

METHOD #: 310.2	Approved for NPDES (Editorial Revision 1974)
TITLE:	Alkalinity (Colorimetric, Automated, Methyl Orange)
ANALYTE:	Alkalinity
INSTRUMENTATION:	Autoanalyzer
STORET No.	00410

1.0 Scope and Application

- 1.1 This automated method is applicable to drinking, surface, and saline waters, domestic and industrial wastes. The applicable range is 10 to 200 mg/L as CaCO₃.
- 1.2 This method is not an approved NPDES method as cited in the Federal Register December 1, 1976 for samples containing turbidity or color.

2.0 Summary of Method

- 2.1 Methyl orange is used as the indicator in this method because its pH range is in the same range as the equivalence point for total alkalinity, and it has a distinct color change that can be easily measured. The methyl orange is dissolved in a weak buffer at a pH of 3.1, just below the equivalence point, so that any addition of alkalinity causes a loss of color directly proportional to the amount of alkalinity.

3.0 Sample Handling and Preservation

- 3.1 Sample should be refrigerated at 4°C and run as soon as practical. Do not open sample bottle before analysis.

4.0 Interferences

- 4.1 Sample turbidity and color may interfere with this method. Turbidity must be removed by filtration prior to analysis. If sample is filtered, this method is not approved for NPDES monitoring. Sample color that absorbs in the photometric range used will also interfere.

5.0 Apparatus

- 5.1 Technicon Auto Analyzer consisting of:
 - 5.1.1 Sampler I.
 - 5.1.2 Manifold.
 - 5.1.3 Proportioning pump.
 - 5.1.4 Colorimeter equipped with 15 mm tubular flow cell and 550 nm filters.
 - 5.1.5 Recorder equipped with range expander.

6.0 Reagents

- 6.1 Methyl Orange: Dissolve 0.125 g of methyl orange in 1 liter of distilled water.
- 6.2 pH 3.1 Buffer: Dissolve 5.1047 g of potassium acid phthalate in distilled water and add 87.6 mL 0.1 N HCl and dilute to 1 liter. Stable for one week.
- 6.3 Methyl Orange-Buffered Indicator: Add 1 liter of pH 3.1 buffer (6.2) to 200 mL methyl orange solution (6.1) and mix well. Stable for 24 hours.
- 6.4 Stock Solution: Dissolve 1.060 g of anhydrous sodium carbonate (oven-dried at 250°C for 4 hours) in distilled water and dilute to 1000 mL. 1.0 mL = 1.00 mg CaCO₃.
- 6.4.1 Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 mL with distilled water. The following dilutions are suggested:

mL of Stock Solution	Conc., mg/L as CaCO ₃
1.0	10
2.0	20
4.0	40
6.0	60
8.0	80
10.0	100
18.0	180
20.0	200

7.0 Procedure

- 7.1 No advance sample preparation is required. Set up manifold as shown in Figure 1.
- 7.2 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.
- 7.3 Place distilled water wash tubes in alternate openings on sampler and set sample timing at 2.0 minutes.
- 7.4 Place working standards in sampler in order of decreasing concentration. Complete filling of sampler tray with unknown samples.
- 7.5 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 known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

