CHEMTEX
INTERNATIONAL CHEMTEX CORPORATION

Technical Topics

Test Procedures

"Explanation of methods and possible interferences"

TT-026-0196

The following are some of the more common tests performed by water treatment service personnel. An explanation of the test method and some possible interference's that may be encountered are included.

This information should help in understanding what is actually happening when performing these tests and also why sometimes they do not work. This can save possible headaches in the field when problems are encountered. Use this as a handy reference.

TOTAL HARDNESS

TESTING PROCEDURE:
Complexometric titration with EDTA

Add "buffered" indicator powder to the sample as required. Magnesium is required to be present in order to achieve a satisfactory endpoint. To insure this, a small amount of complexometrically neutral magnesium salt of EDTA is added to the buffered indicator powder - 129P.

Titrate slowly, with continuous stirring, until the last reddish tinge disappears. Add the last drops of titrant at 3 - 5 second intervals because the last color change occurs at a slow rate. The endpoint is a true blue color.

INTERFERENCES

Sharpness of endpoint increases at an increased pH. A pH of 10 + or - 0.1 is satisfactory but should not be exceeded because $CaCO_3$ or $Mg(OH)_2$ can precipitate and because the dye changes color at high pH values.

Take only 5 minutes to perform this test so as to minimize the tendency toward $CaCO_3$ precipitation.

Some metal ions interfere by causing fading or indistinct endpoints or by stoichiometric consumption of EDTA and will give a false high reading.

Titrations should be conducted at or near normal room temperatures. Color change becomes impractically slow in cold samples and indicator composition becomes a factor in hot water.

The endpoint after titration is a true blue color. Ordinary incandescent lights tend to produce a reddish tinge in the blue endpoint. Daylight or daylight florescent lighting is recommended.

CALCIUM HARDNESS

TESTING PROCEDURE:
Complexometric titration with EDTA

When EDTA is added to water containing both calcium and magnesium, it combines first with the calcium. Calcium can be determined directly with EDTA when the pH is made sufficiently high so that the magnesium is largely precipitated as the hydroxide and the indicator used combines with the calcium only. Adding D-652 increases the pH sufficiently to precipitate $Mg(OH)_2$.

Because of the high pH used in this procedure, titrate immediately after adding the alkali due to the fact that the indicator becomes unstable under alkaline conditions.

The color changes from pink to bright purple during titration. The endpoint is reached when there is no further color change when additional titrant is added.

INTERFERENCES

Alkalinity in excess of 300 ppm may cause an indistinct endpoint in hard waters. Dilution of the sample with distilled water may be necessary.

The following concentrations of ions should cause no interference problems with this test: (Cu^{2+} - 2 ppm), (Fe^{2+} - 20 ppm), (Fe^{3+} - 20 ppm), (Mn^{2+} - 10 ppm), (Zn^{2+} - 5 ppm), (Pb^{2+} - 5 ppm), (Al^{3+} - 5 ppm) and (Sn^{4+} - 5 ppm).

Orthophosphate precipitates calcium at the pH of this test and can cause low readings.

CHLORIDE

TESTING PROCEDURE:
Argentometric Method

Silver Nitrate plus Chromate Indicator plus Chlorides yields a white precipitate of silver chloride. Once all Cl^- ions have been precipitated, b) the Silver Nitrate then reacts with the Chromate Indicator to form an orange precipitate of Silver Chromate

a) $AgNO_3 + K_2CrO_4 + Cl^-$ ----------> AgCl
(white precipitate)

b) $AgNO_3 + K_2CrO_4$ ----------> Ag_2CrO_4
(orange precipitate)

The sample is titrated until the bright lemon-yellow color just stars to turn orange. A dark reddish-orange color will appear if excess silver nitrate is added.

A consistent choice of endpoint is really what is required. If a darker endpoint is easier for you to see, always titrate to the same point with all samples to achieve reproducibility from sample to sample. (Be careful when comparing your test results with others).

INTERFERENCES

Sulfide, thiosulfate and sulfite can interfere. Add 1 ml of 30% H_2O_2 per 100 ml of sample and wait one minute before performing the test.

