Bromide, colorimetric, fluorescein, automated-segmented flow

Parameter and Code:
Bromide, dissolved, I-2129-85 (mg/L as Br): 71870

1. Application

This method may be used to analyze natural water containing from 0.010 to 0.40 mg/L of bromide. Samples containing greater concentrations need to be diluted.

2. Summary of method

The sample is buffered to pH 5.6 with an acetic acid buffer solution and then reacted with chloramine T to oxidize the bromide to hypobromous acid. The hypobromous acid formed then reacts with fluorescein to form the pink eosin (tetrabromo fluorescein), which is proportional to the bromide concentration.

$$Br^{-1} + HOCl \rightarrow BrOH + Cl^{-1}$$

$$BrOH + \text{Fluorescein} \rightarrow \text{Tetrabromo Fluorescein (pink)}$$

3. Interferences

Iodide interferes quantitatively, but in most waters the iodide concentration is negligible. It is recommended that a determination for iodide be performed and that the concentration that is found be subtracted from the apparent bromide concentration. Cyanide, as much as 0.50 mg/L, and chloride, as much as 500 mg/L, do not interfere. Thiocyanate interferes linearly, but in most waters its concentration is negligible.

4. Apparatus

4.1 *Technicon AutoAnalyzer II,* consisting of a sampler, proportioning pump, cartridge manifold, colorimeter, voltage stabilizer, recorder, and printer.

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 0.010 to 0.40 mg/L bromide.

Absorption cell ----- 50 mm
Wavelength -------- 520 nm
Cam ---------- 30/h (2/1)

5. Reagents

5.1 *Bromide standard solution I,* 1.00 mL= 0.100 mg Br^{-1}: Dissolve 0.149 g KBr, dried overnight over concentrated H_2SO_4, in demineralized water and dilute to 1,000 mL with demineralized water.

5.2 *Bromide standard solution II,* 1.00 mL= 0.010 mg Br^{-1}: Dilute 100.0 mL bromide standard solution I to 1,000 mL with demineralized water.

5.3 *Bromide working standards:* Prepare a blank and 1000 mL each of a series of bromide working standards by appropriate quantitative dilution of bromide standard solution II as follows:

Bromide standard solution II (mL)	Bromide concentration (mg/L)
1.0	0.010
5.0	.050
10.0	.100
25.0	.250
40.0	.400

5.4 *Buffer solution:* Dissolve 9.426 g NH_4Cl in 500 mL demineralized water and add 57 mL glacial acetic acid (sp. gr. 1.06). Add dropwise, 5*N* KOH solution until the pH of the solution is 5.6. Dilute to 1,000 mL with demineralized water.

5.5 *Chloramine-T solution,* 0.5 g/100 mL: Dissolve 0.500 g chloramine-T in 100 mL of demineralized water. Prepare fresh daily.

5.6 *Fluorescein stock solution,* 0.125 g/100 mL: Dissolve 0.125 g fluorescein in 25 mL 0.1*N* NaOH and dilute to 100 mL with demineralized water. This solution is stable for one week if stored in a light-proof bottle.

5.7 *Fluorescein working solution:* Pipet 10 mL Fluorescein stock solution into a 100-mL volumetric flask; dilute to the mark with demineralized water. This solution must be prepared fresh daily.

5.8 *Sodium hydroxide solution,* 0.1*N:* Dissolve 4.0 g NaOH in demineralized water and dilute to 1 L with demineralized water.

5.9 *Potassium hydroxide solution,* 5.0*N:* **CAUTIOUSLY** dissolve 280 g KOH in demineralized water, cool, and dilute to 1 L with demineralized water.

6. Procedure

6.1 Set up manifold (fig. 18).

6.2 Allow colorimeter and recorder to warm up for at least 30 min.

6.3 Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample line.

6.4 Place a complete set of standards and a blank in the first positions of the first sample tray, beginning with the most concentrated standard. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples.

6.5 Begin analysis. When the peak from the most concentrated standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective empirical bromide concentration.

