3. RESULTS

3.1 Determinations of Anions with IonPac AS4A Column

3.1.1 Investigation of retention times of ions of interest

The most common anions in geological samples are generally F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-} and SO_4^{2-} which are likely to be found as contaminating anions in geological samples. The retention times of these anions found in the investigated samples are given in **Table 3.1.**

Table 3.1 Retention times of anions obtained with IonPac AS4A column using 1.80 mM Na_2CO_3/1.70 mM $NaHCO_3$ as eluent, at flow rate 2.0 ml/min

Ion	t_r (min)
F^-	0.92
Cl^-	1.40
NO_2^-	1.68
Br^-	2.48
NO_3^-	2.87
PO_4^{3-}	4.90
SO_4^{2-}	6.33

3.1.2 Optimization of IC conditions

3.1.2.1 Results of effect of eluent concentration

(a) Retention time

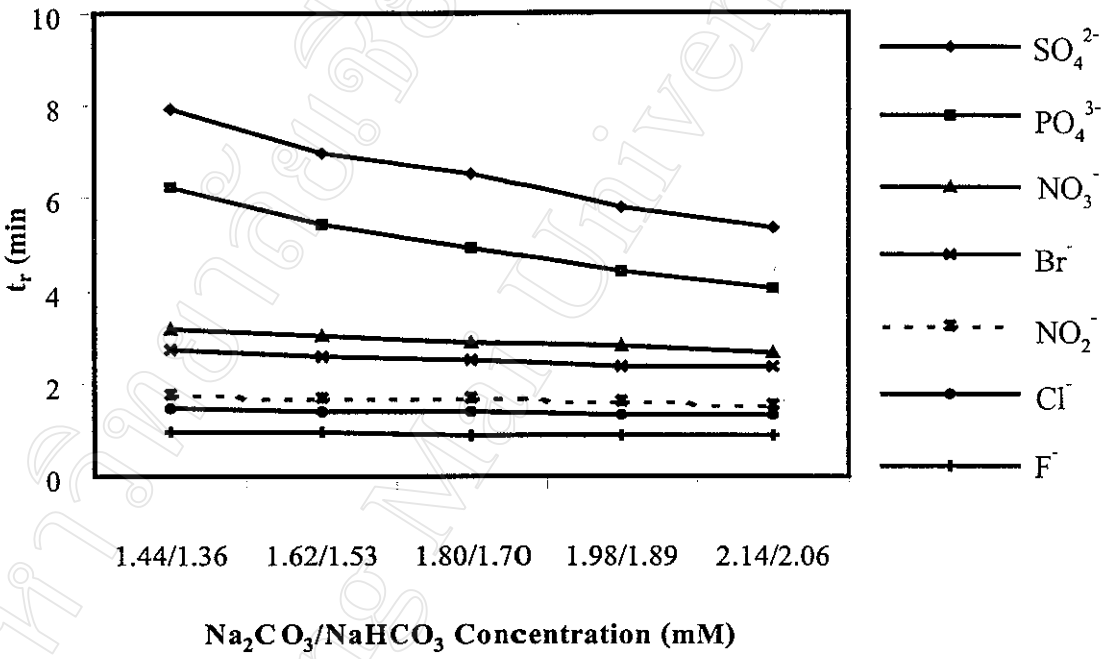


Figure 3.1 Plot of the retention time of each anion against the $Na_2CO_3/NaHCO_3$ concentration.

(b) Peak area

Table 3.2 Peak areas of each anion at various eluent concentration

Anions	Peak area ($1x10^5$) at Na_2CO_3/$NaHCO_3$ (mM)				
	1.44/1.36	1.62/1.53	1.80/1.70	1.98/1.89	2.14/2.06
F^-	1.53	1.70	1.64	1.67	1.92
Cl^-	2.03	1.97	2.03	1.94	1.86
NO_2^-	1.34	1.32	1.26	1.23	1.23
Br^-	0.89	0.83	0.85	0.84	0.83
NO_3^-	1.07	1.06	1.14	1.10	1.06
PO_4^{3-}	0.78	0.76	0.88	0.78	0.80
SO_4^{2-}	1.55	1.58	1.67	1.54	1.63

(c) Resolution

Table 3.3 Resolution of each anion pair at various eluent concentration

Anions	Resolution of each anion pair at Na_2CO_3/$NaHCO_3$ (mM)				
	1.44/1.36	1.62/1.53	1.80/1.70	1.98/1.89	2.14/2.06
F^-&Cl^-	5.33	4.98	4.85	4.54	4.26
Cl^-&NO_2^-	3.00	2.83	2.78	2.62	2.44
NO_2^-&Br^-	7.48	7.14	7.06	6.55	6.46
Br^-&NO_3^-	3.18	2.98	2.97	2.94	2.71
NO_3^-&PO_4^{3-}	14.04	12.35	10.60	9.46	8.54
PO_4^{3-}&SO_4^{2-}	5.49	5.60	6.16	6.10	5.92

3.1.2.2 Results of effect of eluent flow rate

(a) Retention time

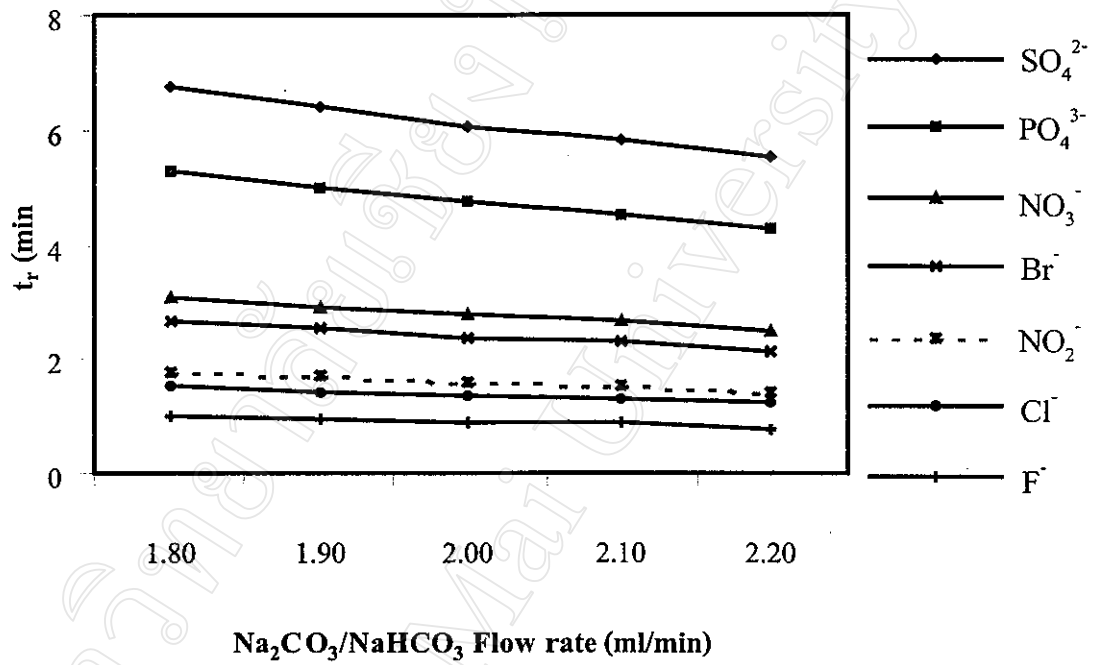


Figure 3.2 Plot of the retention times of each anion against the $Na_2CO_3/NaHCO_3$ flow rate.

(b) Peak area

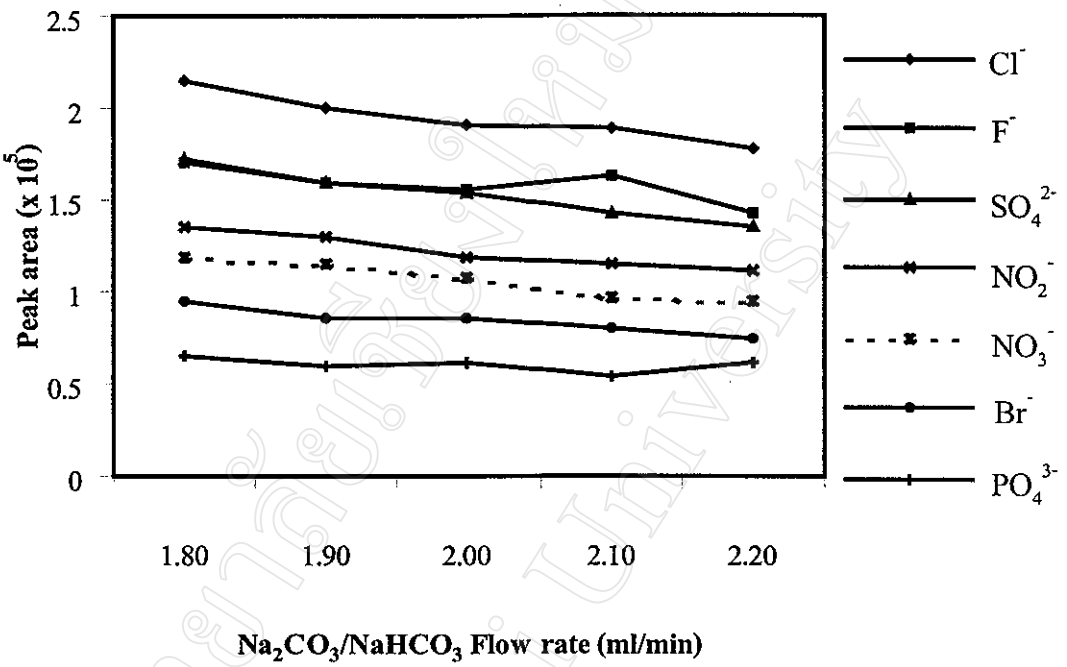


Figure 3.3 Plot of each anion peak area against the $Na_2CO_3/NaHCO_3$ flow rate.

(c) Resolution

Table 3.4 Resolution of each anions pair at various $Na_2CO_3/NaHCO_3$ flow rate

Anions	Resolution of each anion pair at $Na_2CO_3/NaHCO_3$ flow rate (ml/min)				
	1.80	1.90	2.00	2.10	2.20
F^-&Cl^-	4.86	4.59	4.52	4.35	4.26
Cl^-&NO_2^-	2.52	2.66	2.54	2.39	2.29
NO_2^-&Br^-	7.07	6.75	6.36	6.43	6.42
Br^-&NO_3^-	2.88	2.88	2.89	2.77	2.75
NO_3^-&PO_4^{3-}	11.79	11.26	10.83	11.19	10.88
PO_4^{3-}&SO_4^{2-}	5.99	5.84	5.67	5.71	5.58

(d) Theoretical plates (N)

Table 3.5 Theoretical plates of each anion at $Na_2CO_3/NaHCO_3$ flow rate

Anions	N at $Na_2CO_3/NaHCO_3$ flow rate (ml/min)				
	1.80	1.90	2.00	2.10	2.20
F^-	1424	1361	1146	1120	1066
Cl^-	3169	2912	2696	2628	2430
NO_2^-	3989	3773	3534	3510	3233
Br^-	6546	6251	5363	5781	5496
NO_3^-	7074	6579	6264	6448	6400
PO_4^{3-}	8624	8051	7365	7890	6840
SO_4^{2-}	9768	9403	8995	8812	9149

3.1.2.3 Summary of optimized IC conditions

The optimized IC conditions obtained with IonPac AS4A column established in this work are listed in **Table 3.6.**

Table 3.6 Optimized IC conditions yielding high sensitivity and good resolution of analysis obtained with IonPac AS4A.

Operation	Optimal conditions
Eluent	1.80 mM Na_2CO_3/1.70 mM $NaHCO_3$
Eluent flow rate	2.00 ml/min
Detector	conductivity
Detector temperature compensation	1.7 %/ °C
Background conductivity (output range)	3 μS
Sample loop volume	25 μl

3.1.3 Repeatability and reproducibility of results

3.1.3.1 Repeatability of results

Table 3.7 Repeatability of results obtained with IonPac AS4A column, 1.80 mM Na_2CO_3/1.70 mM $NaHCO_3$ as eluent, eluent flow rate 2.0 ml/min, conductivity detector with temperature compensation 1.7%/°C and output range 3 μS.