Samples must be titrated in the pH range from 7 to 10. The sample can be adjusted to pH of 8.3 by performing the "P" Alkalinity test if the pH is too high. If the pH is too low, add NaOH to reach the desired range.

Orthophosphate in excess of 25 ppm interferes by precipitating as silver phosphate causing a high reading.

Iron in excess of 10 ppm masks the endpoint.

Bromide, iodide or cyanide in the sample will read as equivalent chloride concentrations.

SULFITE

TESTING PROCEDURE:
Titration

An acidified sample containing sulfite (SO_3^{-2}) is titrated with a potassium iodide-iodate titrant. Free iodine (provided by the DT-402 reagent) reacts with SO_3^{-2}. The titration endpoint is signaled by the blue color resulting from the first excess of iodine reacting with the starch indicator.

The pH of the sample during titration should be 8.0 or less. The more acidified the sample the better.

Sample must be at room temperature.

INTERFERENCES

Sulfide, thiosulfate and Fe^{+2} ions (soluble ferrous form), can cause high results for sulfite.

Some metal ions such as Cu^{2+} may catalyze the oxidation of SO_3^{-2} to SO_4^{-2} when the sample is exposed to air which leads to low results.

NO_2^- will react with SO_3^{-2} in the acidic reaction medium and lead to low sulfite results. Sulfamic acid in the starch-acid indicator powder (I-501) helps destroy the nitrite.

ORGANOPHOSPHONATE

TESTING PROCEDURE:
Direct titration

A sample containing phosphonate, acidified to a narrow range of pH 2.5 - 3.0 is titrated with a solution of thorium nitrate using a xylenol orange indicator.

The thorium forms a stable, colorless complex with the phophonate present in the sample. A xylenol orange-thorium complex will form only when all of the phosphonate has been used up by first complexing with the thorium because the xylenol orange-thorium complex is less stable than the thorium-phosphonate complex. The xylenol orange-thorium complex formed in the acid range results in a color described as pink, rose, violet and purple. The endpoint of this titration is when the first pink color starts to appear.

INTERFERENCES

Below pH 2.5, sulfate interferes with the endpoint by causing a false high reading. At this low pH, The SO_4 ion forms a complex with thorium. In order for the pink endpoint to be developed, all thorium demand by SO_4 must be satisfied.

Iron (Fe^{+3} - insoluble ferric) forms stable complexes with phosphonates at pH of 2.5 - 3.0 as well as at higher pH values. As a consequence, since the Fe^{+3} - phosphonate complex is stronger than the thorium-phosphonate complex, the presence of Fe^{+3} ions will give a false low reading. In effect, the phosphonate is complexed by the iron and rendered undetectable because the thorium complex is not strong enough to displace the iron. If enough iron is present, a zero phosphonate result by thorium titration is possible. Removal of the iron by filtration is necessary.

Calcium and magnesium ions do not form stable complexes with phosphonates at pH 2.5 - 3.0 and do not interfere with the titration at this low pH.

Polyphosphates can complex with the thorium causing false high readings. Municipal water supplies adding a polyphosphate stabilizer can often cause a higher titration result in cooling water samples. An accurate blank test should be run on makeup water supply in order to minimize the effects of polyphosphates. Cooling treatment products also may contain polyphosphates and can cause problems if you are controlling a system with organophosphonate.

Fluoride ion present in the city water used as the makeup supply or cooling water known to contain fluoride ion will cause a false high reading. 1 ppm of fluoride can produce high results by as many as 3-5 drops depending upon strength of the titrant. Use of a fluoride suppressing agent is necessary. Reagent 987 in the K-800 kit is used for this purpose.

Chlorine causes the xylenol orange indicator to fade causing extreme difficulty in determining the endpoint. Chlorine interference is removed by the addition of thiosulfate solution prior to adding the xylenol orange indicator. D-801 in the K-800 kit performs this function.

The xylenol orange indicator is a mono-hydrated form (contains one attached water molecule) when you first receive it for use. If an additional water molecule becomes attached (becomes a dihydrate form), the indicator will not produce accurate results. If you notice your indicator is wet and not free-flowing it should be discarded and replaced.