CHELOMETRIC TITRATION METHOD

Thomas M. Robertson, La Grange, and Charles J. Overbeck and James J. Hickey, Chicago, Ill., assignors to Nalco Chemical Company, Chicago, Ill., a corporation of Delaware

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8 Claims

ABSTRACT OF THE DISCLOSURE

A method for quantitatively determining the presence of amino polycarboxylic acids or alkali metal salts thereof by a chelometric titration method where an alkaline earth metal halide-Xylyl Blue II titrant indicator system is used.

The present invention relates to an analytical method involving a chelometric titration. More specifically, the instant invention is concerned with a method for quantitatively determining the presence of aminopolycarboxylic acids or alkali metal salts thereof.

Aminopolycarboxylic acids or their alkali metal salt derivatives are employed as complexing additives for a variety of end-uses. For example, the above class of materials find excellent use in inhibiting scale formation in boiler waters by complexing the hardness constituents of calcium and magnesium, thereby maintaining the substances in a dissolved condition. For optimum results, it has been determined that the aminopolycarboxylic acid complexing agents should be present in excess amounts during the boiler operation. However, to date, no simple method exists for determining amounts of free, uncomplexed aminopolycarboxylic acids present in such aqueous media as boiler water.

It would be of benefit to the art if a simple, yet accurate method were discovered for determining amounts of free aminopolycarboxylic acids or their salts present in aqueous media. By employing such an analytical tool, the amounts of complexing agent present in a system being protected could be suitably adjusted after periodic analysis of a test sample from the system, thereby maintaining proper treatment control. Thus, by periodically measuring amounts of complexing agents present in such systems as boilers, cooling towers, etc. by systematic analytical checks, the system could be protected against scale formation at all times by maintenance of excess complexing agents. After each analysis, additional complexing agent could be added to the system if needed, as determined by appropriate analytical procedure wherein a test sample is withdrawn from the boiler and determined for residual or excess complexing agent content.

It therefore becomes an object of the invention to provide an improved chelometric titration method.

A more specific object of the invention is to determine the content of aminopolycarboxylic acids or their alkali metal salts in water samples withdrawn from such systems as boilers or cooling towers. Other objects will appear hereinafter.

In accordance with the invention, a unique method for determining the content of aminopolycarboxylic acids or alkali metal salts has now been discovered. In its broadest aspects, this method comprises the steps of titrating with an alkaline earth metal halide and preferably magnesium halide a buffered solution having a pH range of 8—11 and containing at least one of said acids or salts and Xylyl Blue II indicator until a color change in said solution of blue to pink is noted.

More specifically, the method of the invention includes the steps of first buffering a test sample containing at least one of said acid or salt compounds to a pH range of 8—11. Subsequently, a chelometric titration of said test sample is effected in presence of Xylyl Blue II indicator. The titrant is most preferably a standardized solution of magnesium chloride which is titrated during the titration by complexing the free acid or salt present in said test sample. At a time when all aminopolycarboxylic acid or salt has complexed with added magnesium, an endpoint is reached indicated by a color change in the sample from blue to pink. Routine calculations will indicate concentration or normality of acid or salt compound present in the test sample. Thus, by knowing volume $V_2$ of magnesium chloride employed, as well as the normality $N_A$ of the standardized titrant solution and volume $V_1$ of test sample, only a routine calculation remains to determine normality $N_I$ of aminopolycarboxylic acid or salt in the measured volume of test sample as set forth below:

$$N_I = \frac{N_A V_2}{V_1}$$

As indicated above, the analytical method is applicable for determination of both aminopolycarboxylic acids and alkali metal salts capable of complexing alkaline earth metals as magnesium. For purpose of simplicity, the compound under measurement will be referred to as the free acid, although as above stated equivalent results can be obtained when the acid is in alkali metal salt form. Excellent success has been realized in correctly determining content of nitritolactic acid or trisodium salt thereof, or ethylenediaminetetraacetic acid or its alkali metal salt. Thus, the content of free aminopolycarboxylic acid or its alkali metal salt may be determined with equal facility whether the material is in free acid form, or partially or completely neutralized with an alkali metal base such as sodium hydroxide.

The process of the invention may also be carried out by selecting a known volume $V_1$ of a sample being tested and buffering the test sample to a pH range as stated above, more preferably, to about 8.5—10.5, and most preferably to a pH of about 9.5. A standard solution of magnesium chloride is employed as the titrant having a known concentration $C_1$. Xylyl Blue II (3-hydroxy-4 (O-hydroxyphenyl) azo-2-naphthol-2',4'-xylidide, sodium derivative) indicator is then added to the test sample. The titration with magnesium chloride is carried out until a color change occurs in the sample from blue to pink. The volume $V_2$ of the magnesium chloride titrant employed to reach the endpoint is then measured and the concentration of aminopolycarboxylic acid or salt complexing agent present in the test sample is calculated by means of the following formula where $C_1$ is the concentration of acid or salt being determined:

$$C = \frac{C_1 V_2}{V_1 K}$$

where $K$ is a number obtained by division of the molecular weight of magnesium chloride by the molecular weight of the compound being determined.

It has been discovered that the above method is valid even when other ions are present, particularly in amounts present in such aqueous media as boiler water. Appratable amounts of copper ion will interfere somewhat with the determination. Therefore, it is a preferred embodiment of the invention to first remove copper by suitable means. One such method is to form a water-insoluble precipitate of copper and remove the precipitate by conventional methods as filtration. One particularly advantageous reagent which may be used as a copper precipitant is diethyldithiocarbamic acid sodium salt. This material forms a water-insoluble complex with copper,
which carbamate crystal precipitate may be conveniently removed from the test sample by filtration. Likewise, any iron present will also be removed as a water-insoluble material, although iron ions in amounts usually present are not considered to substantially interfere with the analytical method of the invention.