(a) Retention times of each anion investigated

Run	t_r (min)						
	F^- 0.5 μg/ml	Cl^- 1.0 μg/ml	NO_2^- 1.0 μg/ml	Br^- 1.0 μg/ml	NO_3^- 1.0 μg/ml	PO_4^{3-} 2.0 μg/ml	SO_4^{2-} 1.0 μg/ml
1	0.90	1.37	1.63	2.43	2.82	4.70	6.05
2	0.90	1.37	1.63	2.43	2.82	4.72	6.07
3	0.90	1.35	1.63	2.42	2.80	4.72	6.05
4	0.92	1.38	1.65	2.45	2.83	4.73	6.08
5	0.90	1.37	1.63	2.43	2.82	4.73	6.07
Mean	0.90	1.37	1.63	2.43	2.82	4.72	6.06
SD	0.01	0.01	0.01	0.01	0.01	0.01	0.01
%RSD	1.11	0.82	0.61	0.46	0.40	0.26	0.23

Table 3.7 (continued)

(b) Peak areas of each anion investigated

Run	Peak area ($1x10^5$) (arbitrary unit)						
	F^- 0.5 µg/ml	Cl^- 1.0 µg/ml	NO_2^- 1.0 µg/ml	Br^- 1.0 µg/ml	NO_3^- 1.0 µg/ml	PO_4^{3-} 2.0 µg/ml	SO_4^{2-} 1.0 µg/ml
1	1.75	1.82	1.10	0.74	0.98	0.61	1.53
2	1.60	1.83	1.13	0.79	1.00	0.61	1.52
3	1.85	1.83	1.13	0.78	1.00	0.61	1.50
4	1.75	1.88	1.14	0.78	1.00	0.61	1.52
5	1.75	1.90	1.13	0.76	1.00	0.60	1.51
Mean	1.74	1.85	1.13	0.77	1.00	0.61	1.52
SD	0.09	0.04	0.02	0.02	0.01	0.01	0.01
%RSD	5.14	1.93	1.40	2.60	1.00	0.82	0.81

3.1.3.2 Reproducibility of results

Table 3.8 Reproducibility of results obtained with IonPac AS4A column, 1.80mM Na_2CO_3/1.70 mM $NaHCO_3$ as eluent, eluent flow rate 2.00 ml/min, conductivity detector with temperature compensation 1.7%/°C and output range 3 μS

(a) Retention times of each anion investigated

Run	t_r (min)						
	F^- 0.5 μg/ml	Cl^- 1.0 μg/ml	NO_2^- 1.0 μg/ml	Br^- 1.0 μg/ml	NO_3^- 1.0 μg/ml	PO_4^{3-} 2.0 μg/ml	SO_4^{2-} 1.0 μg/ml
1	0.90	1.37	1.63	2.43	2.82	4.70	6.05
2	0.90	1.37	1.63	2.43	2.82	4.72	6.07
3	0.87	1.35	1.62	2.47	2.85	4.52	5.82
4	0.92	1.38	1.65	2.45	2.83	4.73	6.08
5	0.88	1.37	1.63	2.48	2.87	4.53	5.83
6	0.95	1.40	1.67	2.48	2.88	4.68	5.98
Mean	0.90	1.37	1.64	2.46	2.84	4.65	5.97
SD	0.02	0.02	0.02	0.02	0.03	0.08	0.12
%RSD	2.48	1.22	1.12	0.96	0.93	1.76	1.99

Table 3.8 (continued)

(b) Peak areas of each anion investigated

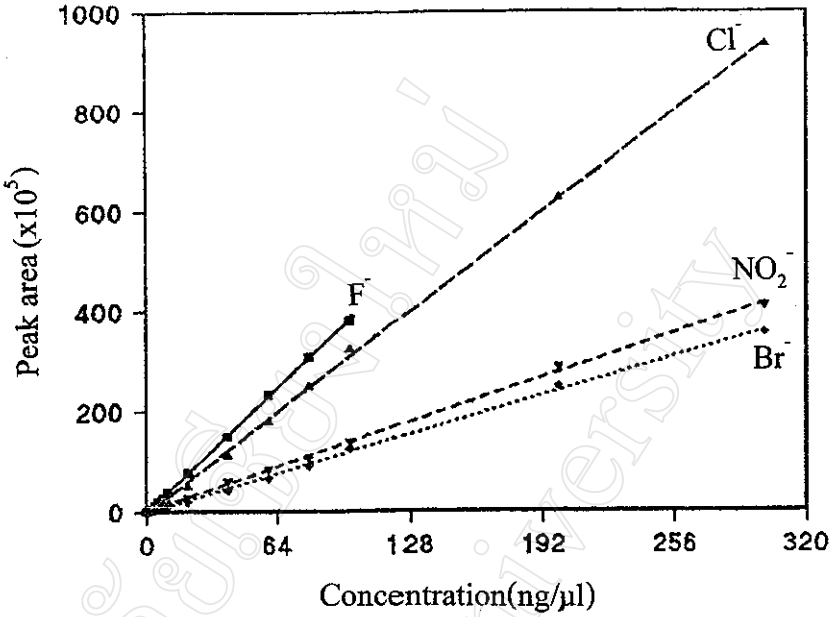
Run	Peak area ($1x10^5$) (arbitrary unit)						
	F^- 0.5 µg/ml	Cl^- 1.0 µg/ml	NO_2^- 1.0 µg/ml	Br^- 1.0 µg/ml	NO_3^- 1.0 µg/ml	PO_4^{3-} 2.0 µg/ml	SO_4^{2-} 1.0 µg/ml
1	1.75	1.82	1.10	0.74	0.98	0.61	1.53
2	1.78	1.87	1.13	0.78	1.00	0.61	1.52
3	1.72	1.87	1.19	0.79	1.02	0.61	1.54
4	1.75	1.90	1.14	0.76	1.00	0.60	1.51
5	1.77	1.88	1.13	0.81	1.01	0.58	1.52
6	1.85	1.83	1.13	0.78	1.00	0.61	1.50
Mean	1.77	1.86	1.14	0.78	1.00	0.60	1.52
SD	0.07	0.03	0.03	0.02	0.01	0.01	0.01
%RSD	2.39	1.65	2.62	3.14	1.34	2.07	0.93

3.1.4 Results of determination of linearity

Table 3.9 Relationship between peak areas and concentration of anions for determination of linearity obtained with IonPac AS4A column and 1.80 mM Na_2CO_3/1.70 mM $NaHCO_3$ as eluent at flow rate 2.0 ml/min, using a conductivity detector.

Concentration	Peak area ($1x10^5$) (arbitrary unit)						
(ng/µl)	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
0.20	0.80	0.63	0.24	0.15	0.22	-	0.30
0.40	1.35	0.95	0.50	0.38	0.45	-	0.69
0.60	1.94	1.32	0.77	0.62	0.65	0.35	1.18
0.80	2.59	1.74	1.07	0.76	0.86	0.51	1.46
1.00	3.22	2.14	1.33	0.93	1.10	0.66	1.90
2.00	6.60	4.12	2.54	1.85	2.11	1.31	2.97
4.00	13.13	8.16	5.41	3.93	4.42	2.88	6.24
6.00	21.60	12.60	8.30	5.40	6.50	3.96	8.28
8.00	27.70	18.20	11.10	7.40	8.80	5.82	12.35
10.00	37.62	23.43	13.86	9.24	10.89	7.07	14.49
20.00	76.56	49.17	29.04	18.81	21.78	15.45	30.24
40.00	149.90	111.87	61.05	41.58	51.81	36.41	68.36
60.00	233.05	179.63	85.30	67.09	78.63	52.87	97.32
80.00	309.69	249.54	108.50	91.24	114.49	73.75	135.54
100.00	381.16	322.87	139.02	124.41	134.01	100.16	187.20
200.00	-	626.49	288.54	249.70	287.69	-	376.70
300.00	-	933.96	409.67	356.46	429.80	292.91	533.75

(a)



(b)

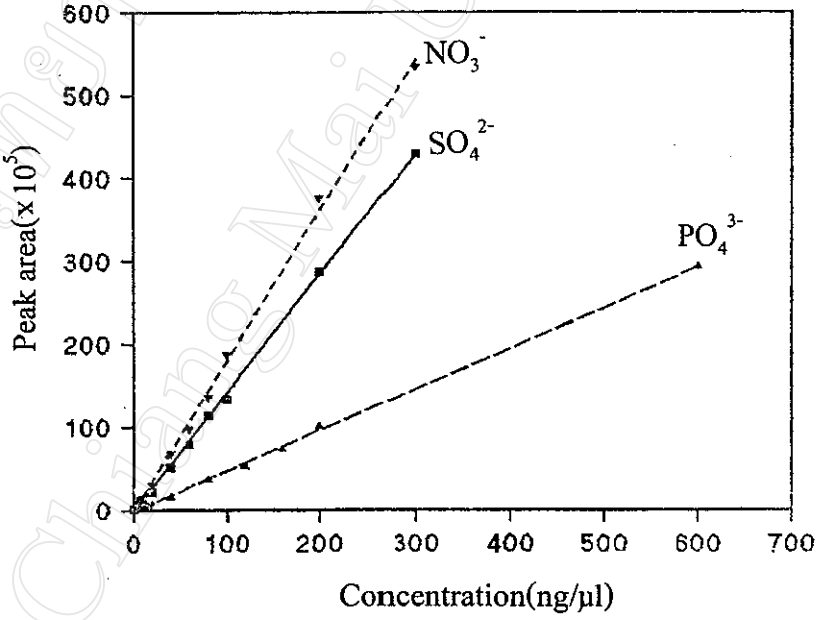


Figure 3.4 Linearity curves for anions obtained with IonPac AS4A column and 1.80 mM Na_2CO_3/1.70 mM $NaHCO_3$ as eluent at flow rate 2.00 ml/min, using a conductivity detector:

(a) for F^-, Cl^-, NO_2^- and Br^-

(b) for SO_4^{2-}, NO_3^- and PO_4^{3-}

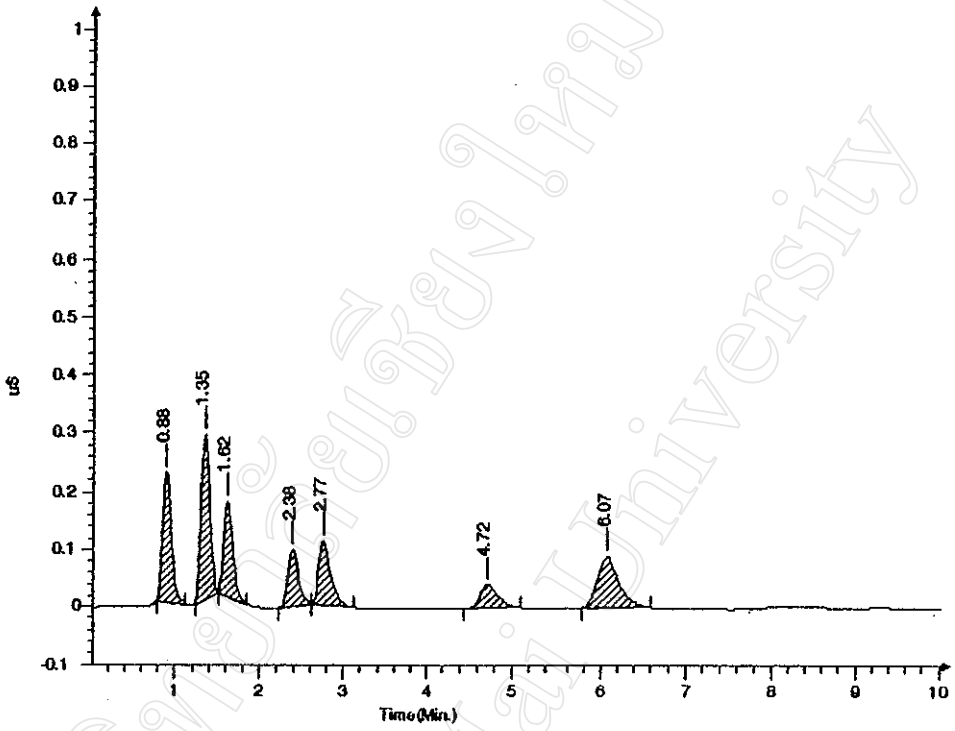


Figure 3.5 Chromatogram of 0.5 ppm F^-, 1.0 ppm Cl^-, 1.0 ppm NO_2^-, 1.0 ppm Br^-, 1.0 ppm NO_3^-, 2.0 ppm PO_4^{3-} and 1.0 ppm SO_4^{2-} obtained with IonPac AS4A column and 1.80 mM Na_2CO_3/1.70 mM $NaHCO_3$ as eluent at flow rate 2.00 ml/min, using a conductivity detector.

3.1.5 Results of detection limit and minimum detectable quantity

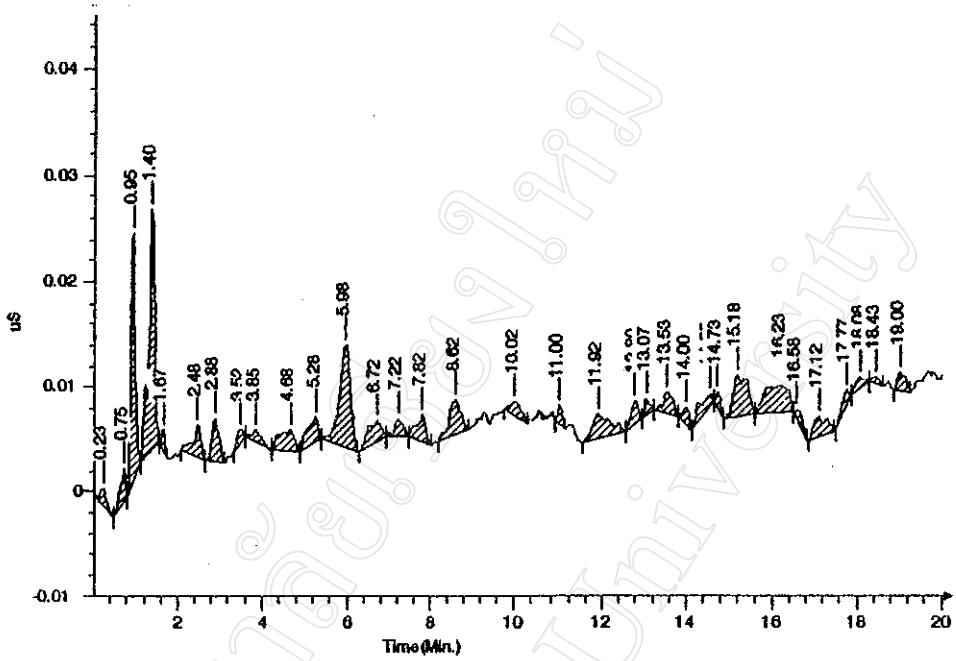


Figure 3.6 Chromatogram illustrating peak height, peak-half width and noise level.

