CHAPTER 4

Determination of Hydroxide by Spectrophotometric Flow Injection Analysis Using *m*-Cresol Purple

4.1 Introduction

Bone char is a popular adsorbent for fluoride removal in Thailand. Adsorption of fluoride by bone char levels up a hydroxide quantity, i.e. the pH of fluoride solution shifts from neutral to basic after the removal. In order to study a relationship between an amount of fluoride adsorbed and hydroxide released during defluoridation, a method for hydroxide measurement must be developed with flexibility to adapt to the method for the simultaneous determination of both ions. Spectrophotometric flow injection analysis of hydroxide with an indicator is unquestionably the most suitable method due to its simplicity and ease of operation. In addition, it can be straightforwardly adopted to flow injection determination of fluoride for online detection of the two ions. The aim of this work is to develop the flow injection method for hydroxide determination by spectrophotometry.

4.2 Experimental

4.2.1 Apparatus and reagents

A manifold for hydroxide determination was utilized as previous described (Figure 3.1c). All chemicals were of analytical reagent grade. Doubly distilled water was used throughout. Phenol red (FLUKA), cresol red (FLUKA), *m*-cresol purple (MERCK) and thymol blue (MERCK) were prepared as described in the literature [1]. Hydrochloric acid (BDH) and sodium hydroxide (BDH) were used in adjusting the pH.

4.3 Results and discussion

4.3.1 Selection of a suitable indicator

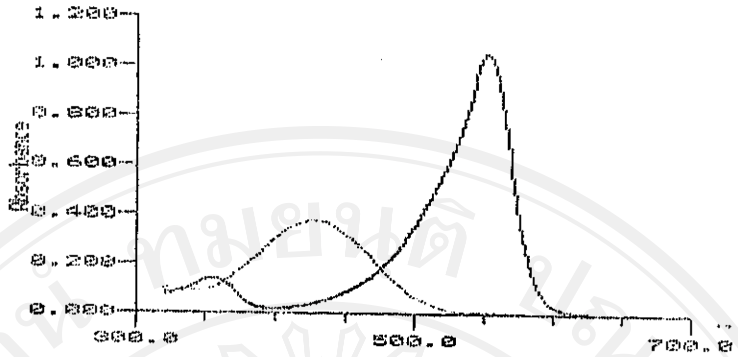
Phenolphthalein with a transition range of 8.3 – 10.0 was first studied. The color of its basic form was expected to be observed in a solution of pH greater than 8.3, but in fact the solution turned pale pink when the pH was nearly 10 which was closed to its pK_I of 9.5.

Other indicators were therefore investigated. Four phthalein indicators showing the transition range in a basic solution (Table 4.1) were considered owing to no interference from the color absorption of an acid form when measuring the maximum wavelength of the basic form for the determination of hydroxide. Absorption spectra of four phthaleins, i.e. phenol red, cresol red, *m*-cresol purple and thymol blue, were shown in Figure 4.1. Each of the four phthaleins clearly shows that its maximum absorption of the basic form is well separated from that of the acid form.

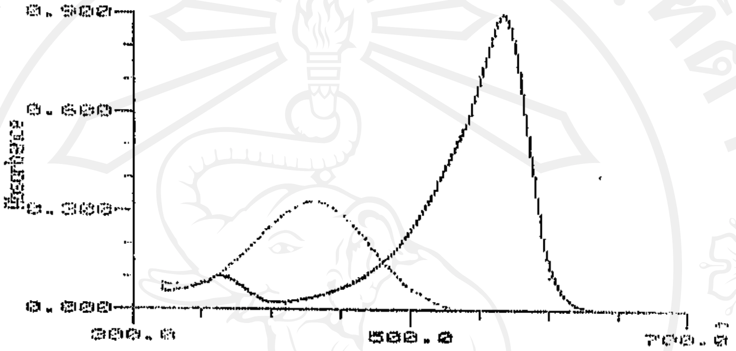
Table 4.1 Four phthalein indicators in a basic solution [1].

