtered bleach at various vacuums. If you don't know the pull of your in-house water aspirator filtration system, you can estimate your water aspirator vacuum using the procedure below:

Estimating the vacuum (only necessary if utilizing equipment whereby vacuum is unknown)

- Set-up the water aspirator filtration system to filter 1 liter of tap water
- Filter 1 liter of tap water and record the time
- Refer to the filtration time vs. vacuum graph and find the filtration time on the y-axis
- Draw a straight line from the y-axis to the curve and extrapolate to the x-axis
- The x-axis extrapolation provides an estimate of vacuum.

Filtration Time vs. Vacuum



Bleach Filtration - The following chart and table show typical filtration times for 1 liter of tap water, filtered bleach and non-filtered bleach. When pulling 25 mm Hg, the average filtration time for tap water is 27 seconds (about 1/2 minute). Under the same conditions, filtered bleach takes 103 seconds (about 13/4 minutes). This is a good bleach clarity filtration time. By comparison, 1 liter of non-filtered bleach takes significantly longer. Actual times may vary slightly depending on the quality of the tap water in your area of the country.

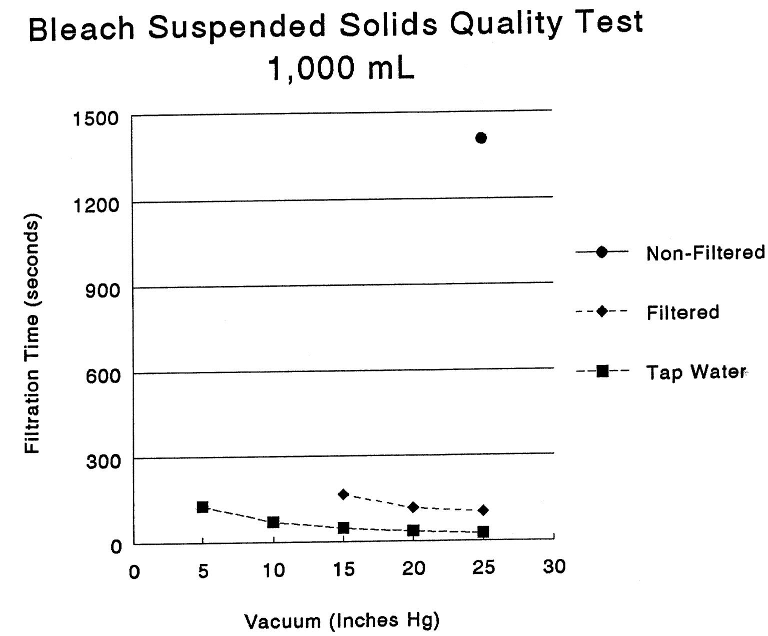
Typical Filtration Times

1 liter

Inches Hg	Mm Hg	Set Point	Tap Water (Seconds)	Filtered Bleach (Seconds)	Non-Filtered Bleach (Seconds)
5	127	635	127		
10	254	508	71		
15	381	381	48	170	
20	508	254	35	120	
25	635	127	27 (~1/2 min)	105 (~ ¾ min)	1,400 (>20 min)

Note: Error of replicate filtration times was typically <5%

In the following chart, note the similar filtration times for tap water and high clarity bleach. Also note that large difference in the filtration time for the low clarity (unfiltered) bleach.



The suspended solids test requires the use of a 0.8 micron filter. Our studies show that the most durable and reliable filter is the Millipore Type AA 0.8 micron filter. It does not matter which side of the filter paper faces up (e.g., "shiny" side up or down). In total 6 filters (nylon, and polycarbonate) were tested. A variety of problems were encountered including the tearing of the filter, poor sealing around the edges of the filter, and in some cases the filter became brittle and broke apart.

We recommend that the suspended solids test be performed pulling 20 inches of Hg. Under these conditions, the following results are typical.

Typical Filtration Times @ 20 in. Hg
(15 Trade %)

Filtered A	Unfiltered A	Filtered B	Unfiltered B	Filtered C	Unfiltered C
< 2 min	> 6 min	< 1 min	> 15 min	< 2 min	> 60 min

It is interesting to note the large difference in the filtration times of the unfiltered bleach samples. These samples were chosen as examples of membrane caustic with softened water (A), membrane caustic with city water (B) and diaphragm caustic with city water (C).

The data indicate that filtration removes unwanted turbidity (i.e. improves the clarity) in bleach due to the presence of transition metal ions. Filtration also helps to eliminate the adverse effects (decomposition) of reactive metal ion complexes that form during bleach production. The Suspended Solids Quality Test for Bleach Using Vacuum Filtration is the simplest way to assess bleach clarity at the time of delivery. If 1 liter of delivered bleach takes more than 3 minutes to filter, there is an increased likelihood that the product is not high clarity bleach.