Table 3.10 Detection limits and minimum detectable quantities of anions obtained with IonPac AS4A column and 1.80 mM Na_2CO_3/1.70 mM $NaHCO_3$ as eluent at flow rate 2.0 ml/min, using a conductivity detector.

Anions	Concentration m_x (ng/µl)	Noise signal n (cm)	Peak height R (cm)	$W_{1/2}$ (min)	L (ng)	MDQ (ng.sec)
F^-	0.02	0.16	2.39	0.06	0.03	0.002
Cl^-	0.02	0.23	2.29	0.06	0.05	0.003
NO_2^-	0.02	0.25	0.20	0.04	0.62	0.025
Br^-	0.02	0.12	0.29	0.08	0.21	0.016
NO_3^-	0.02	0.13	0.40	0 10	0.16	0.016
PO_4^{3-}	0.02	0.08	0.20	0.23	0.20	0.046
SO_4^{2-}	0.02	0.11	0.99	0.13	0.06	0.007

3.2 Determination of Anions in Geological Samples by IC.

3.2.1 Geological water samples

From the investigation described in Section 2.3.1, it was found that IonPac AS4A column could be used to separate F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-} and SO_4^{2-} isocratically in less than 8 minutes. So this column was used for the determination of anions in geological water samples. The condition obtained was applied to determine the amounts of anions in some geological water samples.

3.2.1.1 Standard calibration curves of F^-, Cl^-, NO_3^- and SO_4^{2-}

Analysis for these anions in geological water samples were constructed from the data in **Tables 3.11-3.14**. The resultant calibration curves are shown in **Figures 3.7-3.10**.

Table 3.11 The data used for construction of the standard calibration curve of F^-.

Concentration (ng/μl)	Peak area ($1x10^5$)(arbitrary unit)
0.30	0.94
0.50	1.57
1.00	3.22
6.00	22.80
10.00	37.62
20.00	76.56
30.00	113.40

Table 3.12 The data used for construction of the standard calibration curve of Cl^-.

Concentration (ng/μl)	Peak area ($1x10^5$)(arbitrary unit)
0.20	0.63
1.00	1.87
2.00	4.16
4.00	8.69
10.00	23.43
20.00	49.17

Table 3.13 The data used for construction of the standard calibration curve of NO_3^-.

Concentration (ng/μl)	Peak area ($1x10^5$)(arbitrary unit)
0.20	0.22
0.40	0.44
0.80	0.86
1.00	1.00
2.00	2.03
6.00	5.86

Table 3.14 The data used for construction of the standard calibration curve of SO_4^{2-}.

Concentration (ng/μl)	Peak area ($1x10^5$)(arbitrary unit)
1.00	1.63
6.00	8.29
10.00	14.49
20.00	30.24
40.00	65.34

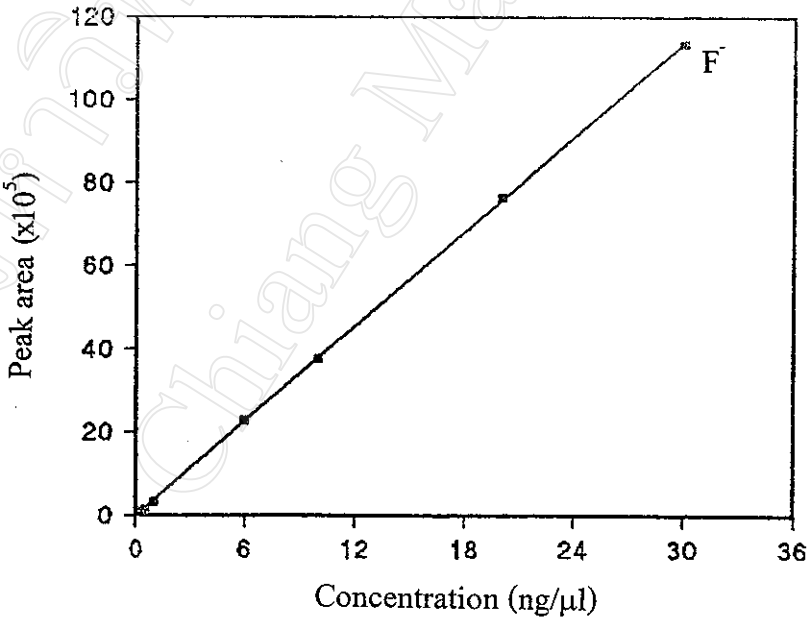


Figure 3.7 Calibration curve of F^-.

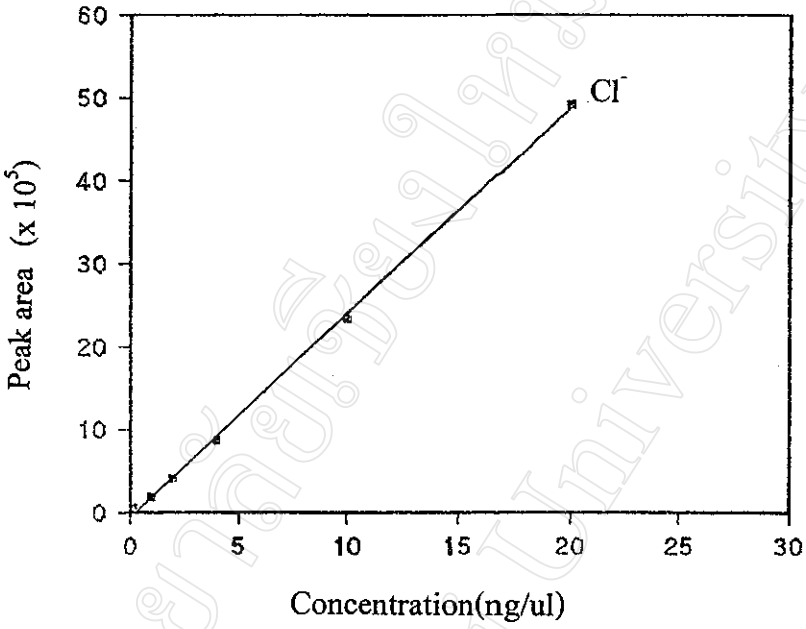


Figure 3.8 Calibration curve of Cl^-.

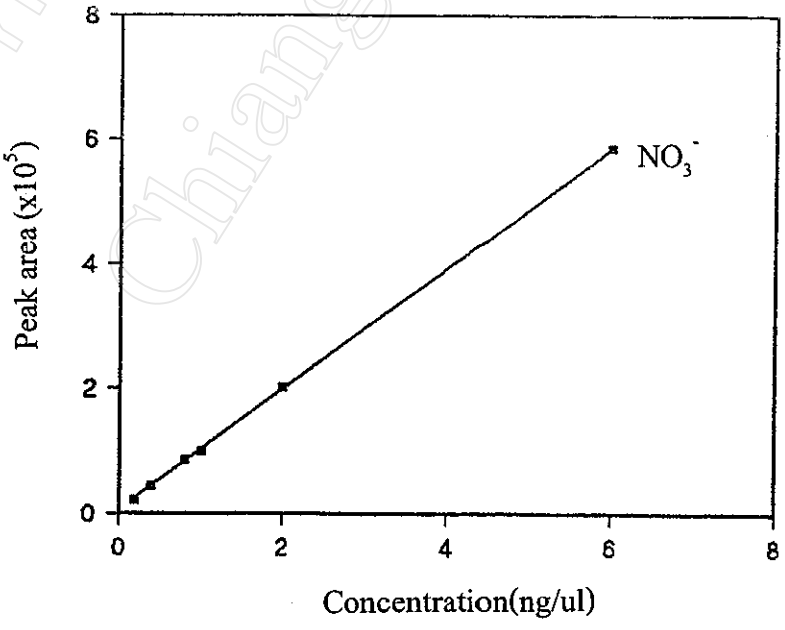


Figure 3.9 Calibration curve of NO_3^-

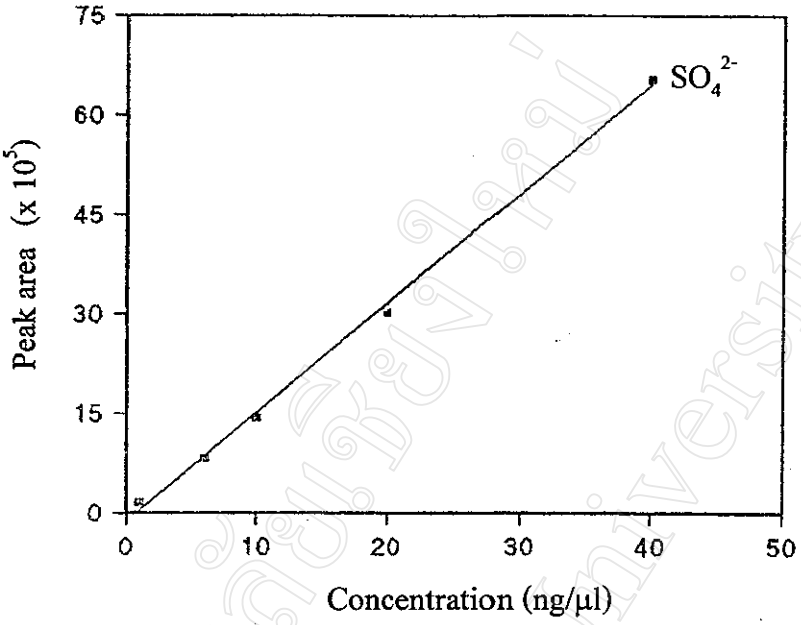


Figure 3.10 Calibration curve of SO_4^{2-}.

3.2.1.2 The amounts of F^-,Cl^-, NO_3^- and SO_4^{2-} in geological water samples

The amounts of F^-,Cl^-, NO_3^- and SO_4^{2-} in geological water samples were obtained with IonPac AS4A column. The results of analysis are shown in **Tables 3.15 and 3.16**.

Table 3.15 Peak areas of analyte anions in geological water samples obtained with IonPac AS4A column.

Sample	Peak area (arbitrary unit)*			
	F^-	Cl^-	NO_3^-	SO_4^{2-}
1	8428890	2254030	NF.	5099790
2	7247497	840316	NF.	3569576
3	358837	666270	34995	520066
4	434865	859013	517399	476390
5	326054	620702	181238	1112330
6	305022	208203	448131	290348
7	184399	310469	291231	115794
8	NF.	85819	44996	74431
9	NF.	50491	9140	27764
10	NF.	36560	11945	23424
11	237022	87876	29154	45188
12	164472	89408	8206	331969
13	NF.	207651	17000	29967
14	115054	188788	20242	57094
15	NF.	200448	28680	44176
16	197844	227656	10289	23420
17	NF.	79302	10965	17174
18	NF.	43784	2674	11303
19	111879	52870	52100	71638

* averaged from 3 runs.

Table 3.16 Concentration of analyte anions in geological water samples obtained with IonPac AS4A column.

Sample	Concentration (ng/µl)*			
	F^-	Cl^-	NO_3^-	SO_4^{2-}
1	22.22	9.39	NF.	31.60
2	19.12	3.67	NF.	22.21
3	1.01	2.96	0.30	3.49
4	1.02	3.74	5.28	3.22
5	0.92	2.78	1.81	7.13
6	0.87	1.11	4.57	2.08
7	0.55	1.47	2.61	0.78
8	NF.	0.45	0.43	0.50
9	NF.	0.29	0.11	0.18
10	NF.	0.22	0.14	0.15
11	0.69	0.46	0.28	0.30
12	0.50	0.46	0.10	0.21
13	NF.	1.00	0.16	0.23
14	0.38	0.91	0.19	0.40
15	NF.	0.96	0.27	0.32
16	0.67	1.09	0.10	0.19
17	NF.	0.38	0.10	0.15
18	NF.	0.21	0.03	0.11
19	0.36	0.11	0.43	0.44

* averaged from 3 runs.