Indicator	pK_I	pH range	Color change
Phenol red	8.00	6.6 – 8.0	yellow - red
Cresol red	8.46	7.0 – 8.8	yellow - red
m-Cresol Purple	8.3	7.4 – 9.0	yellow - purple
Thymol blue	9.20	8.0 – 9.6	yellow - blue

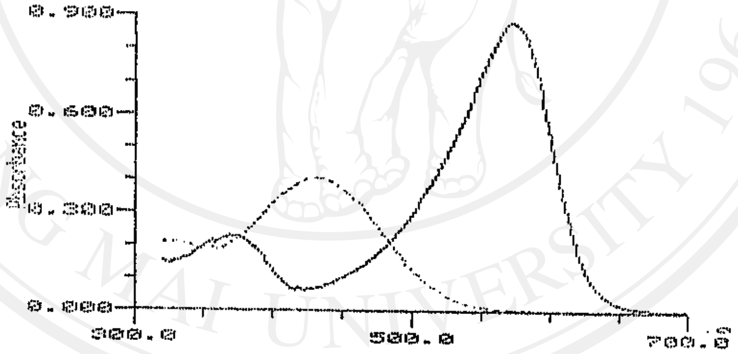
4.1a Phenol red



4.1b Cresol red



4.1c *m*-Cresol Purple



4.1d Thymol blue

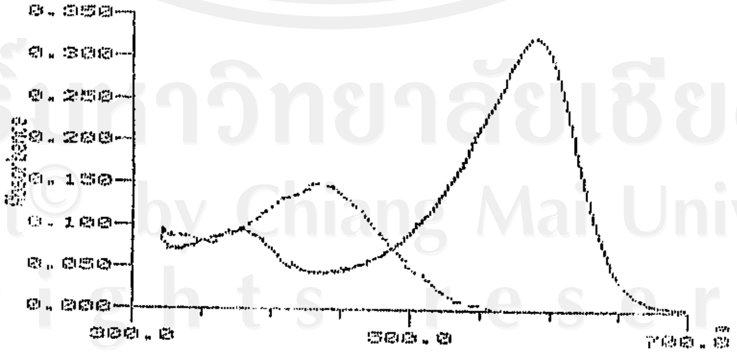


Figure 4.1 Absorption spectra of four phthalein indicators.

(- - - - acid form , —— basic form)

The sensitivity of the investigated indicators was tabulated in Table 4.2. All phthalein dyes had the same concentration but their sensitivity decreased from phenol red, cresol red, *m*-cresol purple to thymol blue, respectively, corresponding to the decrease in their absorbances. Therefore their qualitative molar absorptivities were compared as follow: $\varepsilon_{\text{phenol red}} > \varepsilon_{\text{cresol red}} \cong \varepsilon_{m\text{-cresol purple}} >> \varepsilon_{\text{thymol blue}}$.

Table 4.2 Absorbance of the basic form of phthalein dyes.

Indicator	**λ_{max} of the basic form (nm)**	**Absorbance***
Phenol red	555.0	1.051
Cresol red	570.0	0.898
m-Cresol Purple	576.0	0.881
Thymol blue	596.0	0.325

* indicator concentration 2.00% v/v

The absorbance of indicator solutions at different pH were also investigated. Although four indicators have the transition range in a basic solution, the exact transition region was slightly different as illustrated in Figure 4.2. This figure reveals that *m*-Cresol purple is superior to the rest because the absorbance change is in the range of 7 – 10 which covers the pH range of the samples and is the most linear. Beside its acceptable sensitivity, it is not much different from that of phenol red and cresol red. *m*-Cresol purple was therefore preferable for the later experiments.

