
Hardness

For water, wastewater and seawater

EDTA Titration and Calmagite Colorimetric
Methods

Introduction

Hardness in water is caused by dissolved minerals, primarily divalent cations, including calcium (Ca^{2+}), iron (Fe^{2+}), strontium (Sr^{2+}), zinc (Zn^{2+}) and manganese (Mn^{2+}). Calcium and magnesium ions are usually the only ions present in significant concentrations; therefore, hardness is generally considered to be a measure of the calcium and magnesium content of water. Considerations should be given when other cations contributing to hardness are present in significant amounts.

Titration methods

Hardness in water can be determined quickly by titration and the use of color indicators. By proper choice of pH, total hardness (Ca^{2+} and Mg^{2+}) or the portion contributed by calcium and magnesium individually can be measured. The traditional test for hardness involves pH adjustment to 10.1 with an ammonium buffer, addition of Eriochrome Black T indicator [1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulfonic acid] and then titration with Na_2EDTA (ethylenediaminetetraacetic acid, disodium salt) solution.

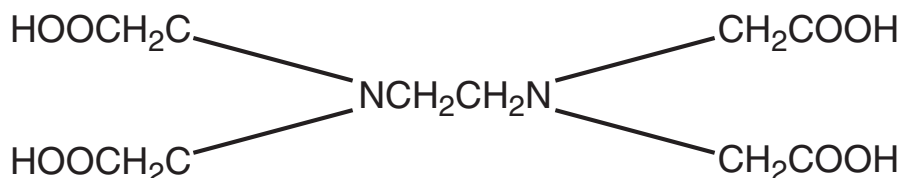


Figure 1 Chemical structure of EDTA-Ethylenediaminetetraacetic acid

Some other indicators are more stable, giving a faster reaction and a more distinct end point than Eriochrome Black T. One of the best is calmagite, 1-(1-hydroxyl-4-methyl-2-phenylazo)-2-naphthol-4 sulfonic acid, which is used in Hach total hardness tests.

Colorimetric method

The Colorimetric Method is for low level measurement of hardness. The interference of some metals with the Titration Methods will be rendered inconsequential after diluting the sample to bring it into the range of this test. Calmagite indicator and two chelating agents, EGTA and EDTA, are used in the test.

Chemical reactions

Total hardness

Several solutions including digital titrator cartridges are described in the following section for titrating prepared water samples containing calmagite indicator. Titraver™ Hardness Titrant (0.020 N EDTA) is the most widely used. Other strengths of Titraver Hardness Titrant are available for titrating high hardness samples. Hexaver™ Hardness Titrant also is available. Hexaver is CDTA (cyclohexanediaminetetraacetic acid, disodium salt). It gives slightly sharper end points and can tolerate higher levels of iron interference than Titraver.

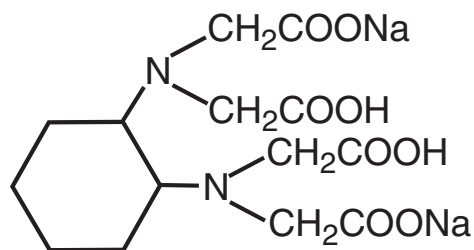


Figure 2 Chemical structure of CDTA, disodium salt

Calmagite indicator is available in special formulations as ManVer™ and UniVer™. The ManVer formulations of calmagite have been specially prepared to enhance stability and to be free from most interferences. Interferences caused by metal ions, such as copper or iron, can be removed or masked by the use of the magnesium salt of CDTA. It is effective, yet safe to use. Cyanide compounds also may be used to overcome interferences. Their use is avoided where possible because of potential environmental and health hazards.

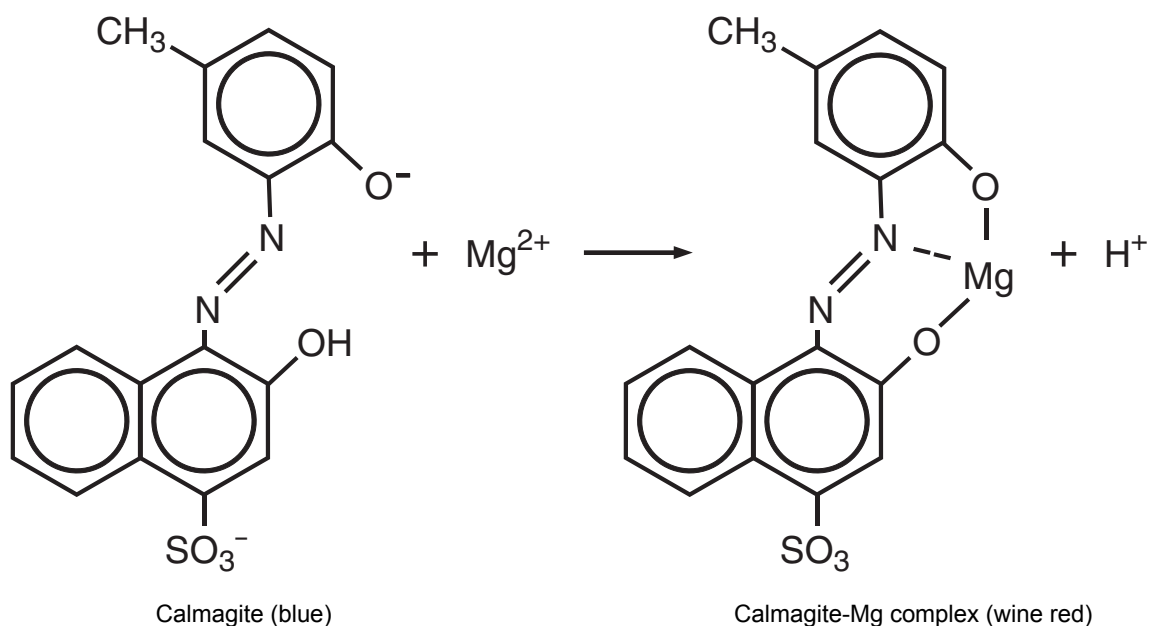


Figure 3 Reaction between magnesium and calmagite indicator

The reaction of calmagite is pH-dependent; it has been determined that a pH of 10.1 is ideal. Traditionally, ammonia buffers have been used; however, they have a strong odor. Each method uses Hardness 1 Buffer (2-amino-2-methyl-1-propanol), which is stable, safe to use and has a less objectionable odor.