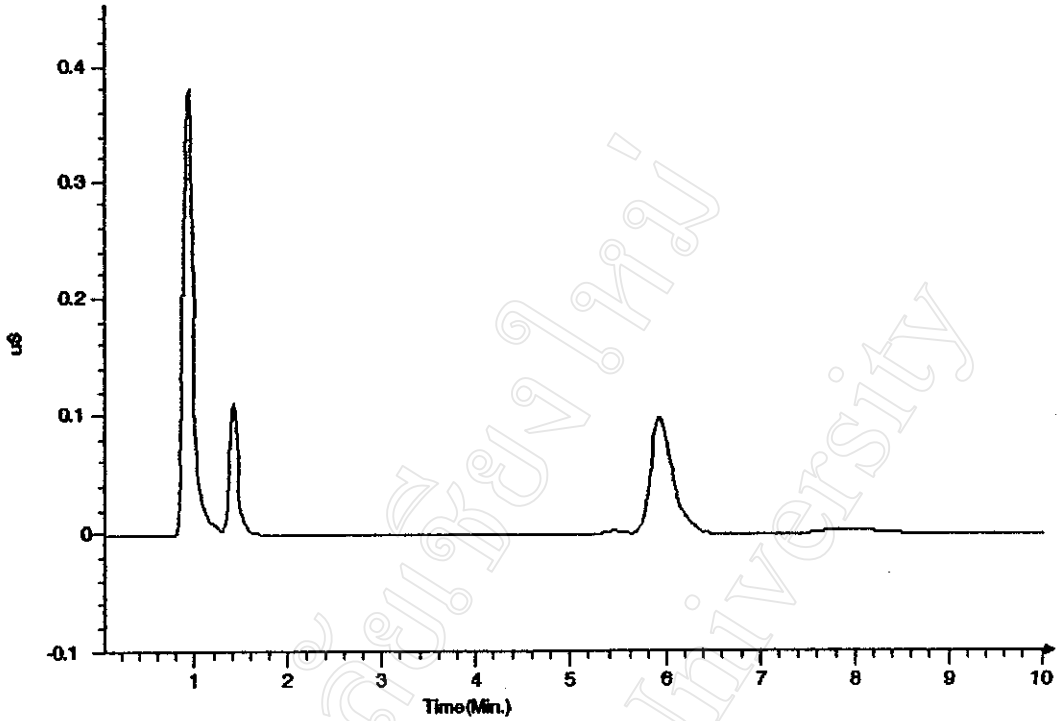


Figure 3.11 Typical chromatogram of sample #1 obtained with IonPac AS4A column

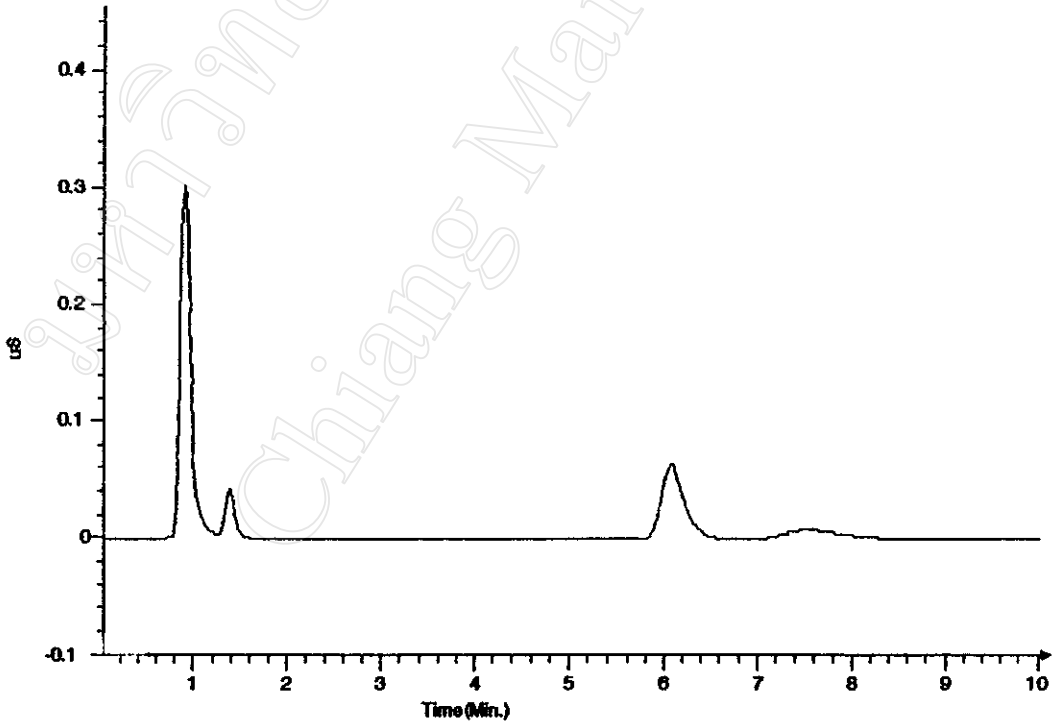


Figure 3.12 Typical chromatogram of sample #2 obtained with IonPac AS4A column

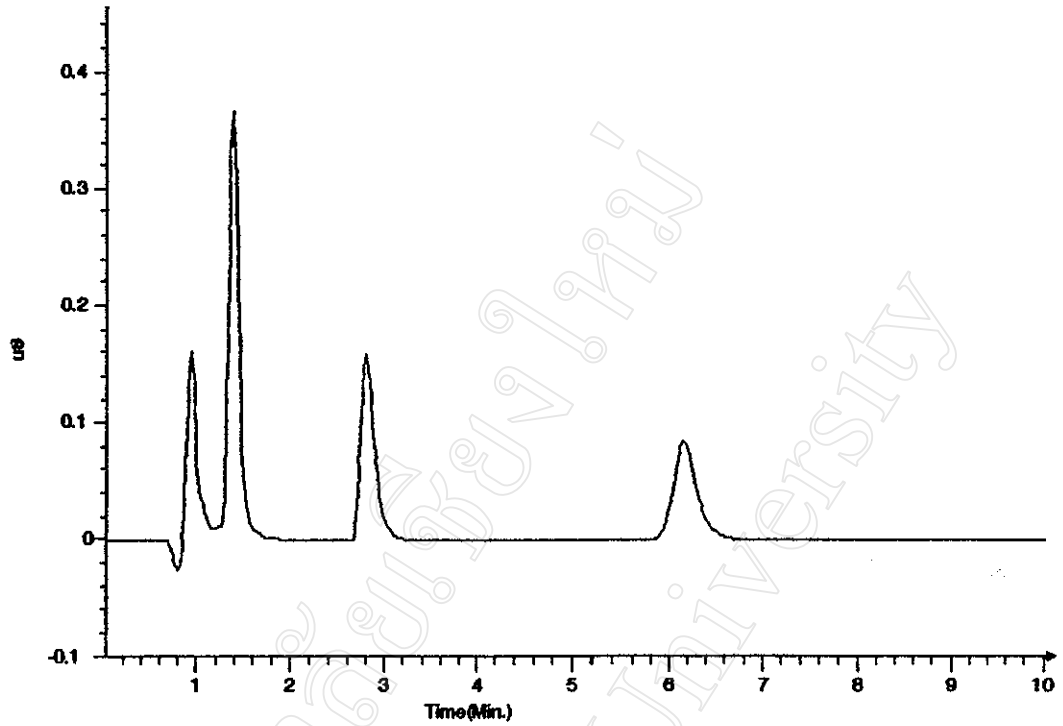


Figure 3.13 Typical chromatogram of sample #4 obtained with IonPac AS4A column

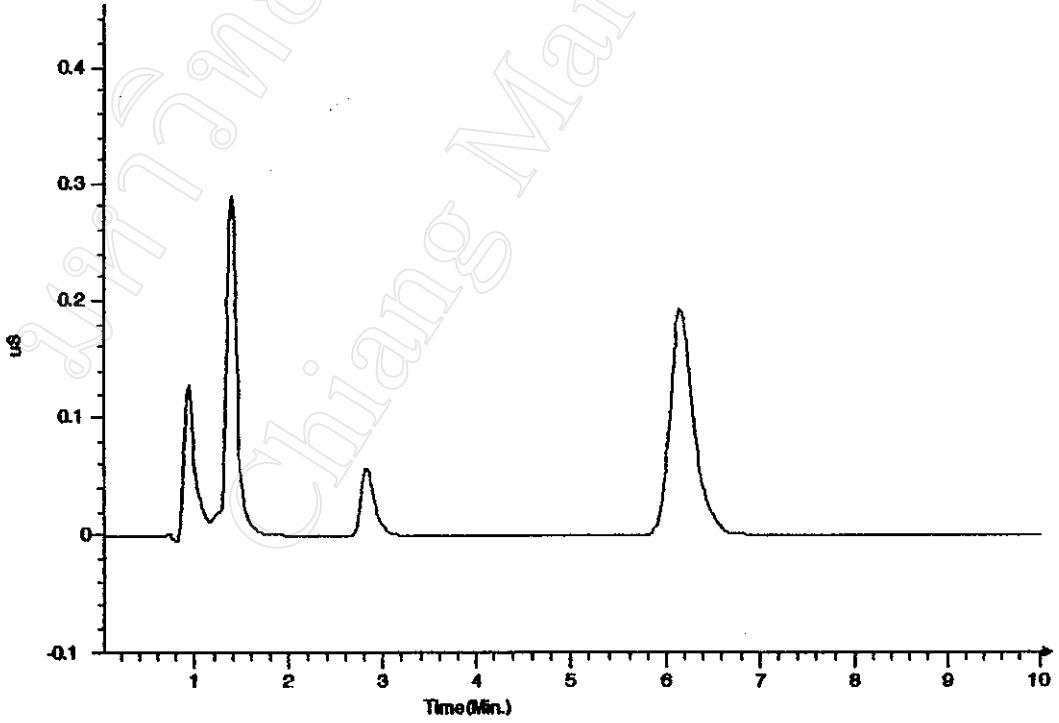


Figure 3.14 Typical chromatogram of sample #5 obtained with IonPac AS4A column

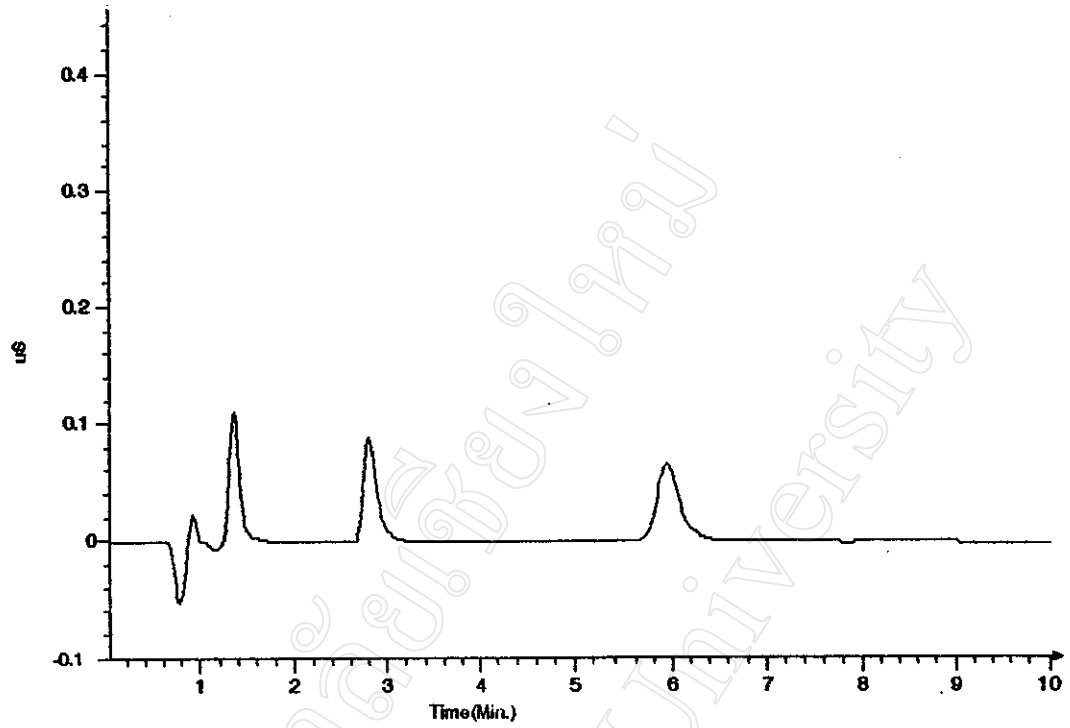


Figure 3.15 Typical chromatogram of sample #7 obtained with IonPac AS4A column

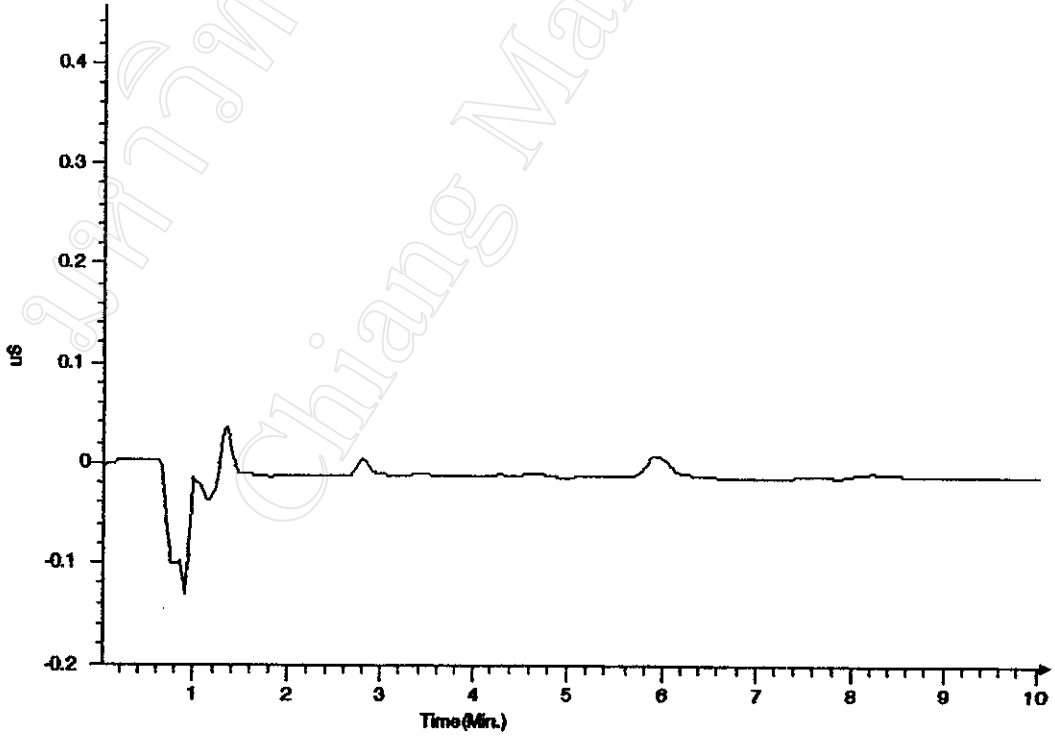


Figure 3.16 Typical chromatogram of sample #10 obtained with IonPac AS4A column

3.2.1.3 The amounts of anions in coal samples

The amounts of anions in samples #20 and 21 (coal samples) were obtained with IonPac AS4A column. The results of analysis are shown in **Tables 3.17-3.26, Figures 3.17-3.19.**