Bleach Filtration and Transition Metal Ion Catalysis

The formation of oxygen from decomposing OCl^- is a very slow side reaction in solutions of pure OCl^-. However, in the presence of transition metal ions the rate of bleach decomposition by the oxygen pathway is increased.

$$OCl^- + OCl^- \rightarrow O_2 + 2Cl^-$$

The effect of various metal ions (Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+}) on the catalyzed decomposition of OCl^- in basic solution was recently investigated by Gordon[1]. Nickel ion appears to strongly catalyze bleach decomposition either alone or in combination with other transition metal ions. Thus, bleach strength will be reduced in the presence of transition metal ions (Ni > Co > Cu > Fe > Mn > Hg)[2].

The role of transition metal ion catalysis in liquid bleach is complex. In general, nickel ion appears to effectively catalyze decomposition either alone or in combination with other transition metal ions. The maximum concentration of transition metal ions that will not significantly affect the decomposition of bleach is ~0.1 mg/L Ni^{2+} and ~1 mg/L Cu^{2+}. Ferric ion (Fe^{3+}) and Mn^{2+} when present alone, are not considered to be effective catalysts for bleach decomposition and readily precipitate.

Soluble transition metals are generally present as M^{n+}-hydroxide complexes or as anionic complexes such as phosphates, chlorides, or hypochlorites. The metal complexes also may be present as dimeric (or oligomeric) M^{n+}-hydroxide complexes, which eventually may or may not precipitate. In the manufacture of bleach, many types of metal complexes undoubtedly form both in solution and as precipitates. The bleach manufacturers are aware of metal ion precipitates and thus filter the bleach or allow the precipitates to "settle" so that what is typically sold is a clear solution free of precipitates. However, precipitates are frequently observed in holding tanks at utilities using liquid bleach that is mixed with unsoftened water. In addition, dissolved metal ion complexes are most probably also formed. Any or all of these metal-complex species can lower the bleach content in the holding tank once again resulting in the formation of oxygen.

Sources of Transition Metal Ions in Commercial Bleach

The electrolytic cells used to manufacture caustic are categorized into three classes: diaphragm (e.g., commercial grade), mercury (e.g., rayon), and membrane cells. The level of impurities in the caustic is directly related to the type of process. Many bleach manufacturers use caustic produced by diaphragm cells because of its lower cost. Unfortunately, this type of caustic also has the highest level of impurities. Membrane and mercury cell caustic are the most expensive and have the fewest impurities.

Thus, the primary quality issue with respect to caustic type is the product impurities. In caustic, the transition metal ions (Fe, Cu, and Ni) are soluble and most likely present as the sodium salts of various anionic complexes. However, if the caustic is diluted, precipitates of virtually unknown composition will slowly appear.

Bleach is regarded of poor quality when it contains turbidity and color other than clear bright yellow. Bleach quality is directly related to the caustic used in manufacturing. The metal ions contained in bleach can originate from numerous sources. A few are listed below[3]:

Nickel	The origin of nickel in 50% caustic is from the nickel evaporators used to concentrate dilute caustic from the electrolytic cells. It can also come from nickel containing Na_2CO_3 and NaCl sediments from the bottom of the caustic storage tanks. In terms of quality, nickel in excess of 0.3 ppm results in black residues.
Iron	15% NaOH from cell liquor generally contains 0.6 ppm iron that is concentrated to about 3 ppm in 50% caustic. Iron also will concentrate in the sludge at the bottom of storage tanks resulting in more than 5 ppm Fe in 50% caustic. Caustic is generally transported in lined steel tanks and dilution and storage operations are generally carried out in unlined steel tanks. During these operations, the tank will corrode resulting in iron buildup. Iron in excess of 3 ppm in 50% caustic leads to off colored, brownish bleach.
Calcium Magnesium	The levels of calcium and magnesium in caustic is low. However, if hard water is used for diluting the caustic, the calcium and magnesium levels will undoubtedly increase. Excessive levels can also result from the sludge at the bottom of storage tanks that are low in caustic. Calcium and magnesium in excess of 6 and 9 ppm respectively cause light colored turbidity and sediments.

The use of bleach filtration improves the quality of concentrated bleach. Color and turbidity are easily removed using in-line filtration, and the product will have a longer storage lifetime with much less pluggage and buildup in the feed system. In the coming months, the quality and storage issues will become more important as more utilities begin to purchase bleach and test the delivered product. Thus, in the future, it will be an advantage to provide high clarity bleach.

References

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2. Redemann, C.E. “The Chemistry of Hypochlorous Acid and the Hypochlorites with Applications to Bleaching and Bleach-making” Second Edition, October 1970, Purex.
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