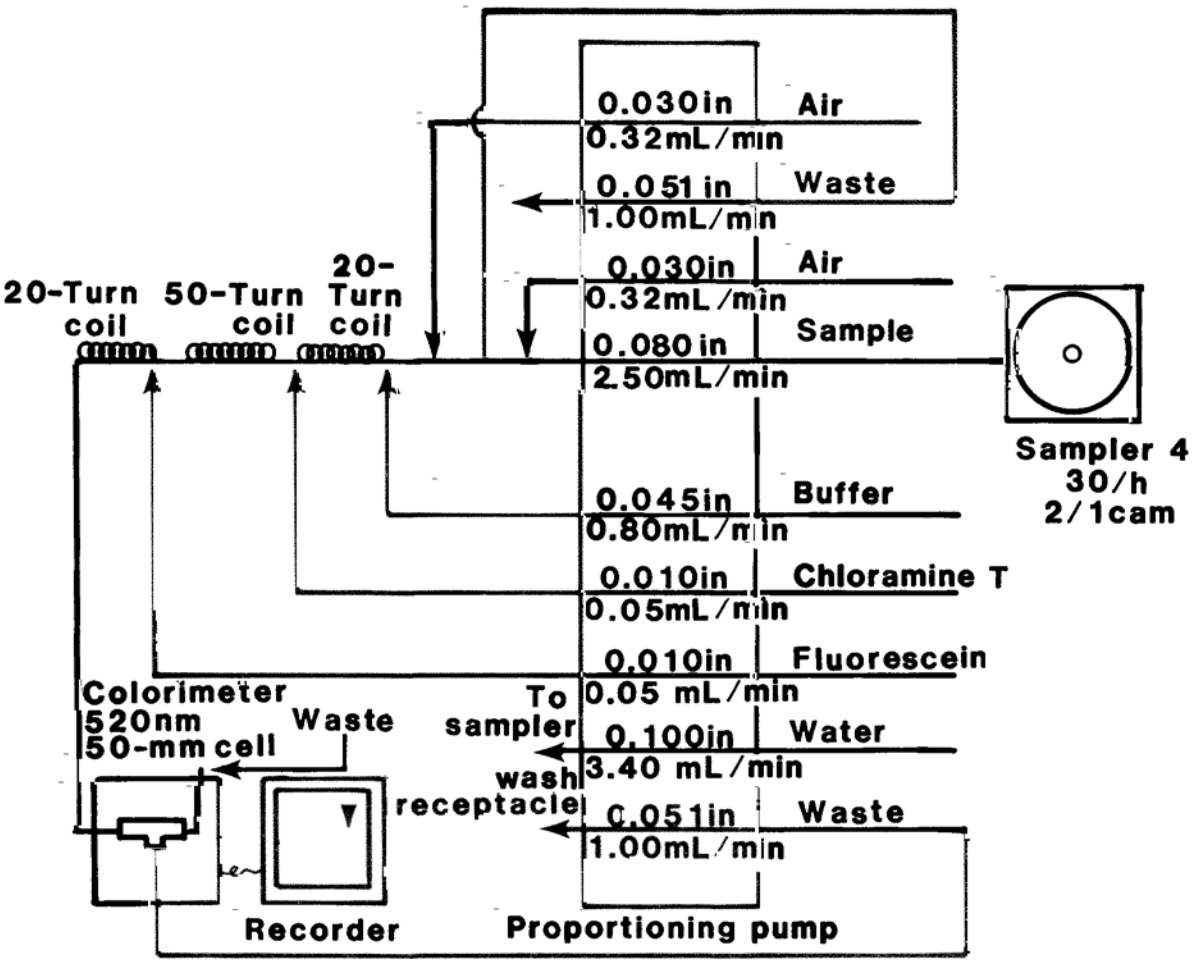

Figure 1. - Bromide, fluorescein manifold

7.2 Compute the apparent bromide concentration of each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

7.3 Compute the iodide concentration of each sample in accordance with method I- 2371.

7.4 Compute the bromide concentration as follows:

Br^{-1}(Mg/L)=

mg/L apparent concentration-mg/L iodide concentration

8. Report

Report bromide, dissolved (71870), concentrations as follows: less than 0.1 mg/L, two decimals; 0.1 mg/L and above, two significant figures.

9. Precision

Single-operator precision for dissolved bromide for six samples expressed in terms of percent relative standard deviation is as follows:

Number of Replicates	Concentration (mg/L)	Relative standard deviation (percent)
10	0.010	15.0
10	.050	10.0
10	.100	5.0
10	.350	2.0
10	.550	1.8
10	.860	2.0

References

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