Extraction method with DMSO

(a) Temperature of extraction

Table 3.17 Concentration of anions in sample #20 obtained by the extraction method with DMSO at various temperature of extraction

Anion	Concentration (ng/µl) of anions at temperature extraction of *			
	Room temperature		70-90 °C	
	From calibration curve (ng/µl)	Actual amount in original sample (%w/w)	From calibration curve (ng/µl)	Actual amount in original sample (%w/w)
F^-	0.60	0.30	0.64	0.32
Cl^-	0.52	0.26	0.56	0.28
SO_4^{2-}	3.27	1.64	4.15	2.07

* averaged from 3 runs

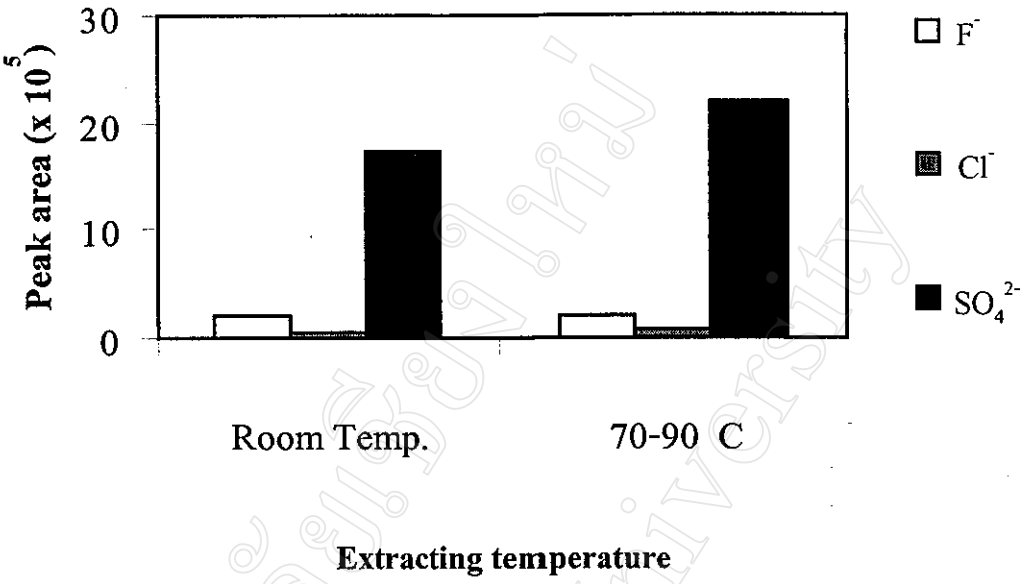


Figure 3.17 Results of the temperature of extraction in sample #20.

(b) Ratio of extracting solvent

Table 3.18 Concentration of anions in sample #20 obtained by the extraction method with DMSO at various DMSO/KNO_3 ratio.

Anion	Concentration (ng/µl) of anions at various DMSO/KNO_3 ratio *							
	1.0		1.5		3.0		9.0	
	A*	B**	A*	B**	A*	B**	A*	B**
F^-	0.52	0.26	0.36	0.18	0.47	0.24	0.52	0.26
Cl^-	0.46	0.23	0.41	0.20	0.44	0.22	0.49	0.24
SO_4^{2-}	3.76	1.88	3.90	1.95	3.72	1.86	4.07	2.04

* averaged from 3 runs

A* = from calibration curve (ng/µl)

B** = actual amount in original sample (%w/w)

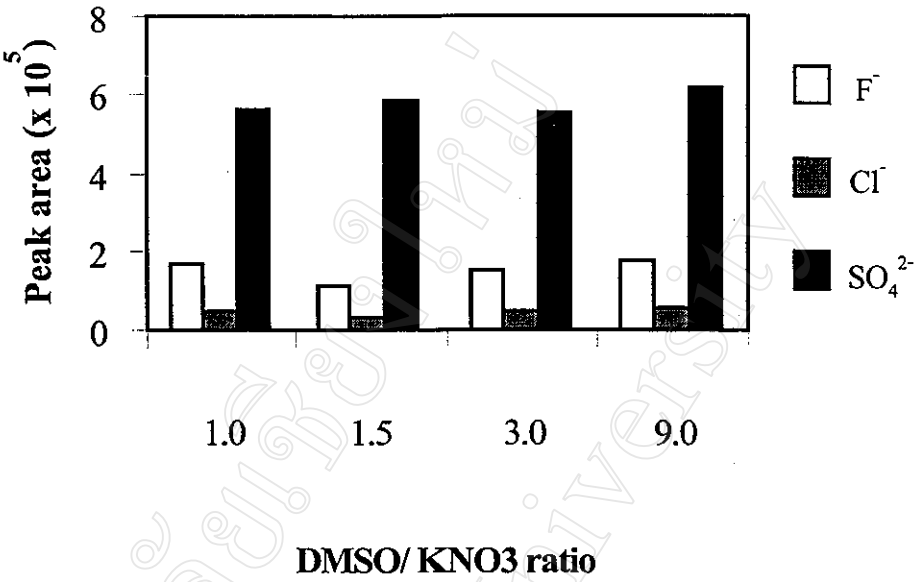


Figure 3.18 Results of the ratio of extracting solvent in sample #20.

Na_2O_2 fusion method and Na_2CO_3 fusion method

Table 3.19 Concentration of anions in sample #20 by Na_2O_2 fusion and Na_2CO_3 fusion method

Anion	Concentration (ng/μl) of anions in sample #20 by *					
	Na_2O_2 fusion		Na_2CO_3 fusion			
			Furnace at 860 °C		Bunsen burner	
	A*	B**	A*	B**	A*	B**
NO_3^-	8.55	0.29	-	-	-	-
SO_4^{2-}	3.16	7.04	65.65	6.60	58.84	5.94

* averaged from 3 runs

A* = from calibration curve (ng/μl)

B** = actual amount in original sample (%w/w)

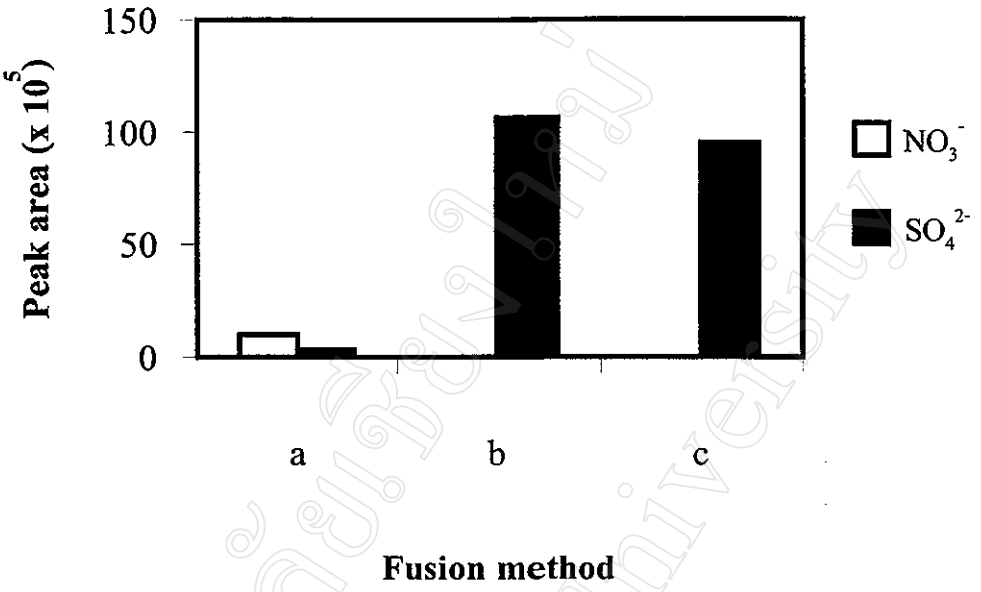


Figure 3.19 Results of the fusion methods of sample #20, (a) is Na_2O_2 fusion, (b) and (c) are Na_2CO_3 fusion by furnace at 860 °C and Bunsen burner, respectively.

Leaching with water

(a) Results of the leaching temperature

Table 3.20 Peak areas of each of anion in sample #20 obtained by leaching with water at various leaching temperature

Anions	Peak areas (1x 10^5) of each of anion in sample #20 obtained by water leaching at *								
	Room temp.			50.0 ± 0.2 °C			100.0 ± 0.2 °C		
	Step 1	Step 2	Step 3	Step 1	Step 2	Step 3	Step 1	Step 2	Step 3
F^-	6.38	4.14	-	6.48	8.07	-	7.51	10.16	-
Cl^-	1.86	3.65	1.70	1.69	5.46	1.86	2.25	6.25	1.83
SO_4^{2-}	349.01	31.28	3.21	367.91	21.99	4.75	381.27	18.06	2.28

* averaged from 3 runs

Table 3.21 Concentration of anions in sample #20 obtained by leaching with water at various leaching temperature

Anions	Concentrations (ng/µl) of each of anion in sample #20 obtained by water leaching at *								
	Room temp.			50.0 ± 0.2 °C			100.0 ± 0.2 °C		
	Step 1	Step 2	Step 3	Step 1	Step 2	Step 3	Step 1	Step 2	Step 3
F^-	1.84	1.16	-	1.71	2.19	-	2.04	2.74	-
Cl^-	1.02	1.74	0.98	0.92	2.50	1.04	1.15	2.80	1.06
SO_4^{2-}	214.50	19.50	2.27	226.18	13.82	3.23	234.12	11.63	1.69

* From calibration curve and averaged from 3 runs

Table 3.22 Total concentration of anions in sample #20 obtained by leaching with water at various leaching temperature

Anions	Total concentrations (ng/μl) of each of anion in sample #20 obtained by water leaching at *					
	Room temp.		50.0 ± 0.2 °C		100.0 ± 0.2 °C	
	A*	B**	A*	B**	A*	B**
F^-	3.00	0.047	3.90	0.055	4.78	0.067
Cl^-	3.74	0.056	4.45	0.063	5.02	0.072
SO_4^{2-}	236.27	4.42	243.23	4.65	247.44	4.79

* averaged from 3 runs

A* = from calibration curve (ng/μl)

B** = actual amount in original sample (%w/w)

(b) Results of the time of leaching

Table 3.23 Peak areas of each of anion in the sample #20 obtained by water leaching at various the time of leaching.

Anions	Peak areas ($1x10^5$) of each of anion in the sample #21 Obtained by water leaching at *					
	1 hour	2 hours	4 hours	8 hours	16 hours	24 hours
F^-	4.48	4.68	5.26	4.56	4.71	6.69
Cl^-	3.10	3.32	4.54	2.41	2.15	5.89
SO_4^{2-}	137.20	137.83	138.28	134.83	104.93	127.85

* averaged from 3 runs

Table 3.24 Actual amount of anions in sample #20 obtained by water leaching at various the time of leaching.

Anions	Actual amount in the original sample #20 (%w/w) Obtained by water leaching at *					
	1 hour	2 hours	4 hours	8 hours	16 hours	24 hours
F^-	0.06	0.06	0.07	0.06	0.06	0.09
Cl^-	0.07	0.08	0.10	0.06	0.05	0.13
SO_4^{2-}	4.20	4.12	4.31	4.14	2.89	3.86

* averaged from 3 runs

Table 3.25 Peak areas of each of anion in the sample #21 obtained by water leaching at various the time of leaching.

Anions	Peak areas ($1x\ 10^5$) of each of anion in the sample #21 obtained by water leaching at *						
	1 hour	2 hours	4 hours	6 hours	8 hours	10 hours	24 hours
F^-	2.96	1.97	3.16	2.12	1.69	1.64	2.97
Cl^-	2.98	2.63	2.92	2.99	0.46	0.63	2.84
SO_4^{2-}	1.49	1.91	2.87	2.79	2.67	2.85	2.41

* averaged from 3 runs

Table 3.26 Actual amount of anions in sample #21 obtained by water leaching at various the time of leaching.

Anions	Actual amount in original sample #21 (%w/w) obtained by water leaching at *						
	1 hour	2 hours	4 hours	6 hours	8 hours	10 hours	24 hours
F^-	0.05	0.02	0.05	0.03	0.02	0.03	0.04
Cl^-	0.08	0.06	0.09	0.08	0.02	0.03	0.07
SO_4^{2-}	0.06	0.06	0.12	0.11	0.09	0.10	0.09

* averaged from 3 runs

3.2.2 %Recovery of each anion in geological water samples

Reliability of the % recovery obtained from geological water samples were confirmed using the "spike" method. The results are shown in **Table 3.27-3.30** and confirmation of analyte anion peaks in geological water samples is illustrated in **Figures 3.20-3.22.**

Table 3.27 %Recovery of F^- in sample#1 when spiked with standard F^- at various concentrations (ng/µl).

Spiked standard F^- (ng/µl)	Peak area (arbitrary unit)	Concentration (ng/µl)	%Recovery
Sample#1	8681600	22.88	-
Sample#1 + 10 ng/µl	12487000	32.89	100.10
Sample#1 + 20 ng/µl	16246700	42.78	99.50
Sample#1 + 30 ng/µl	19587000	51.56	95.60
Sample#1 + 40 ng/µl	23243700	61.17	95.57
		Mean	97.69

Table 3.28 %Recovery of Cl^- in sample#2 when spiked with standard Cl^- at various concentrations (ng/µl).