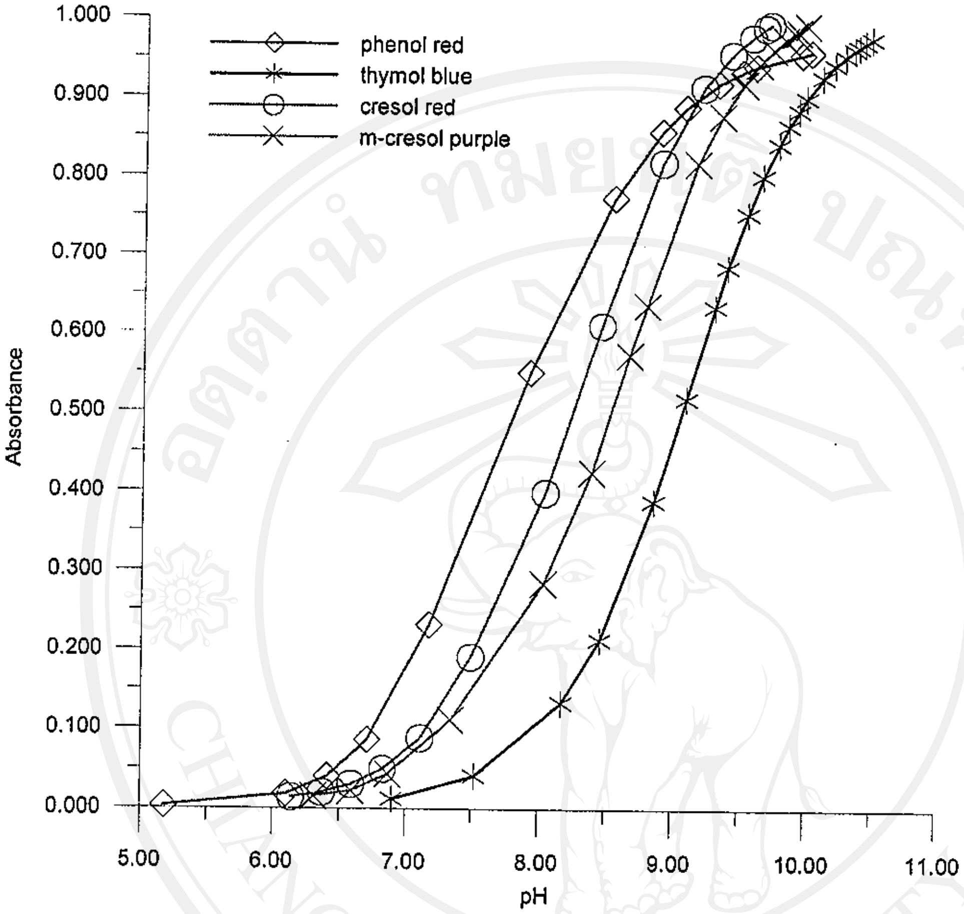


Figure 4.2 Absorbance change of phthalein indicators.

4.3.2 Optimization of the parameters

Once the indicator for spectrophotometric detection of the pH is chosen, an optimization of the parameters is studied. By selecting the double-line manifold as previously used in Chapter 3 (Figure 3.1c), chemical optimizations, i.e. indicator concentration and its initial pH, were investigated. The *m*-cresol purple concentrations were varied from 0.40 to 12.0 %v/v, showing the maximum sensitivity at 4.00 %v/v (Figure 4.3). Note that the values between 2.00 and 8.00 %v/v rendered a satisfactory sensitivity.

On the other hand, the initial pH of the indicator tremendously affected the slope of the calibration curve for hydroxide determination (Figure 4.4); changing in the pH sharply changes the sensitivity. The peak value was obviously obtained at pH 8.85 bringing about the pH at the outlet of the manifold of 8.3 which was closed to the pK_I of *m*-cresol purple.