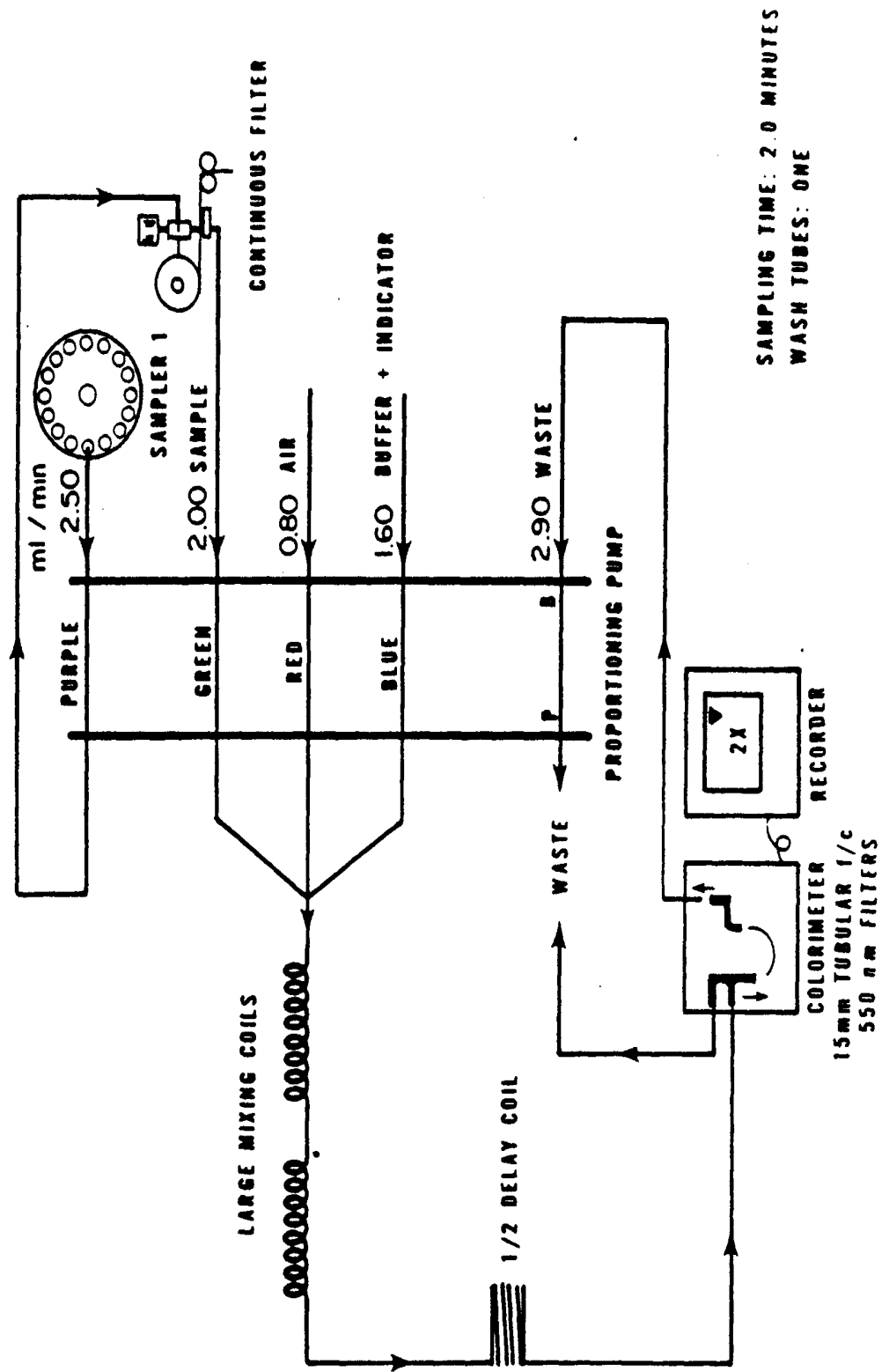
9.0 Precision and Accuracy

- 9.1 In a single laboratory (EMSL), using surface water samples at concentrations of 15, 57, 154, and 193 mg/L as CaCO₃ the standard deviation was ± 0.5.

9.2 In a single laboratory (EMSL), using surface water samples at concentrations of 31 and 149 mg/L as CaCO₃ recoveries were 100% and 99%, respectively.

Bibliography

1. Technicon Auto Analyzer Methodology, Bulletin 1261, Technicon Controls, Inc., Chauncey, N.Y. (1961).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 278, Method 403 (1975).



SAMPLING TIME: 2.0 MINUTES
WASH TUBES: ONE

FIGURE 1. ALKALINITY MANIFOLD AA-1