A number of buffer solutions may be added to the test sample to maintain the desired pH range. One particularly desired buffer solution is sodium borate. Clearly visible end-points are reached through use of this buffer solution.

It was also found that if the test sample contained only several p.p.m. of uncomplexed aminopolycarboxylic acid, the titration was not as clear cut as is desired. To eliminate this problem, a known amount of an aminopolycarboxylic acid or salt is added to the test sample prior to the magnesium chloride titration. The amount added, of course, has to be taken into account in the final calculation which can then be carried out as follows:

\[ N_1 = \frac{(V_2 - V_3)}{V_1} \]

where \( V_2 \) is the volume of magnesium chloride used to titrate the added known amount of aminopolycarboxylic acid compound. Since the amount of complexing acid added is known, it is a simple matter to calculate the volume of magnesium chloride which was added to complex the added acid. The remaining magnesium chloride titrant, of course, is used in the determination of uncomplexed acid already present in test sample. Lastly, after test sample normality \( N_1 \) is calculated, it is a routine matter to calculate concentration in any desired dimension.

For best results, when waters being tested have an unknown quantity of free acid complexing agent, an excess of about 10 p.p.m. of acid or salt complexing agent is added to the sample being tested.

The Xylydyl Blue II indicator is best employed as a solution in organic solvents such as chloroform, pyridine, triethanolamine, ethanol, methanol, etc. In a typical indicator solution preparation 20 mgs. of Xylydyl Blue II is dissolved in 50 mls. of ethanol. \( \frac{1}{2} \) to \( \frac{2}{3} \) milliliters of the indicator may be used with 1 milliliter giving the best end-point.

The following example illustrates a typical titration procedure of the invention. It is understood, of course, that this example is merely illustrative, and the invention is not to be limited thereto.

**EXAMPLE I**

100 milliliters of test sample are placed in a clean 300 milliliter casserole. 1.0 milliliter of a standard trisodium nitritrolactic acid is then added to the above sample in order to insure that excess complexing acid is present. This standard trisodium nitritrolactic monohydrate acid solution may be prepared as follows: 1.100 grams of the above acid salt is dissolved in deionized water and diluted to 1 liter. The solution then contains 1.1 milligrams of acid salt per milliliter. Then 3 milliliters of a buffer solution are added to the test sample. This buffer solution of pH 9 is made up by dissolving 17 grams of sodium hydroxide, 62 grams of H_{3}BO_{3} and 75.6 grams KCl in deionized water. 160 milliliters of triethanolamine are then added and the entire mixture diluted to 1 liter with deionized water. Then approximately 0.1 gram of diethylthiocarbamic acid sodium salt is added to the buffered test sample. If a deep yellow color develops which will interfere with the end-point, the sample is filtered through filter paper. A slight amount of color developed at this point does not cause any problem with the end-point. A 40% solution of isopropanol in methanol is prepared and 100 milliliters added to test sample. At this point, the casserole is heated on a hot plate until the solution is almost boiling. One milliliter of Xylydyl Blue II indicator is then added. This indicator solution is made up by dissolving 200 milligrams of Xylydyl Blue II in 50 milliliters of ethanol. 50 milliliters of triethanolamine are then added and the solution stirred.

The titration is then carried out with a magnesium chloride titrating solution. The solution has previously been prepared by dissolving 5.5 grams of MgCl_{2}·6H_{2}O in 1 liter of deionized water. This solution contains 2.7 milligrams magnesium measured as calcium carbonate per milliliter. The titration is carried out until there is a color change from blue to pink. Dropping devices should be held in a vertical position during the titration and thorough mixing effected between each drop. In this example, each drop of magnesium chloride solution is equivalent to 5 p.p.m. of nitritrolactic acid trisodium monohydrate salt.

The invention is hereby claimed as follows:

1. A quantitative method for determining the concentration of a compound selected from the group consisting of aminopolyacrylic acids and alkali metal salts thereof which comprises the step of titrating with an alkaline earth metal halide a buffered solution having a pH within the range of 8-11 and containing at least one of said compounds and Xylydyl Blue II indicator until a color change in said solution of blue to pink is noted.

2. The method of claim 1 wherein one of said compounds is the trisodium salt of nitritrolactic acid.

3. A quantitative method for determining the concentration of a compound selected from the group consisting of aminopolyacrylic acids and alkali metal salts thereof which comprises the steps of buffering a test sample containing at least one of said compounds to a pH within the range of 8-11, effecting a chelometric titration of said sample in presence of Xylydyl Blue II indicator by means of a standardized solution of magnesium chloride, and calculating the amount of said compound present.

4. The method of claim 3 wherein one of said compounds is the trisodium salt of nitritrolactic acid.

5. The method of claim 3 wherein said test sample is buffered to a pH of about 9.5.

6. The method of claim 3 wherein a measured amount of at least one of said compounds is initially added to said test sample in an amount of at least 10 p.p.m.

7. The method of claim 3 wherein prior to said chelometric titration copper is removed from said test sample.

8. The method of claim 7 wherein said copper is removed as a precipitate by addition of diethylthiocarbamate.

**References Cited**

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**MORRIS O. WOLK, Primary Examiner.**

**E. A. KATZ, Assistant Examiner.**

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U.S. DEPARTMENT OF COMMERCE
PATENT OFFICE
Washington, D.C. 20231

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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Thomas M. Robertson et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, line 4, "200" should read -- 20 --.

Signed and sealed this 21st day of April 1970.

(SEAL)
Attest:

Edward M. Fletcher, Jr. WILLIAM E. SCHUYLER, JR.
Attesting Officer Commissioner of Patents