CHAPTER 2

EXPERIMENTAL

2.1 Instruments and apparatus

1. Conductometer-pH meter, Cole-Parmer, Model 5800-05, U.S.A.
2. Fluoride combination electrode, Cole-Parmer, Model 800-323-4340, U.S.A.
3. Incubator shaker, GALLENKAMP, Serial No. 8060131, U.K.
4. Jaw crusher machine, Japan
5. Magnetic stirrer, Cole-Parmer, model 4658, U.S.A.
6. pH meter, Cole-Parmer, Model 5986-25, U.S.A.
7. Sieve size of 6 and 20 mesh, Maruto testing machine MFG.Co. Ltd., Japan

2.2 Chemicals

1. Calcium chloride, $CaCl_2.2H_2O$, Puriss, Fluka, Switzerland
2. Firebrick, From Pong-Noi Village, Chiang Mai, Thailand
3. Glacial acetic acid, CH_3COOH, RPE, Carlo Erba, Italy
4. Magnesium chloride, $MgCl_2$, Puriss, Fluka, Switzerland
5. Sodium nitrate, $NaNO_3$, A.R., BDH, England
6. Sodium phosphate, Na_3PO_4, A.R., BDH, England
7. Sodium sulphate,Na_2SO_4, A.R. Carlo Erba, Italy
8. Sodium hydroxide, NaOH, A.R., Labscan, Ireland
9. Sodium chloride, NaCl, RPE, Carlo Erba, Italy
10. Sodium fluoride, NaF, Pure, Merck, Darmstadt, Germany

11. Tran-1,2 Diaminocyclohexane-N,N,N',N'–tetraacetic acid(CDTA), $C_{14}H_{22}N_2O_8$, A.R., Fluka, Switzerland

2.3 Preparation of the standard solution and reagents

Distilled water was used for the preparation of all solutions.

2.3.1 Stock standard fluoride solution, 5000 mg/l

A 11.050 g of NaF was dissolved and then diluted to 1000 ml with distilled water.

2.3.2 Standard fluoride solutions, 10, 20, 50, 70, 100, 150, 300 and 400 mg/l

The fluoride standard solutions were prepared from 5000 mg/l stock standard fluoride solution to different concentrations in 1 liter volumetric flask. Pipetted the desired volume of stock solution into the volumetric flask. The desired volume for each concentration was listed in Table 2.1

Table 2.1 The volume desired for diluting stock standard fluoride solution to obtain working standard fluoride solutions

Fluoride concentration (mg/l)	Pipetted volume (ml)
10	2.00
20	4.00
50	10.00
70	14.00
100	20.00
150	30.00
300	60.00
400	80.00

2.3.3 Sodium hydroxide, 6 M (NaOH)

Prepared by dissolving 242.42 g of NaOH in water and diluting to 1liter.

2.3.4 Stock phosphate ion solution, 2000 mg/l

Phosphate stock solution was prepared by dissolving 8.003g $Na_3PO_4.12H_2O$ in distilled water and dilution was made in 1liter volumetric flask.

2.3.5 Stock sulfate ion solution, 2000 mg/l

Prepared 1 liter of 2000 mg/l of sulfate ion by weighing 2.9592 g of Na_2SO_4 into 1liter volumetric flask. Dissolved and filled to the mark with distilled water.

2.3.6 Stock nitrate ion solution, 2000 mg/l

Prepared by dissolving 2.7461 g of $NaNO_3$ in water and diluting to 1000 ml with distilled water.

2.3.7 Stock chloride ion solution, 2000 mg/l.

Chloride ion solution was prepared by dissolving 3.2957 NaCl in distilled water and diluting to 1 liter in a volumetric flask.

2.3.8 Stock calcium ion solution, 2000 mg/l.

A 7.3510g of $CaCl_2.2H_2O$ was dissolved and then diluted to 1000 ml with distilled water

2.3.9 Stock magnesium ion solution, 2000 mg/l.

Prepared 1 liter of 2000 mg/l magnesium ion by weighing 8.3632g of $MgCl_2.6H_2O$ into 1 liter of volumetric flask. Dissolved and filled to the mark with distilled water.

2.3.10 Stock sodium ion solution, 2000 mg/l.

Sodium ion solution was prepared by dissolving 5.0869g of NaCl in distilled water and diluting to the mark in 1 liter volumetric flask.

2.3.11 Acetic acid, 0.1 M

Pipetted 1.00 ml. of acetic acid into 100 ml volumetric flask and diluting to the volume with the distilled water.

2.3.12 Sodium hydroxide, 0.1 M

Prepared by dissolving 2.0202 g of NaOH in water and diluting to 500 ml with distilled water.

2.3.13 Total ionic strength adjustment buffer; TISAB(II)

In a 1 liter beaker containing 500 ml of distilled water, 58 g of NaCl, 57 ml of CH_3COOH and 1 g of CDTA were dissolved. The solution was cooled and adjusted to pH 5-5.5 with 6M NaOH. The solution was cooled down further to the room temperature, transferred it to a 1000 ml volumetric flask and diluted to the volume with distilled water.

2.3.14 Mixture of fluoride ion and interfering ions at ratio 1:1 to 1:100 by weight

Pipetted 100 mg/l of fluoride solution and 2000 mg/l of interfering ion (Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, Na^+, Mg^{2+} and Ca^{2+}) solutions with appropriate volumes as indicated in Table 2.2, and diluted to the volume in 50 ml volumetric flask.