Spiked standard Cl^- (ng/µl)	Peak area (arbitrary unit)	Concentration (ng/µl)	%Recovery
Sample#2	862181	3.72	-
Sample#2 + 2 ng/µl	1324334	5.63	95.50
Sample#2 + 4 ng/µl	1839449	7.71	99.75
Sample#2 + 6 ng/µl	2345232	9.76	100.67
Sample#2 + 8 ng/µl	2885978	11.95	102.87
		Mean	99.70

Table 3.29 %Recovery of NO_3^- in sample#5 when spiked with standard NO_3^- at various concentrations (ng/µl).

spiked standard NO_3^- (ng/µl)	Peak area (arbitrary unit)	Concentration (ng/µl)	%Recovery
Sample#5	180739	1.81	-
Sample#5 + 1 ng/µl	278152	2.81	100.00
Sample#5 + 2 ng/µl	367502	3.74	96.50
Sample#5 + 3 ng/µl	466696	4.76	98.33
Sample#5 + 4 ng/µl	562297	5.74	98.25
		Mean	98.27

Table 3.30 %Recovery of SO_4^{2-} in sample#1 when spiked with standard SO_4^{2-} at various concentrations (ng/µl).

Spiked standard SO_4^{2-} (ng/µl)	Peak area (arbitrary unit)	Concentration (ng/µl)	%Recovery
Sample#2	3749763	23.32	-
Sample#2 + 10 ng/µl	5382162	33.33	100.10
Sample#2 + 20 ng/µl	7023870	43.40	100.40
Sample#2 + 30 ng/µl	8456354	52.20	96.27
Sample#2 + 40 ng/µl	10092791	62.48	97.90
		Mean	98.67

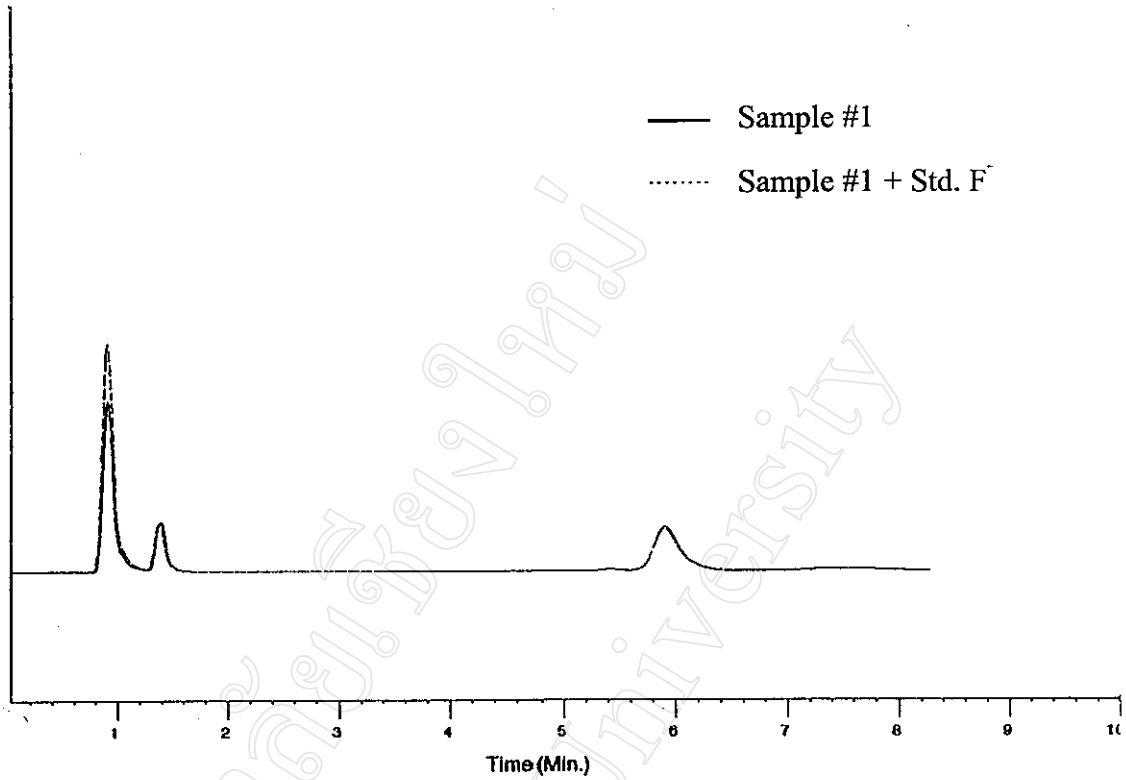


Figure 3.20 Chromatogram of sample #1 (——) and chromatogram of sample #1 spiked with standard of F^- (·····)

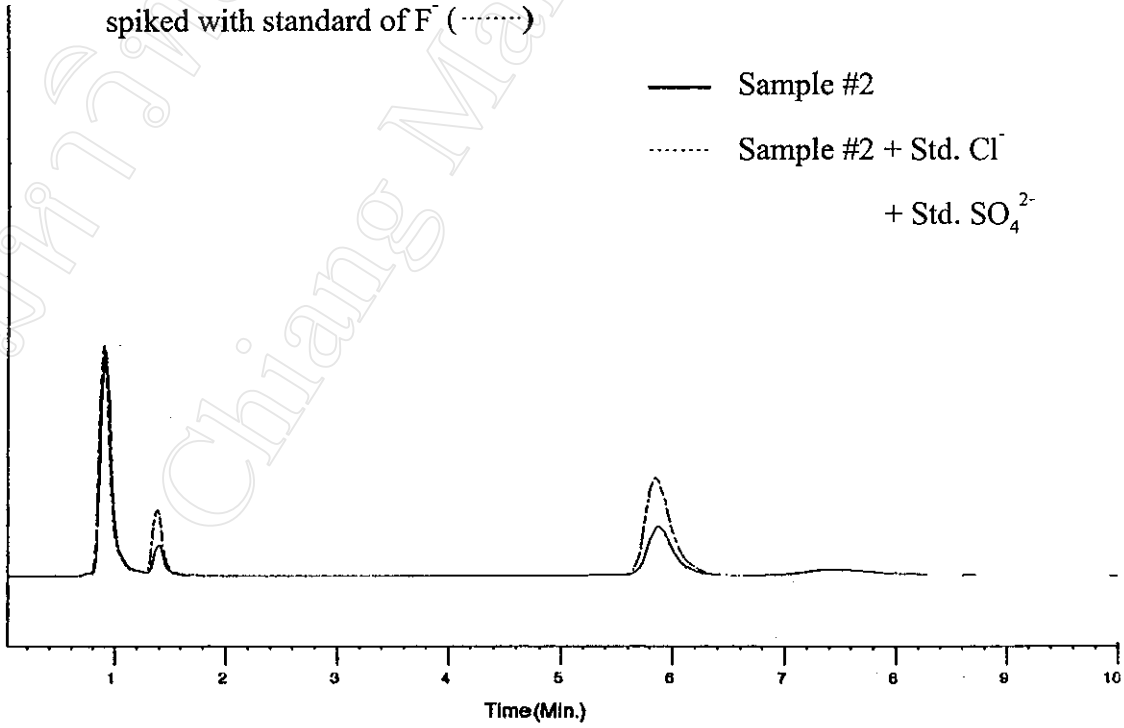


Figure 3.21 Chromatogram of sample #2 (——) and chromatogram of sample #2 spiked with standard of Cl^- and SO_4^{2-} (·····)

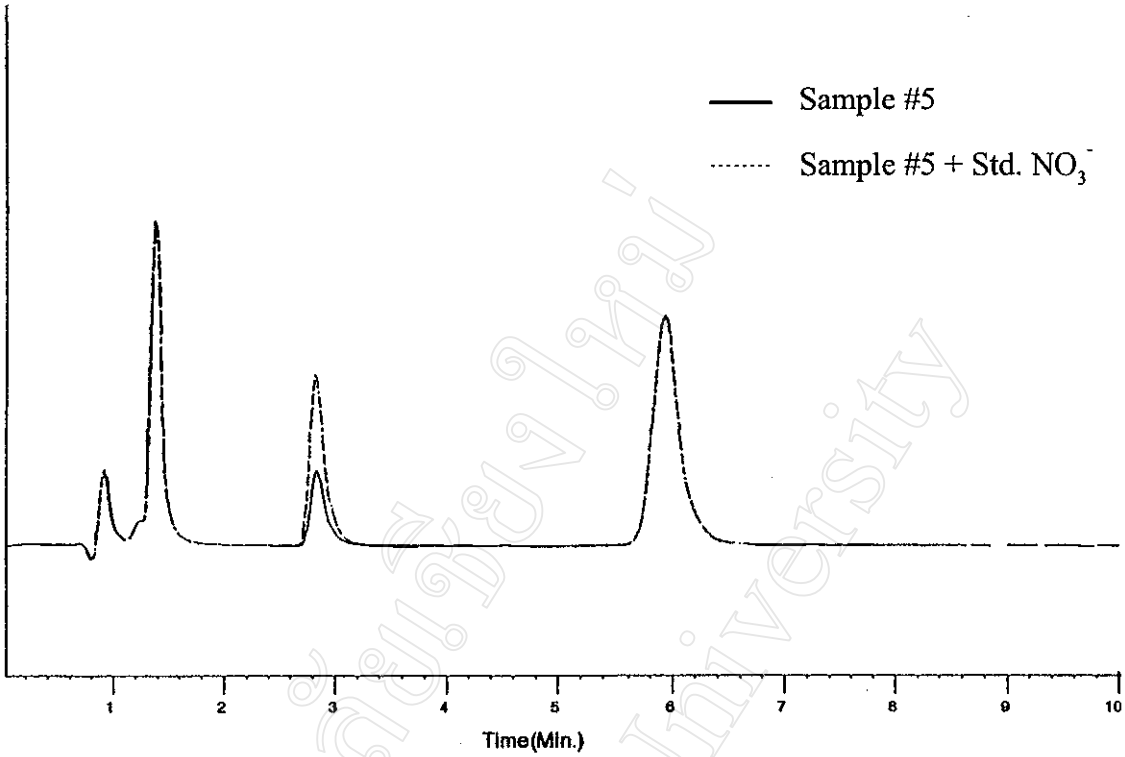


Figure 3.22 Chromatogram of sample #5 (——) and chromatogram of sample #5 spiked with standard of NO_3^- (·····)

3.2.3 Analysis for F^-,Cl^-,NO_3^- and SO_4^{2-} by spectrophotometric technique.

The amounts of F^-,Cl^-,NO_3^- and SO_4^{2-} in geological water samples were determined by spectrophotometric technique[28]. The results of analysis were compared with the results of IC technique in **Table 3.31-3.34**.

Table 3.31 Comparison of the results of F^- analysis in geological water samples by IC and by spectrophotometric techniques (SPADNS method).

Sample	IC technique (ng/μl)	Spectrophotometric technique (ng/μl)	Di	$(Di-\bar{D})$	$(Di-\bar{D})^2$
1	22.22	21.61	0.61	0.34	0.1156
2	19.12	19.02	0.10	0.17	0.0289
3	1.01	1.27	0.26	0.01	0.0001
5	0.92	1.03	0.11	0.16	0.0256
			$\sum$ 1.08		$\sum$ 0.17
$\bar{D}$					0.27
SD					0.24
t_{calc}					2.27

Table 3.32 Comparison of the results of Cl^- analysis in geological water samples by IC and spectrophotometric techniques (Mercury (II) thiocyanate method).

Sample	IC technique (ng/μl)	Spectrophotometric technique (ng/μl)	Di	$(Di-\bar{D})$	$(Di-\bar{D})^2$
1	9.39	9.56	0.17	0.07	0.0049
2	3.67	3.67	0.00	0.10	0.0100
3	2.96	2.88	0.08	0.02	0.0004
5	2.78	2.91	0.13	0.03	0.0009
			$\sum$ 0.38		$\sum$ 0.02
$\bar{D}$					0.10
SD					0.07
t_{calc}					2.59

Table 3.33 Comparison of the results of NO_3^- analysis in geological water samples by IC and spectrophotometric techniques (Ultraviolet spectrophotometric screening method).

Sample	IC technique (ng/µl)	Spectrophotometric technique (ng/µl)	Di	(Di -$\bar{D}$)	(Di - $\bar{D}$)^2
3	0.30	0.31	0.01	0.02	4×10^{-4}
5	1.81	1.74	0.07	0.04	1.6×10^{-3}
7	2.61	2.60	0.01	0.02	4×10^{-4}
8	0.43	0.45	0.02	0.01	1×10^{-4}
			$\sum$ 0.11		$\sum$0.0025
$\bar{D}$					0.03
SD					0.03
t_{calc}					1.91

Table 3.34 Comparison of the results of SO_4^{2-} analysis in geological water samples by IC and spectrophotometric techniques (Turbidimetric method).

