Technical Assistance
HYDROLOGY PROJECT

World Bank & Government of The Netherlands funded

Training module # WQ - 36

How to measure Fluoride: SPADNS Spectrophotometric Method

New Delhi, February, 2000

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with
HALCROW, TAHAL, CES, ORG & JPS

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1. Module context

This module concerns measurement of fluoride by SPADNS method. Other related modules are listed below.

While designing a training course, the relationship between this module and the others, would be maintained by keeping them close together in the syllabus and place them in a logical sequence. The actual selection of the topics and the depth of training would, of course, depend on the training needs of the participants, i.e. their knowledge level and skills performance upon the start of the course.

No.	Module title	Code	Objectives
1.	Basic water quality concepts	**WQ - 01**	• Discuss the common water quality parameters • List important water quality issues
2.	Basic chemistry concepts	**WQ - 02**	• Convert units from one to another • Discuss the basic concepts of quantitative chemistry • Report analytical results with the correct number of significant digits.
3.	Advanced aquatic chemistry: solubility equilibria	**WQ – 29**	• Explain the principles of chemical equilibrium • Define solubility product and explain how this relates to water quality assessment • Define the octanol-water partition coefficient and explain how this relates to water quality assessment.
4.	Use of ion selective probes	**WQ - 33**	• Precautions required in use of ion selective probes
5.	Absorption Spectroscopy	**WQ - 34**	• Understand the principles of absorption spectroscopy • Explain the use of absorption spectroscopy for chemical analyses

2. Module profile

Title	:	How to measure Fluoride: SPADNS Spectrophotometric Method
Target group	:	HIS function(s): Q2, Q3, Q5, Q6
Duration	:	One lecture session of 30 min., one laboratory session of 120 min. and one concluding session of 30 min.
Objectives	:	After the training the participants will be able to*:* • measure fluoride by SPADNS method • appreciate interference by salts
Key concepts	:	• SPADNS method • Interference
Training methods	:	Lecture, Laboratory
Training tools required	:	Board, flipchart, OHS, chemical laboratory, spectrophotometer
Handouts	:	As provided in this module
Further reading and references	:	• Chemistry for environmental engineers - C. N. Sawyer, P. L. McCarty & G. F. Parkin, McGraw - Hill, Inc., 1994 • Standard methods for the examination of water and wastewaters, AWWA, 19th edition, 1995

3. Session plan

No	Activities	Time	Tools
1	***Preparations*** • Reagents as described in SAP • Samples: A – Tap water, B – Tap water IL + Stock fluoride 50 mL C – Sample B 500 mL + Na_2SO_4 1g D – Sample B 500 mL + NaCl 1g.		
2	***Introduction***: • Describe significance of fluoride • Ask participants if they know of areas where fluoride is a problem	10 min	OHS
3.	***SPADNS method*** • Describe briefly the method, interferences and the aim of the experiment • Ask participants to read the SAP	20 min	OHS
4.	***Laboratory*** • Divide the class in groups of 2 to 3 persons • Provide the stock fluoride solution and ask each group to prepare atleast 4 standards • While the participants are preparing standards, demonstrate the working of the spectrophotometer to each group separately. • Ask the participants to complete the experiment	120 min	Laboratory
5	***Report and wrap up*** • Ask the participants to prepare their reports • Discuss results	30 min	

4. Overhead/flipchart master

OHS format guidelines

Type of text	Style	Setting
Headings:	OHS-Title	Arial 30-36, with bottom border line (not: underline)
Text:	OHS-lev1 OHS-lev2	Arial 24-26, maximum two levels
Case:		Sentence case. Avoid full text in UPPERCASE.
Italics:		Use occasionally and in a consistent way
Listings:	OHS-lev1 OHS-lev1-Numbered	Big bullets. Numbers for definite series of steps. Avoid roman numbers and letters.
Colours:		None, as these get lost in photocopying and some colours do not reproduce at all.
Formulas/Equations	OHS-Equation	Use of a table will ease horizontal alignment over more lines (columns) Use equation editor for advanced formatting only

Introduction (1)

- Fluoride is present in most natural waters
- Concentrations vary from 0.05 to 100 mg/L but less than 0.1mg/L is much more common
- Some groundwaters have very high concentrations of fluoride
- In India, at some locations in Andra Pradesh and Tamil Nadu the concentration of fluoride can reach 10 mg/L

Introduction (2)

- Fluoride is both beneficial and toxic to humans:
  - *At low concentrations (≈ 1.0 mg/L) it prevents dental caries*
  - *At high concentrations (> 4.0 mg/L) it causes skeletal fluorosis*
  - *At intermediate concentrations it causes mottling of teeth*
- The Indian standard prescribes the limit for fluoride for waters to be used for drinking as 1.5 mg/L

SPADNS Spectrophtometric Method

- Fluoride reacts with certain zirconium dyes to form a colourless complex and another dye
- The dye becomes progressively lighter as fluoride concentration increases
- Absorbance is measured at 570 nm
- Prepare calibration curve using absorbance values for known standards
- Read fluoride values for the samples

Interference

- Substance causing 0.1 mg error at 1.0 mg F^-/L

Substance	**Conc. mg/L**	**Type of error**
Alkalinity	5000	(-)
Al^{3+}	0.1	(-)
Cl^-	7000	(+)
Fe^{2+}	10	(-)
SO_4^{2-}	200	(-)