The effect of manifold variables, i.e. flow rate, injection volume and mixing coil length, were depicted in Figure 4.5, 4.6 and 4.7 respectively. The dependence of flow rate and loop volume was similar; the selected value appeared at the apex of the graph. However, the effect of reactor coil length on sensitivity was not explicit from 25.0 to 100 cm of length. The peak height was consequently considered instead of the sensitivity. The value of 50 cm was optimum because it gave the highest peak height.

The optimization for hydroxide determination was summarized in Table 4.3.

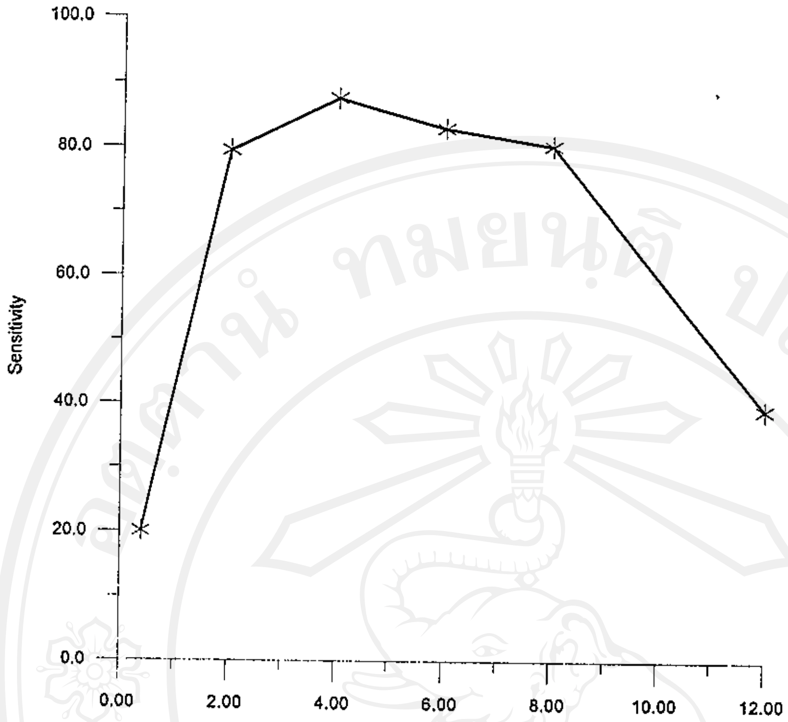


Figure 4.3 Effect of *m*-cresol purple concentration on sensitivity.

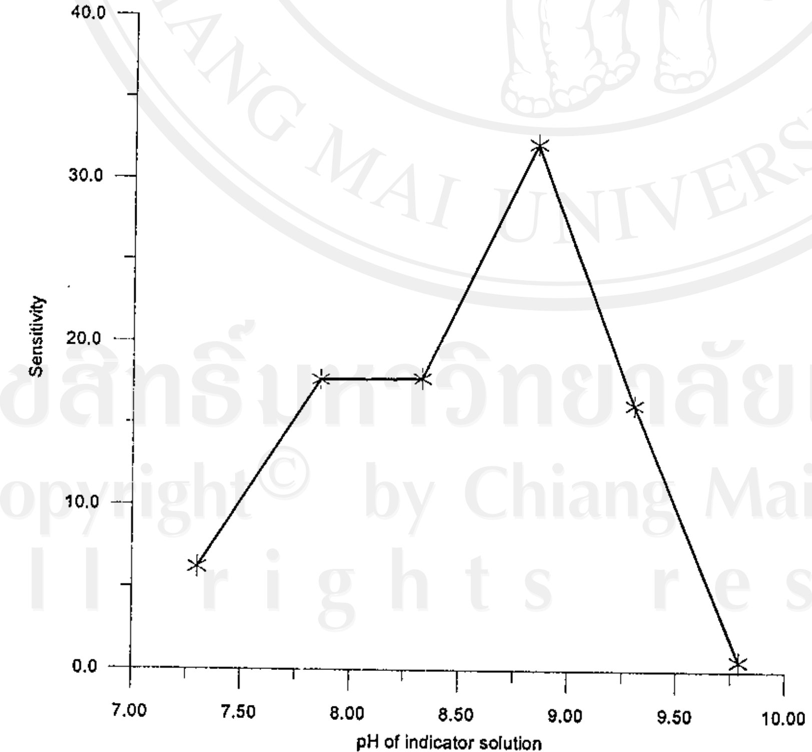


Figure 4.4 Effect of initial pH of indicator solution on sensitivity.