Sample	IC technique (ng/µl)	Spectrophotometric technique (ng/µl)	Di	(Di-$\bar{D}$)	(Di - $\bar{D}$)^2
1	31.60	32.61	1.01	0.47	0.22
2	22.21	21.78	0.43	0.11	0.01
3	3.49	3.24	0.25	0.29	0.08
5	7.13	7.58	0.45	0.09	0.0081
			$\sum$ 2.14		$\sum$ 0.32
$\bar{D}$					0.54
SD					0.32
t_{calc}					3.25

3.2.4 Analysis for F^- and Cl^- by ion selective electrode method

The amount of F^- and Cl^- in geological water sample were determined by ion selective electrode method (ISE method). The results of analysis were compared with the results of IC technique in **Tables 3.35 and 3.36.**

Table 3.35 Comparison of the results of F^- analysis in geological water samples by IC and ISE techniques

Sample	IC technique (ng/µl)	ISE technique (ng/µl)	Di	$(Di-\bar{D})$	$(Di - \bar{D})^2$
1	22.22	20.60	1.62	0.80	0.640
2	19.12	19.60	-0.48	0.34	0.116
3	1.01	0.34	0.67	0.15	0.022
4	1.21	0.26	0.95	0.13	0.017
5	0.92	0.36	0.56	0.26	0.068
6	0.87	0.20	0.67	0.15	0.022
			$\sum$ 4.95		$\sum$ 0.885
$\bar{D}$					0.83
SD					0.42
t_{calc}					4.80

Table 3.36 Comparison of the results of Cl^- analysis in geological water samples by IC and ISE techniques

Sample	IC technique (ng/μl)	ISE technique (ng/μl)	Di	(Di-$\bar{D}$)	(Di - $\bar{D}$)^2
1	9.39	8.40	0.99	0.49	0.240
2	3.67	3.20	0.47	0.03	0.001
3	2.96	2.80	0.16	0.34	0.116
5	2.78	2.40	0.38	0.12	0.014
			$\sum$ 2.00		$\sum$ 0.371
$\bar{D}$					0.50
SD					0.35
t_{calc}					2.84

3.3 Determination of metal ions with IonPac CS5 column

3.3.1 Results of investigation of retention times of ions of interest

The ions of interest in this work were Fe^{3+}, Cu^{2+}, Zn^{2+}, Co^{2+} and Mn^{2+} in geological water samples. The retention time of the mixture of standard cation solutions from section 2.4.2 are given in **Table 3.37**.

Table 3.37 Retention times of the mixture of standard cation solution obtained with IonPac CS5 column using 7.5 mM PDCA/ 66.0 mM KOH/ 5.6 mM K_2SO_4/ 74.0 mM HCOOH pH 4.1 at flow rate 1.0 ml/min as eluent, 0.36 mM PAR in 3.52 M NH_4OH/ 1.0 M CH_3COOH at flow rate as the post-column reagent and wavelength 530 nm.

Cation	t_r (min)
Fe^{3+}	3.47
Cu^{2+}	4.53
Zn^{2+}	5.60
Co^{2+}	6.32
Mn^{2+}	7.38

Table 3.38 Retention times of the mixture of standard cation solution obtained with IonPac CS5 column using; (a) oxalic acid and (b) PDCA as eluent, respectively and 0.36 mM PAR in 3.52 M NH_4OH/ 1.0 M CH_3COOH at flow rate as the post-column reagent and wavelength 530 nm.

Anions	t_r of each anion (min) at eluent	
	Oxalic acid	PDCA
Pb^{2+}	3.17	-
Fe^{3+}	-	3.47
Cu^{2+}	4.58	4.53
Ni^{2+}	13.28	4.77
Zn^{2+}	11.29	5.60
Co^{2+}	-	6.32
Mn^{2+}	5.80	7.38

Table 3.39 Retention times of the mixture of standard cation solution obtained with IonPac CS5 column using PDCA eluents prepared from methods I and II at flow rate 1.0 ml/ min and 0.36 mM PAR in 3.52 M NH_4OH/ 1.0 M CH_3COOH at flow rate as the post-column reagent and wavelength 530 nm.

Anions	t_r (min) at PDCA from mtehod	
	Method I	Method II
Fe^{3+}	3.47	5.23
Cu^{2+}	4.53	6.80
Zn^{2+}	5.60	8.10
Co^{2+}	6.32	9.12
Mn^{2+}	7.38	10.15

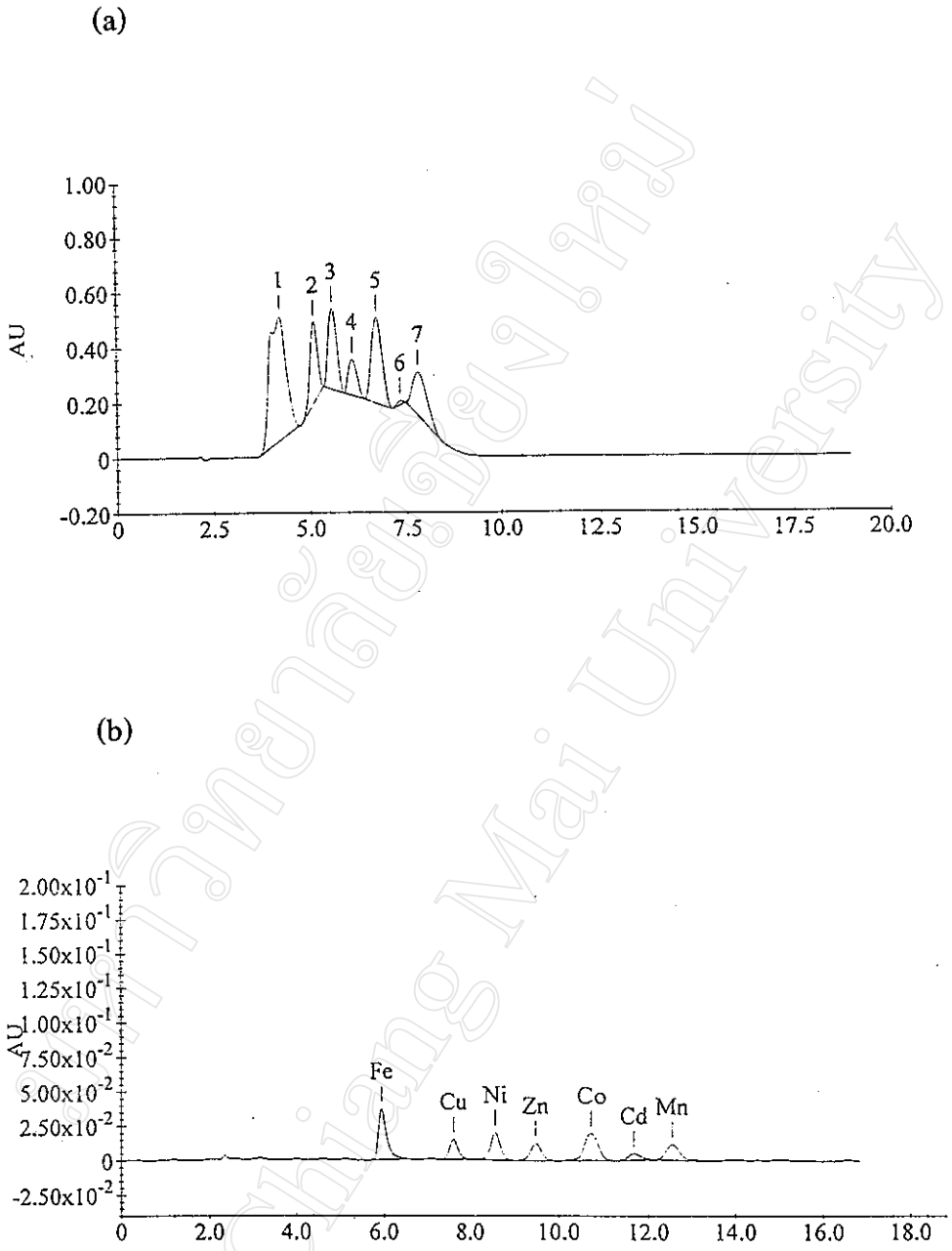


Figure 3.23 Chromatograms of Fe^{3+}, Cu^{2+}, Zn^{2+}, Co^{2+} and Mn^{2+} obtained with IonPac CS5; (a) aged column and (b) new column, 7.5 mM PDCA pH 4.1 as eluent, 0.36 mM PAR in 3.52 M NH_4OH/ 1.0 M CH_3COOH as post-column reagent, at 530 nm.

3.3.2 Optimization of IC conditions

3.3.2.1 Results of effect of eluent concentration.

Table 3.40 Resolution of each metal ion pair at various eluent concentration

Metal ion pair	Resolution at various eluent concentration (mM)				
	6.0	6.5	7.0	7.5	8.0
Fe^{3+} & Cu^{2+}	5.15	4.49	4.04	3.42	3.18
Cu^{2+} & Zn^{2+}	3.90	4.41	4.32	4.13	4.05
Zn^{2+} & Co^{2+}	2.59	2.51	2.54	2.43	2.41
Co^{2+} & Mn^{2+}	3.38	3.35	3.42	3.48	3.57

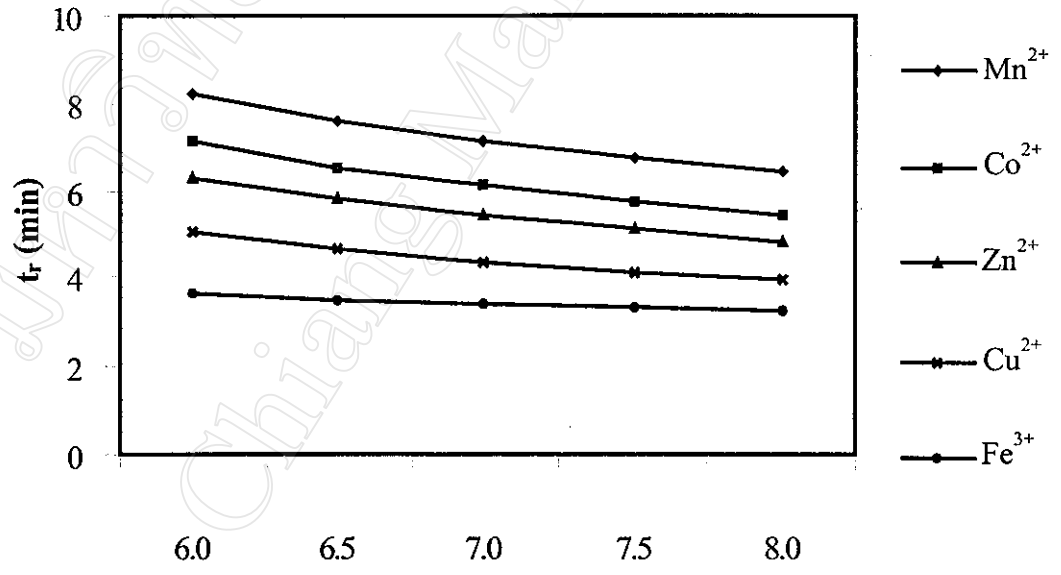


Figure 3.24 Plot of each metal ion retention time against the eluent concentration.

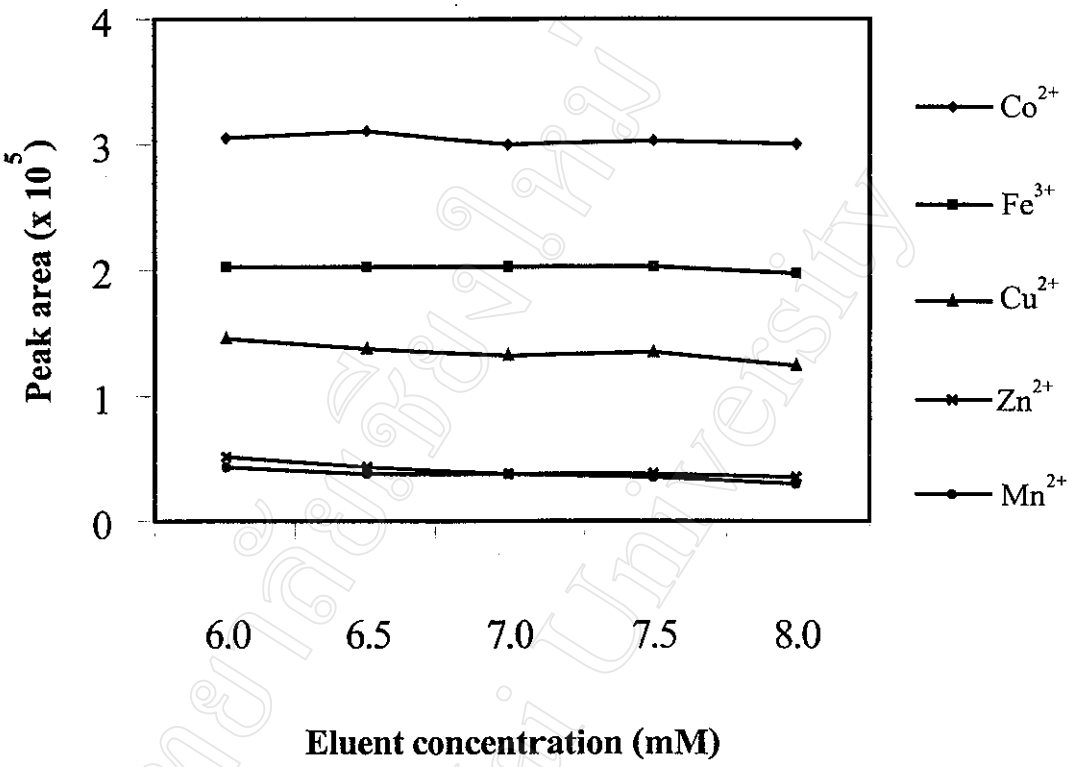


Figure 3.25 Plot of each metal ion peak area against the eluent concentration.