Measurement of Fluoride

- Aim:
  - *To determine the concentration of fluoride in different samples of water*
  - *Study the interference caused by Na_2SO_4 and NaCl*

Sample	Source	Probable concentration
A	Low TDS water	0-1 mg F^-/L
B	Low TDS water	2-3 mg F^-/L
C	Sample B + Na_2SO_4	2-3 mg F^-/L
D	Sample B + NaCl	2-3 mg F^-/L

Report

- The aim of the investigation
- The results that you have produced
- The effect of the added salts
- The need for distillation of samples
- The likely effect on human health if this water is drunk

5. Evaluation sheets

6. Handout

Introduction (1)

- Fluoride is present in most natural waters
- Concentrations vary from 0.05 to 100 mg/L but less than 0.1mg/L is much more common
- Some groundwaters have very high concentrations of fluoride
- In India, at some locations in Andra Pradesh and Tamil Nadu the concentration of fluoride can reach 10 mg/L

Introduction (2)

- Fluoride is both beneficial and toxic to humans as:
  - *At low concentrations (≈ 1.0 mg/L) it prevents dental caries*
  - *At high concentrations (> 4.0 mg/L) it causes skeletal fluorosis*
  - *At intermediate concentrations it causes mottling of teeth*
- The Indian standard prescribes the limit for fluoride for waters to be used for drinking as 1.5 mg/L

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D	Sample B + NaCl	2-3 mg F^-/L

Report

- The aim of the investigation
- The results that you have produced
- The effect of the added salts
- The need for distillation of samples
- The likely effect on human health if this water is drunk

Add copy of Main text in chapter 8, for all participants.

7. Additional handout

These handouts are distributed during delivery and contain test questions, answers to questions, special worksheets, optional information, and other matters you would not like to be seen in the regular handouts.

It is a good practice to pre-punch these additional handouts, so the participants can easily insert them in the main handout folder.

8. Main text

Contents

How to measure Fluoride: SPADNS Spectrophotometric Method

1. Introduction

Fluoride is present in most natural waters at concentrations varying from 0.05 to 100 mg/L although less than 0.1 mg/L is much more common. Some groundwaters, including those in Hawaii, Sri Lanka, Malawi and Tanzania are known to have high concentrations of fluoride ion. In India, there are many areas where groundwater contains high concentrations of fluorides. In Andhra Pradesh, Rajasthan, Madhya Pradesh and Tamil Nadu, at some locations, the concentration may reach as high as 10 mg/L.

Fluoride seems to be both beneficial and toxic to humans depending upon the concentration of the ion in drinking water. At low concentrations (approximately 1.0 mg/L) it has been shown to reduce dental caries, whilst in high concentrations (above approximately 4 mg/L) it can cause skeletal fluorosis, a crippling bone disease. Intermediate concentrations of the ion often cause mottling of teeth in humans.

The Indian standard for fluoride concentration in waters to be used for drinking and bathing is 1.5 mg/L.

2. SPADNS Spectrophotometric Method

This method relies on the fact that when fluoride reacts with certain zirconium dyes, a colourless complex anion and a dye are formed. The complex, which is proportional to the fluoride concentration, tends to bleach the dye which therefore becomes progressively lighter as the fluoride concentration increases.

In the case of the fluoride ion reaction with Zr-SPADNS (sodium 2-(parasulphophenylazo-)-1,8-dihydroxy-3,6-naphthalene disulphonate), the resulting coloured complex is measured in a spectrophotometer at 570 nm.

Distillation is necessary for samples containing high concentration of dissolved solids. The dissolved solids interfere with the fluoride analysis. Alkalinity, aluminium, iron and sulphates have negative effect on the results while chloride and phosphate has positive effect.

3. Aim

To determine the concentration of fluoride in a number of different samples by SPADNS Spectrophotometric Method and to study the interference caused by different salts.

4. Method

a) Collect a sample from each of the buckets marked A, B, C and D.

Sample	Source	Probable concentration
A	Low TDS water	0-1 mg F^-/L
B	Low TDS water	2-3 mg F^-/L
C	Sample B + Na_2SO_4	2-3 mg F^-/L
D	Sample B + NaCl	2-3 mg F^-/L

b) Samples C & D contain two different salts which normally interfere in fluoride analysis.

c) Determine the concentration of fluoride in each sample according to the Standard Analytical Procedure for Fluoride. In case of samples C and D note the level of interference caused by the added salts.

5. Observations & calculations

a) Fill in the following table as you proceed with the test:

Sample	Absorbance at 570 nm
5 μg F^- standard	
10 μg F^- standard	
20 μg F^- standard	
30 μg F^- standard	
50 μg F^- standard	
70 μg F^- standard	
Sample A	
Sample B	
Sample C	
Sample D	

b) Use the values of the standard solutions in the table to plot a calibration curve of fluoride versus absorbance.
c) Read the fluoride content of the four sample aliquots from the standard curve and calculate the F^- concentration as described in the SAP.

6. Report

When writing your report the following aspects should be addressed:

- the aim of the investigation
- the analytical results that you have produced
- the effect of the added salts on the measured value of fluoride
- need for distillation of samples
- the likely effect on human health if sample A or B is drunk.