## CLAIMS:

1. A method of measuring calcium hardness comprising:

extracting a sample of water containing calcium from a process water system;

adding an indicator composition to the sample of water to form an optical analysis solution, the indicator composition comprising a calcium indicator, a range extender, and a buffer;

optically analyzing the optical analysis solution and determining therefrom a concentration of the calcium in the sample of water; and

controlling addition of a calcium control agent to the process water system based on the determined concentration of calcium in the sample of water.

2. The method of claim 1, wherein the calcium indicator comprises chlorophosphonazo III or chlorophosphonazo I.

3. The method of claim 1 or 2, wherein the range extender comprises at least one of a polycarboxylic acid, an acrylate-based polymer, a polymaleic anhydride (PMA), a poly epoxy succinic acid (PESA), a maleic anhydride and sulfonated styrene copolymer (MA/SS), a polyaspartic acid, a chelating agent, and salts thereof.

4. The method of any one of claims 1-3, wherein the range extender comprises an alkali metal citrate.

5. The method of claim 1 or 2, wherein the range extender is a polymer selected from the group consisting of a polyacrylate (PAA), a polymaleic anhydride (PMA), a poly epoxy succinic acid (PESA), a poly(acrylate-co-acrylamide) copolymer (AA/AM), an acrylic acid and hydroxypropylacrylate copolymer (AA/HPA), an acrylic acid and 2-acrylamido-2-methyl propane sulfonate copolymer (AA/AMPS), a maleic anhydride and sulfonated styrene copolymer (MA/SS), an acrylic acid/acrylamide/tertiary butyl acrylamide copolymer (AA/AM/t-BAM), an acrylic acid/2-acrylamido-2-methyl propane sulfonate/tertiary butyl acrylamide (AA/AMPS/t-BAM), an acrylic acid/sulfonated styrene/2-acrylamido-2-methyl

propane sulfonate (AA/SS/AMPS), an acrylic acid/acrylamide/aminomethyl sulfonate copolymer(AA/AM/AMS), polyaspartic acid, and combination thereof.

6. The method of any one of claims 1 to 3, wherein the range extender is a chelating agent selected from the group consisting of L-glutamic acid N-N-diacetic acid tetrasodium salt (GLDA), iminodisuccinic acid ((N-1,2-dicarboxyethyl)-D,L-aspartate acid), ethylenediamine-N,N'-disuccinic acid (EDDS), methylglycinediacetic acid (MGDA), ethyleneglycol-O,O'-bis(2-aminoethyl)-N,N, N',N'-tetraacetic acid (EGTA), ethylenediamine-tetraacetic acid disodium salt (EDTA), ODS (oxygen disuccinic acid), salts thereof, and combinations thereof.

7. The method of any one of claims 1 to 7, wherein the buffer is at least one of lactic acid, acetic acid, formic acid, uric acid, malic acid, tartaric acid, phthalic acid, citric acid, oxalic acid, phosphoric acid, MES (2-(N-Morpholino)ethanesulfonic acid), 4-Morpholineethanesulfonic acid, sulfamic acid, benzyl sulfonic acid, methylbenzyl sulfonic acid, glycine, and salts thereof.

8. The method of any one of claims 1 to 7, wherein the indicator composition is provided as a solid composition.

9. The method of any one of claims 1 to 8, wherein the indicator composition is diluted with water to form a use solution.

10. The method of any one of claims 1 to 9, wherein the optical analysis solution has a pH of less than 7.0.

11. The method of any one of claims 1-4 and 7-10, wherein the indicator composition consists essentially of the calcium indicator chlorophosphonazo III, the range extender an alkali metal citrate, the buffer citric acid and an alkali metal citrate, and water to form an indicator solution, and wherein the indicator solution has a pH less than 7.0.

12. The method of any one of claims 1-11, wherein:

the calcium indicator comprises less than about 0.5 wt % of the indicator composition;

the range extender comprises from about 0.1 wt % to about 10 wt % of the indicator composition; and

the buffer comprises from about 0.1 wt % to about 5 wt % of the indicator composition.

13. The method of any one of claims 1-12, wherein a concentration of calcium in the sample of water ranges from about 1 ppm to about 50 ppm, or greater than about 50 ppm, or from about 250 ppm to about 1000 ppm.

14. The method of any one of claims 1-13, wherein:

extracting the sample of water comprises drawing a side stream from the process water system, and

adding the indicator composition to the sample of water and optically analyzing the optical analysis solution comprises adding the indicator composition to the sample of water and optically analyzing the optical analysis solution using an automated online analysis device.

15. A system comprising:

an optical sensor configured to receive a sample of water containing an unknown concentration of calcium from a process water system;

an indicator composition comprising a calcium indicator, a range extender, and a buffer;

at least one pump fluidly coupled to the indicator composition; and

a controller communicatively coupled to the optical sensor and the pump, wherein the controller is configured to:

control the pump to generate an optical analysis solution by at least combining the sample of water with the indicator composition;

control the optical sensor to optically analyze the optical analysis solution; and

determine a concentration of calcium in the sample of water based on the optical analysis.

16. The system of claim 15, wherein the system further comprises a calcium control agent pump, wherein the controller is communicatively coupled to the calcium control agent pump and configured to control addition of a calcium control agent to the process water system based on the determined concentration of calcium in the sample of water.

17. The system of either of claims 15 or 16, wherein:

the calcium indicator comprises chlorophosphonazo III or chlorophosphonazo I;

the range extender comprises at least one of a polycarboxylic acid, an acrylate-based polymer, a polymaleic anhydride (PMA), a poly epoxy succinic acid (PESA), a maleic anhydride and sulfonated styrene copolymer (MA/SS), a polyaspartic acid, a chelating agent, and salts thereof; and

the buffer is at least one of lactic acid, acetic acid, formic acid, uric acid, malic acid, tartaric acid, phthalic acid, citric acid, oxalic acid, phosphoric acid, MES (2-(N-Morpholino)ethanesulfonic acid), 4-Morpholineethanesulfonic acid, sulfamic acid, benzyl sulfonic acid, methylbenzyl sulfonic acid, glycine, and salts thereof.

18. The system of any one of claims15-17, wherein:

the calcium indicator comprises less than 0.5 wt % of the indicator composition;

the range extender ranges from about 0.1 wt % to about 10 wt% of the indicator composition; and

the buffer ranges from about 0.1 wt % to about 5 wt % of the indicator composition.