

METHOD #: 130.1                                 Approved for NPDES (Issued 1971)

TITLE:    Hardness, Total (mg/L as CaCO<sub>3</sub>) (Colorimetric,  
Automated EDTA)

ANALYTE:   Hardness Total (mg/L as CaCO<sub>3</sub>)

INSTRUMENTATION:                             Spectrophotometer

STORET No.:                                     00900

## 1.0 Scope and Application

1.1 This automated method is applicable to drinking, surface, and saline waters. The applicable range is 10 to 400 mg/L as CaCO<sub>3</sub>. Approximately 12 samples per hour can be analyzed.

## 2.0 Summary of Method

2.1 The magnesium EDTA exchanges magnesium on an equivalent basis for any calcium and/or other cations to form a more stable EDTA chelate than magnesium. The free magnesium reacts with calmagite at a pH of 10 to give a red-violet complex. Thus, by measuring only magnesium concentration in the final reaction stream, an accurate measurement of total hardness is possible.

## 3.0 Sample Handling and Preservation

3.1 Cool to 4°C, HNO<sub>3</sub> to pH < 2.

## 4.0 Interferences

4.1 No significant interferences.

## 5.0 Apparatus

5.1 Technicon AutoAnalyzer consisting of:

- 5.1.1 Sampler I
- 5.1.2 Continuous Filter
- 5.1.3 Manifold
- 5.1.4 Proportioning Pump
- 5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 520 nm filters
- 5.1.6 Recorder equipped with range expander

## 6.0 Reagents

6.1 Buffer: Dissolve 67.6 g NH<sub>4</sub>Cl in 572 mL of NH<sub>4</sub> OH and dilute to 1 liter with distilled water.

- 6.2 Calmagite Indicator: Dissolve 0.25 g in 500 mL of distilled water by stirring approximately 30 minutes on a magnetic stirrer. Filter.
- 6.3 Monomagnesium ethylenediamine-tetraacetate (MgEDTA): Dissolve 0.2 g of MgEDTA in 1 liter of distilled water.
- 6.4 Stock Solution: Weigh 1.000 g of calcium carbonate (pre-dried at 105°C) into 500 mL Erlenmeyer flask; add 1:1 HCl until all CaCO<sub>3</sub> has dissolved. Add 200 mL of distilled water and boil for a few minutes. Cool, add a few drops of methyl red indicator, and adjust to the orange color with 3N NH<sub>4</sub>OH and dilute to 1000 mL with distilled water. 1.0 mL = 1.0 mg CaCO<sub>3</sub>.
- 6.4.1 Dilute each of the following volumes of stock solutions to 250 mL in a volumetric flask for appropriate standards:

Stock Solution, mL	CaCO <sub>3</sub> mg/L
2.5	10.0
5.0	20.0
10.0	40.0
15.0	60.0
25.0	100.0
35.0	140.0
50.0	200.0
75.0	300.0
100.0	400.0

- 6.5 Ammonium Hydroxide, 1N: Dilute 70 mL of conc. NH<sub>4</sub>OH to 1 liter with distilled water.

## 7.0 Procedure

### 7.1 Pretreatment

- 7.1.1 For drinking waters, surface waters, saline waters, and dilutions thereof, no pretreatment steps are necessary. Proceed to 7.2.
- 7.1.2 For most wastewaters, and highly polluted waters, the sample must be digested as given in the Atomic Absorption Methods section of this manual, paragraphs 4.1.3 and 4.1.4. Following this digestion, proceed to 7.2.

7.2 Neutralize 50.0 mL of sample with 1N ammonium hydroxide (6.5) and note volume of NH<sub>4</sub>OH used.

7.3 Set up manifold as shown in Figure 1.

7.4 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

7.5 Place distilled water wash tubes in alternate openings in Sampler and set sample timing at 2.5 minutes.

7.6 Arrange working standards in Sampler in order of decreasing concentrations. Complete loading of Sampler tray with unknown samples.

7.7 Switch sample line from distilled water to Sampler and begin analysis.

## 8.0 Calculation

- 8.1 Prepare standard curve by plotting peak heights of processed standards against concentration values. Compute concentration of samples by comparing sample peak heights with standard curve. Correct for amount of  $\text{NH}_4\text{OH}$  used in 7.2 as follows:

$$\text{mg/L} = (A/50) \times B$$

where:

A = Vol. of sample plus volume of  $\text{NH}_4\text{OH}$

B = Concentration from standard curve

## 9.0 Precision and Accuracy

- 9.1 In a single laboratory (EMSL), using surface water samples at concentrations of 19, 120, 385, and 366 mg/L as  $\text{CaCO}_3$ , the standard deviations were  $\pm 1.5$ ,  $\pm 1.5$ ,  $\pm 4.5$ , and  $\pm 5.0$ , respectively.
- 9.2 In a single laboratory (EMSL), using surface water samples at concentrations of 39 and 296 mg/L as  $\text{CaCO}_3$ , recoveries were 89% and 93%, respectively.