The sequence of analysis in the hardness tests begins with pH adjustment and addition of inhibitors followed by formation of the Mg^{2+} and Ca^{2+} complexes with calmagite. The calcium forms a weak complex with calmagite at this pH. The solution is titrated with TitrVer (EDTA) or HexaVer (CDTA). The titrant first complexes any calcium, then magnesium. Color change from wine red to blue is an indication that all calcium and magnesium have been removed from the calmagite and complexed with the titrant.

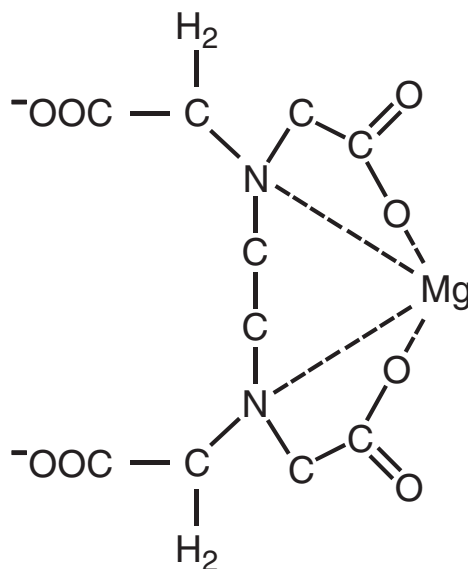


Figure 4 Magnesium complexed with TitraVer

Expression of results of the hardness titration is mg/L as CaCO_3 . The reaction of TitraVer with Ca^{2+} and Mg^{2+} is a 1:1 ratio.

Calcium hardness

The test for calcium hardness is very similar to the total hardness test. Traditionally, either murexide indicator (ammonium purpurate) or Eriochrome Blue-Black R indicator is followed by titration with EDTA. CalVer 2 Calcium Indicator has been developed by Hach to replace these indicators. CalVer 2 (hydroxy naphthol blue) is more sensitive and has a sharper end point color change.

CalVer 2 Calcium Indicator forms a red-violet complex with calcium and changes to pure blue after TitraVer removes calcium from the complex. The pH is elevated to at least 13 to precipitate magnesium. A few drops of Magnesium Standard Solution may be added to the reaction to sharpen the end point color change. This may seem inconsistent because magnesium is precipitated by elevating the pH. However, the added magnesium is chelated preferentially by the dye and the quantity of chelated magnesium is very small; thus any error caused by addition of magnesium is negligible.

The pH adjustment is accomplished by addition of potassium hydroxide prior to addition of CalVer 2. Potassium cyanide may also be added to complex interfering metals prior to the addition of CalVer 2.

Calcium hardness and total hardness may be determined sequentially using the same sample. After the calcium hardness is determined the sample pH can be adjusted downward, using sulfuric acid. Then Hardness Buffer 1 and ManVer 2 are added and titration with TitraVer is resumed.



DO NOT use this procedure if potassium cyanide has been used in determining calcium hardness! The addition of sulfuric acid will cause deadly hydrogen cyanide gas to evolve.

Colorimetric method

Calmagite, contained in Calcium and Magnesium Indicator Solution, is added to a sample and the pH is elevated to about 12.5 by using a buffer. Adding calmagite prior to pH adjustment prevents the calcium and magnesium precipitation that ordinarily would occur at this elevated pH. The sample is then split into three equal portions.

EDTA is added to the first portion to sequester calcium and magnesium, thereby breaking the Ca- and Mg-calmagite complexes. This solution is used as a zero reference blank to standardize the spectrophotometer.

EGTA or ethyleneglycol-bis (2-aminoethylether)-N,N',N'-tetraacetic acid, is added to the second sample portion. EGTA selectively chelates calcium under conditions of the test; only absorbance due to the Mg-calmagite complex remains to be measured. The result is expressed as mg/L Mg as CaCO₃. After measurement, the spectrophotometer is adjusted to read "zero" on this portion.

Absorbance of the third sample portion (containing no chelant) is measured to determine mg/L Ca as CaCO₃. Adjust the spectrophotometer to a reading of zero after measurement of the second sample portion to compensate for absorbance due to magnesium in the sample.

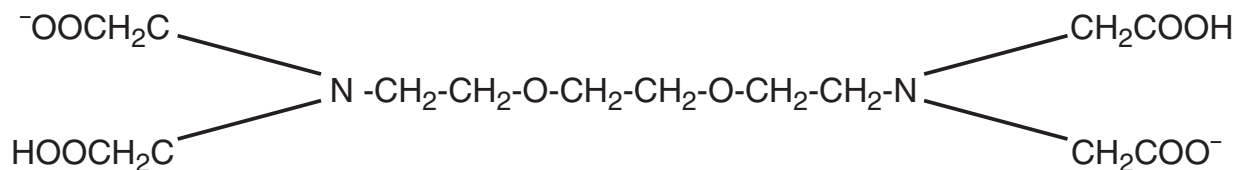


Figure 5 Chemical structure of EGTA