Fluoride Testing

NDEE
Fluoride Seminar
2023

Why Monitor Water Quality?

- Regulations
- Process control

Fluoride Monitoring

- Narrow window for acceptable results:

  Regulatory – 0.8 to 1.5 mg/L (NE Regs)

  Recommended – 1.0 to 1.3 mg/L

  Nebraska Optimum level – 1.0 mg/L (USPHS Recommended, 1962)

Testing Methods

- Determination of the quantity of fluoride present in solution – Total Fluoride.
- Must be precise and highly selective.
- Regulatory (natural level) – Under the SDWA.
- Operational – Do not need to be as precise.

Fluoride Testing Methods

- Three Principal Methods
  - Colorimetric
  - Specific Ion Electrode
  - Ion Chromatography

Increasing skill and ability

Increasing Accuracy

Testing Methods

- SPADNS (colorimetric) Method

Sodium 2-(parasulfophenylazo) – 1,8-dihydroxyl - 3,6-naphthalene disulfonate

- Electrode Method
- Keys in selection
  - Regulatory requirements
  - Speed
  - Economy
  - Test Purpose
  - Interferences

SPADNS

- Zirconium SPADNS dye.
- Fluoride present in the sample removes zirconium from the reaction; decreases the color (red) intensity.
- Photometer detects the differences in color.

SPADNS Method

HACH AccuVac Ampules

SPADNS Concentration Calculation

$$\text{Fluoride, mg/L} = \frac{A_o - A_x}{A_o - A_1}$$

A_o = Absorbance of Blank

A_x = Absorbance of Sample

A_1 = Absorbance of 1 mg/L Fluoride Standard

SPADNS

- High levels of interferences will likely require performance of a distillation process.
- SPADNS reagent (HACH) contains arsenite; eliminate interference from up to 5 mg/L of chlorine.

HACH Pocket Colorimeter

Colorimetric Analysis Sources of Error

- Sample collection
- Sample handling
- Testing cell
- Standards
- Electronic
- Calibration
- Interfering substances

Colorimetric Analysis Sources of Error

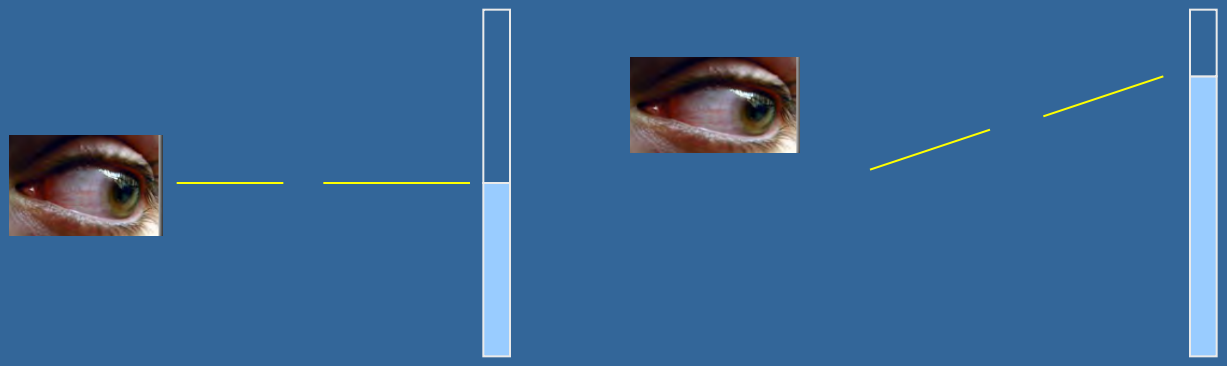
Sample Collection

- Is solution fully mixed?
- Is container used for collection clean?
- Is person introducing contamination?
- Is chlorine a contaminate?

Colorimetric Analysis Sources of Error

Sample Handling

- Skill in using a pipette
- Bulb or pipette may be contaminated
- Parallax in measurement



Colorimetric Analysis Sources of Error

Testing Cell (cuvette)

- Cell might be dirty or smeared
- Residuals could interfere
- Consistent optical clarity between cells
- Chips or scratches

Colorimetric Analysis Sources of Error

Standards

- Use fresh standards
- Appropriate calibration of test
- Use true deionized water (zero fluoride)

Colorimetric Analysis Sources of Error

Electronics

- Weak batteries
- Leaking batteries
- Deterioration of electronics

Colorimetric Analysis Sources of Error

Calibration

- Correct instrument calibration
- Background color or turbidity
- Temperature differences

Electrode

- Specific ion electrode.
- Single crystal through which only fluoride ions can move; specific for fluoride.
- Most accurate way to measure to determine fluoride content in drinking water.
- Generally free from interferences.

Specific Ion Electrode Analysis

Advantages

- Greater Range, 0.1 – 10.0 mg/L
- Fewer Interfering Substances
- Less Susceptible to Technique Errors

Disadvantages

- Expensive

Sample Collection

- A minimum of once per day is recommended.
- Locations where the water is representative of the whole system.
- Sample points should be rotated.

Interferences (mg/L)

	SPADNS	Electrode
Alkalinity ($CaCO_3$)	5,000 (-)	7,000 (+)
Aluminum (Al)	0.1 (-)	3.0 (-)
Chloride (Cl)	7,000 (+)	20,000 (-)
Iron (Fe)	10 (-)	200 (-)
Hexametaphosphate ($[NaPO_3]$)	1.0 (+)	50,000
Phosphate ($P0_4$)	16 (+)	50,000
Sulfate ($S0_4$)	200 (+)	50,000 (-)
Chlorine	Must be completely removed with arsenite	5,000
Color & Turbidity	Must be removed or compensated for	

Strange Readings

- Fluoride is a stable, persistent ion
- Calculations are important
- Low Readings
- High Readings
- Variable Readings

Strange Readings

IT’S THE LAB’S FAULT!!

Low Readings

- Traces of aluminum
- High iron content
- Underdosing – inadequate chemical depth in a saturator or incomplete mixing of dry chemical
- Low chemical purity
- Unfluoridated water entering the system

High Readings

- Polyphosphates
- Chlorine
- Fluctuating natural fluoride level

Variable Readings

- Fluoride feeder delivery rate
- Intermittent unfluoridated water entering the system
- Varying flows