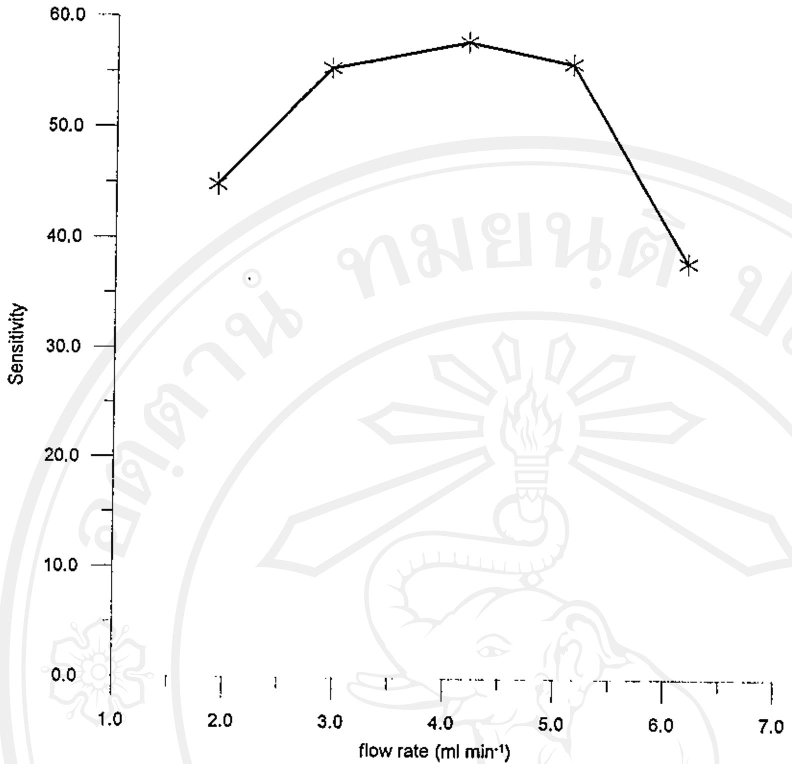


Figure 4.5 Effect of flow rate.