Table 2.2 Preparation of mixed solution of fluoride and interfering ions

Ratio of fluoride ion : interesting ions	Volume of fluoride 100 mg/l solution (ml)	Volume of 2000 mg/l interesting ions (ml)
1:1	5.00	0.25
1:10	5.00	2.50
1:25	5.00	6.25
1:50	5.00	12.50
1:100	5.00	25.00

2.4 Experimental method

2.4.1 Preparation of firebrick sample

Firebrick was broken by using jaw crusher machine and sieved by using sieve size of 6 and 20 mesh, and washed with distilled water before use.

2.4.2 Performance evaluation of fluoride ion selective electrode

Pipetted equal volume of a total ionic strength adjustment buffer (TISAB) solution and fluoride solution with known concentration, in this case, 10.00 ml of 1 and 10 mg/l of fluoride solution into beaker. The mixed solution was always stirred when the potential was measuring. The potential of fluoride solutions were measured by using fluoride ion selective electrode.

2.4.3 Preparation of a fluoride calibration curve

The standard fluoride solutions with concentration ranging from 0.2, 0.4, 0.8, 1.2, 2.0 and 4.0 mg/l were prepared in a total volume of 100 ml by appropriate dilution of 100 and 10 mg/l stock solutions as presented in Table 2.3

Table 2.3 Pipetted volume of stock standard fluoride solutions for preparing a series of working standard solutions.

Initial concentration (mg/l)	Pipetted volume (ml)	Working standard concentration (mg/l)
10	2.00	0.2
10	4.00	0.4
10	8.00	0.8
10	12.00	1.2
100	2.00	2.0
100	4.00	4.0

Each standard fluoride solution was then measured its potential in the same manner as done in the section of electrode evaluations, then a calibration graph was obtained by plotting the readout voltage against the corresponding logarithm of concentration.

2.4.4 A study of equilibration time for fluoride adsorption on firebrick

A 15 g of firebrick (6-20 mesh in size) was accurately weighed into 250 ml Erlenmayer flask. Added 15.00 ml of 10 mg/l of fluoride solution into the flask and shook at 150 rpm. The solutions were equilibrated by shaking at different time intervals ranging from 0.5, 1, 1.5, 2, 2.5 and 3 hours. The supernatant was then separated from the firebrick by filtration and the potential of the solutions was measured to evaluate the residual concentration of fluoride.

2.4.5 A study of the pH effect on fluoride adsorption.

The pH effect on fluoride adsorption were conducted by using 15 g firebrick in 15.00 ml of 10, 20, 50, 70, 100, 150, 300 and 400 mg/l F^- solution, respectively and adjusting the pH of each solution in the range of 3-9. After equilibration for 1 hour the

residual fluoride concentrations were evaluated from their potentials and the amounts of adsorbed fluoride on firebrick were then calculated.

2.4.6 A study of the temperature effect on fluoride adsorption

A weighed amount of firebrick was placed in the 250 ml Erlenmeyer flask and 15 ml of water containing fluoride ion of either 10 or 20 or 50 or 70 or 100 or 150 or 300 or 400 mg/l was added. These mixtures were shaken for 1 hour equilibrating time at 30, 40 and 50 ^{0}C respectively. The supernatant was taken out of each flask by filtration before assaying the fluoride concentration.

2.4.7 A study of the interfering ions

A 15 g of firebrick was weighed into a flask containing 15.00 ml of the solution mixture. The solution mixture consisted of fluoride and interfering ions (Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, Na^+, Mg^{2+} and Ca^{2+}) at different weight ratios of 1:1, 1:10, 1:25, 1:50 and 1:100. The solution-firebrick system was then equilibrated in the usual manner and the residual fluoride remained in the solution was determined later potentiometrically.

2.4.8 Experiments on column operation.

a. Finding a suitable amount of firebrick to be used in a column.

To conduct this experiment, a fixed size glass column (i.d.8 cm. and height 75 cm.) was filled with a different weight of firebrick; namely, 400, 800 and 1200 g of (6-20mesh in size). The synthetic fluoride water with concentration of 10 mg/l was allowed to flow down the column at a flow rate of 3 ml/min. A cotton pad was placed to prevent the clogging of the stopcock passage. Sampling of the fraction was performed at the increment of 100 ml for the first 1000 ml and the increment of

50 and 500 ml for the second and third liters of sample passed through the column. The residual fluoride remained in the solution was determined by the usual procedure.

b. The study on the effect of flow rate on column operation.

To conduct this study with a packed column of 1200 g firebrick, a synthetic fluoride water with concentration of 10 mg/l was flown through the column at different flow rates of 3, 5, 7 and 9 ml/min respectively. Samples of the effluent were periodically collected in the same manner as done in item 2.4.8a. and the volume collected was up to 8 liters. They were then analyzed for residual fluoride concentration.

2.4.9 Defluoridation of real water samples.

Real water samples form two wells in Ban Sankayom, Lamphun province were sampled and the initial fluoride concentrations were determined by ISE measurement.

To evaluate the fluoride removal performance in a flow system, a packed column of 1200 g firebrick was used. This experiment was done by allowing the water sample to flow at the flow rate of 3.0 ml/min through the column while monitoring the potential of the effluent by the same procedure used previously.