## Bibliography

1. Technicon AutoAnalyzer Methodology, Bulletin No. 2, Technicon Controls, Inc., Chauncey, New York (July 1960).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 202, Method 309B (1975).

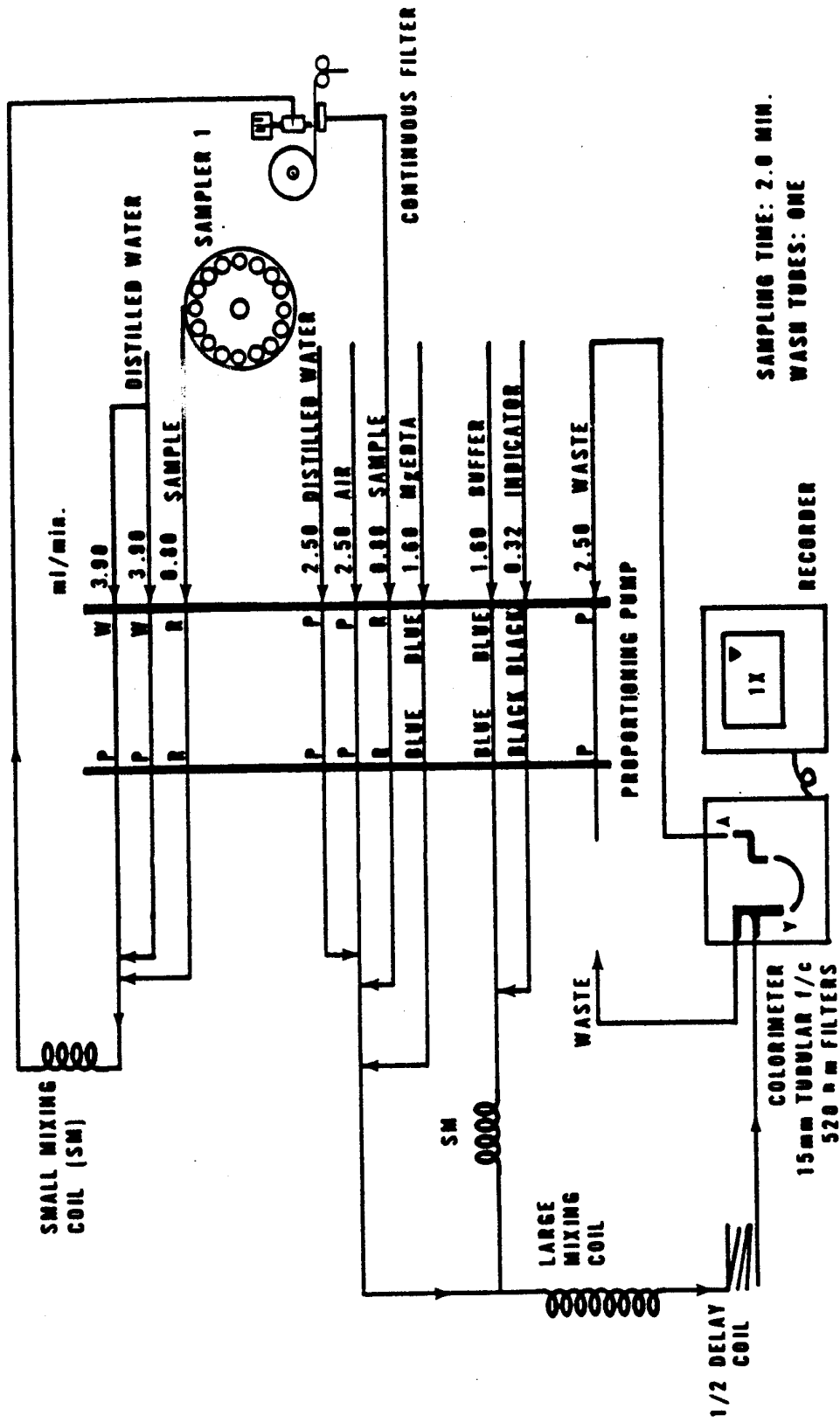


FIGURE 1. HARDNESS MANIFOLD AA-1