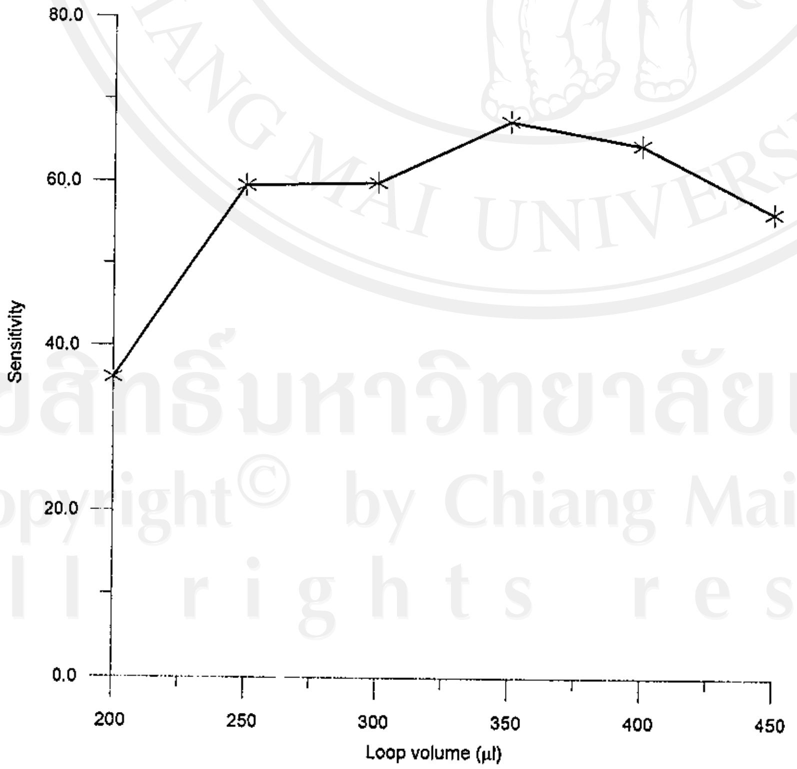


Figure 4.6 Effect of injection volume.

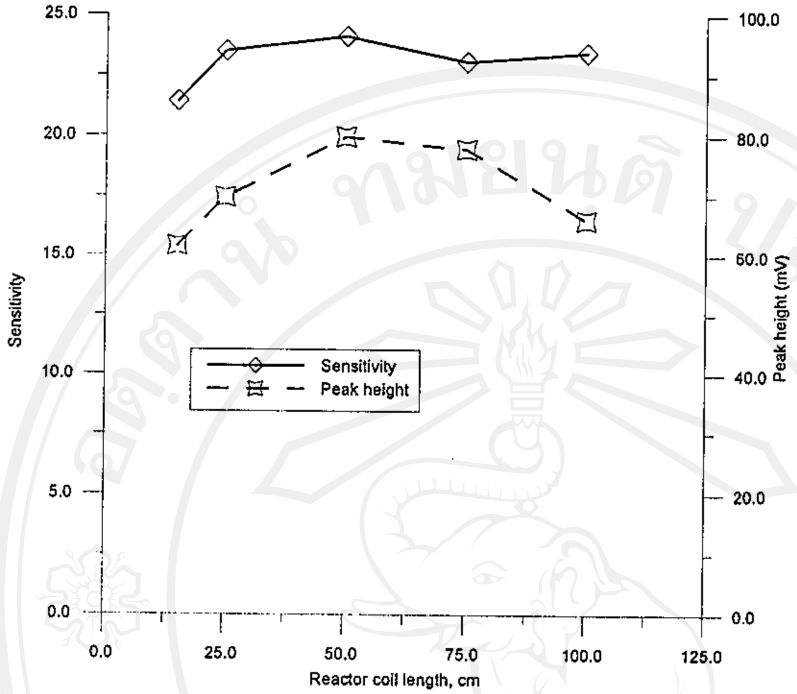


Figure 4.7 Effect of reactor coil length on sensitivity.

Table 4.3 Optimization of chemicals and flow injection variables for pH detection.

Parameters	Range Studied	Selected value
1. Indicator concentration (%v/v)	0.40 – 12.0	4.00
2. pH of indicator solution	7.30 – 9.79	8.85
3. Flow rate (mL min^{-1})	2.0 – 6.0	4.0
4. Injection loop volume (μL)	200 – 450	350
5. Mixing coil length (cm)	15 – 100	50

4.3.3 Analytical characteristics

Under optimized conditions, a typical calibration graph for pH measurement was recorded (Figure 4.8). It was linear from pH 7.14 to 9.06 and 9.06 to 10.06 with the slope of 9.93 and 48.9 respectively. Limit of detection was found to be pH 6.87. The precision of the developed method was expressed as relative standard deviation : 2.5% at pH 8.36 and 2.0% at pH 9.81. The sampling frequency from the t_{base} of 55 s was 65 samples per hour. Analytical features were summarized in Table 4.4.

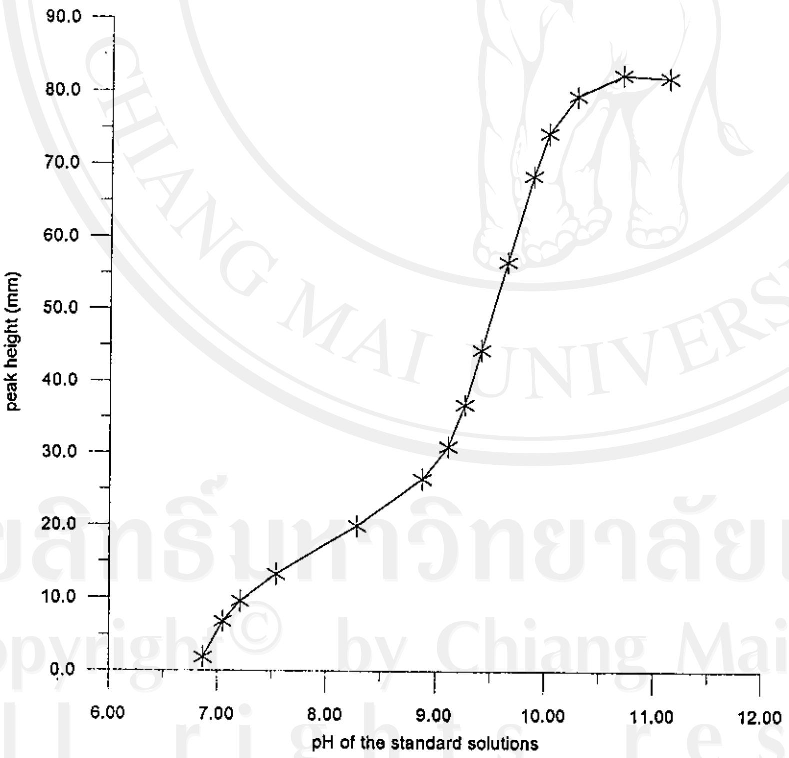


Figure 4.8 The calibration graph for pH measurement.

Table 4.4 Summary of analytical characteristics for hydroxide determination.

Analytical parameters	Characteristics
1. Linearity	pH 7.14 – pH 9.06 $Y = 9.926X - 61.87$, $r^2 = 0.998$ pH 9.06 – pH 10.06 $Y = 48.85X - 414.9$, $r^2 = 0.999$
2. Limit of detection	pH 6.87
3. RSD	2.5 % at pH 8.36 2.0 % at pH 9.81
4. Sampling frequency	65 samples h^{-1}

4.3.4 pH determination in real samples

Samples, supernatant from adsorption of fluoride by bone char, were analyzed for hydroxide level so as to check an accuracy of the present method. Hydroxide quantities in seven samples were measured by the proposed method and the standard one (pH electrode) and the results were compared as tabulated in Table 4.5. t-Test analysis was carried out for the accuracy and indicated that no significant difference between the results from two techniques at 95% confidence interval ($t_{observed} < t_{critical}$).

Table 4.5 Determination of pH by the proposed and standard methods.

Sample	pH from the standard method (pH meter)	pH from the proposed method	x_d
1	7.58	7.48	0.10
2	7.63	7.41	0.22
3	8.78	9.08	-0.30
4	7.64	7.30	0.34
5	7.68	7.64	0.04
6	9.29	9.39	-0.10
7	7.71	7.44	0.27
		$\bar{x}_d$	0.0814
		s_d	0.224
		t_{obs}	0.96*

* Critical t-value at the 0.05 level is 2.45.

4.4 Conclusion

The spectrophotometric flow injection determination of hydroxide by *m*-cresol purple was conducted with satisfactory precision and accuracy. The method was simple and successfully applied to the supernatant from defluoridation by bone char.

4.5 References

1. Lide D.R., *CRC Handbook of Chemistry and Physics*, 76th ed, **1995**, CRC Press.