3.3.2.2 Results of effect of eluent pH

Table 3.41 Resolution of each metal ion pair at various eluent pH

Metal ion pair	Resolution at various eluent pH				
	3.7	4.0	4.1	4.3	4.6
Fe^{3+} & Cu^{2+}	3.62	3.85	3.75	2.85	1.99
Cu^{2+} & Zn^{2+}	4.32	4.28	4.18	3.94	3.60
Zn^{2+} & Co^{2+}	2.27	2.40	2.44	2.29	2.27
Co^{2+} & Mn^{2+}	-	3.10	3.26	3.90	4.13

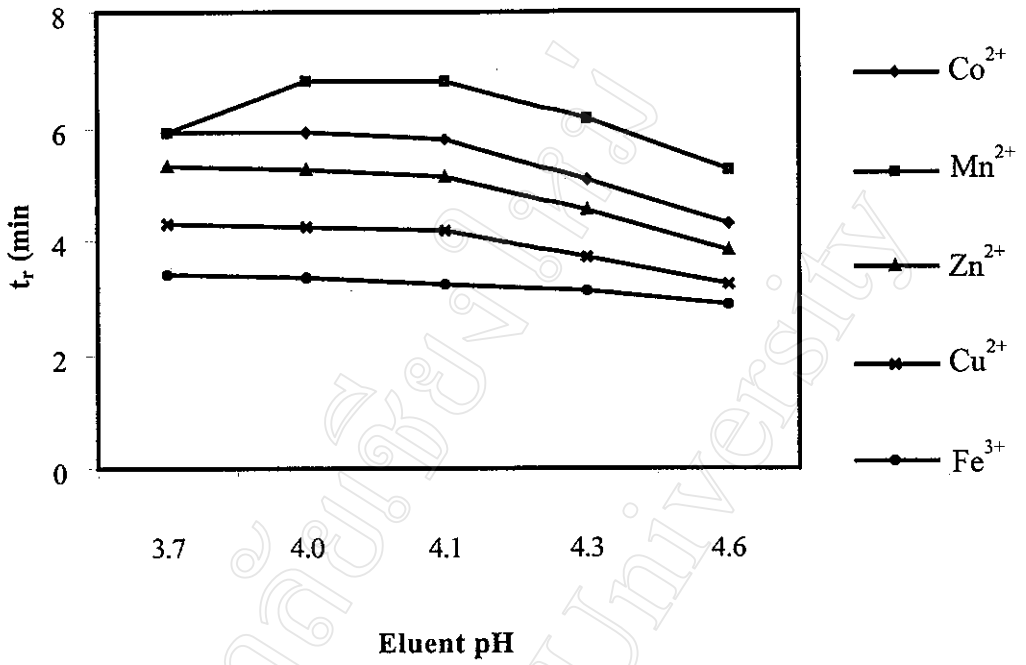


Figure 3.26 Plot of each metal ion retention time against the eluent pH.

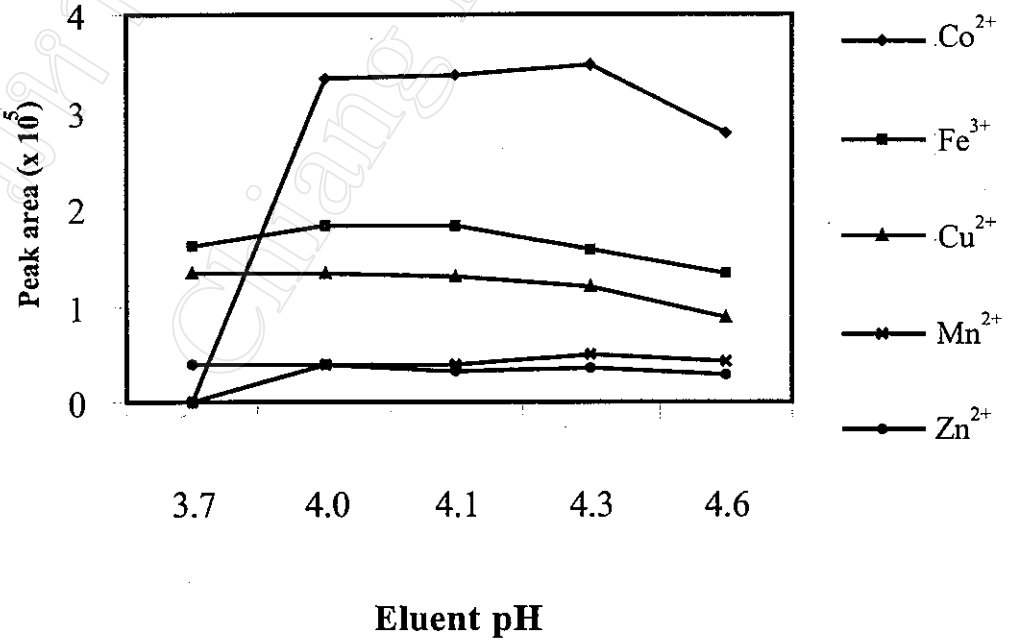


Figure 3.27 Plot of each metal ion peak area against the eluent pH.

3.3.2.3 Results of effect of eluent flow rate

Table 3.42 Resolution of each metal ion pair at various eluent flow rate

Metal ion pair	Resolution at various eluent flow rate (ml/min)				
	0.8	0.9	1.0	1.1	1.2
Fe^{3+} & Cu^{2+}	3.87	4.24	4.26	3.95	3.91
Cu^{2+} & Zn^{2+}	4.27	4.36	4.23	3.96	3.92
Zn^{2+} & Co^{2+}	2.48	2.46	2.50	2.33	2.26
Co^{2+} & Mn^{2+}	3.19	3.24	3.27	3.16	3.14

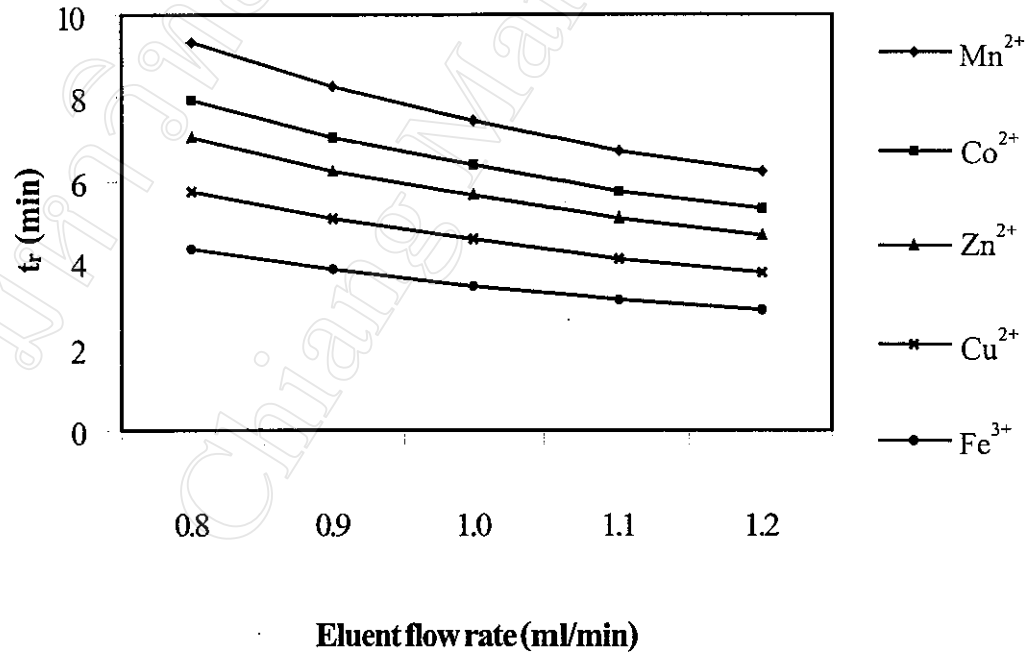


Figure 3.28 Plot of each metal ion retention time against the eluent flow rate (ml/min).

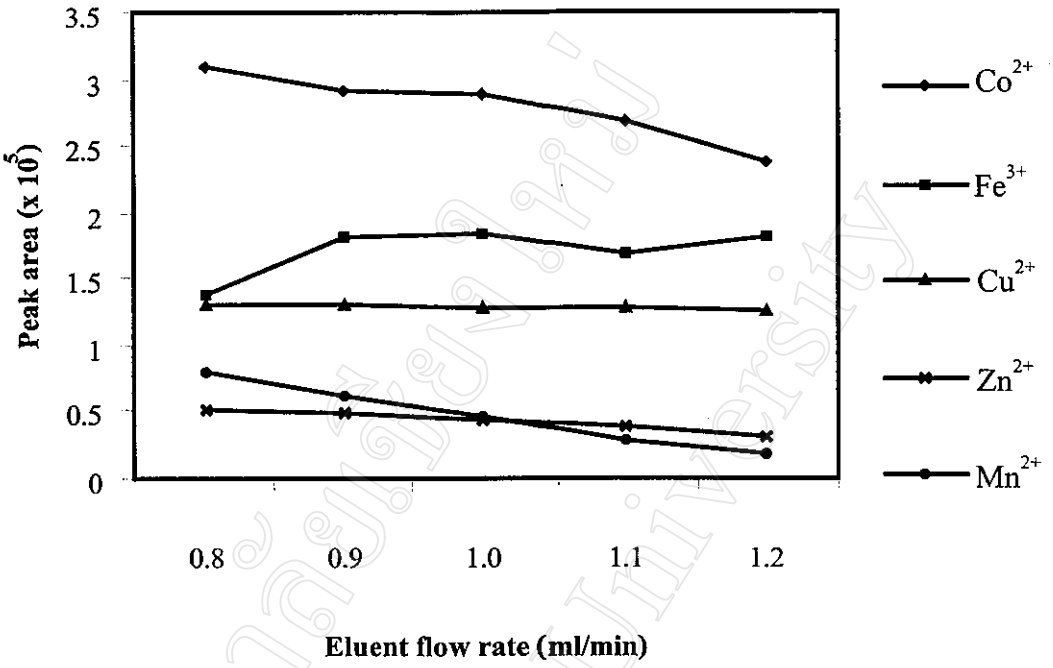
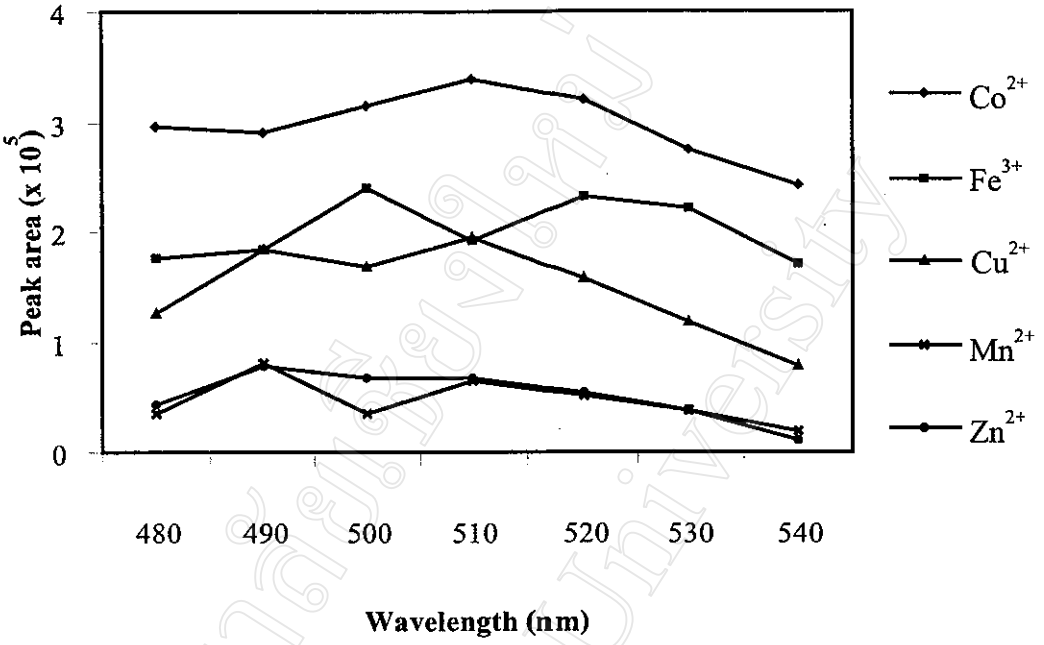


Figure 3.29 Plot of each metal ion peak area against the eluent flow rate (ml/min).

Table 3.43 The number of theoretical plate (N) of each metal ion at various eluent flow rate.

Metal ion	N at eluent flow rate (ml/min)				
	0.8	0.9	1.0	1.1	1.2
Fe^{3+}	2001	2590	2671	2235	2247
Cu^{2+}	5480	5435	5300	4637	4484
Zn^{2+}	7575	7690	7445	6502	6567
Co^{2+}	5845	6003	5926	5170	4994
Mn^{2+}	7552	7782	8204	8798	8252



3.3.2.4 Optimum detection wavelength

Figure 3.30 Relationship between each metal peak area and the wavelength employed.

Table 3.44 Signal to noise ratio at various wavelength

Metal ion	Signal to noise ratio at various wavelength (nm)						
	480	490	500	510	520	530	540
Fe^{3+}	19.9	52.7	70.6	65.2	74.0	125.2	154.58
Cu^{2+}	14.1	52.3	49.4	67.0	54.3	66.9	69.6
Zn^{2+}	4.9	21.9	19.7	22.4	18.6	21.4	10.65
Co^{2+}	33.5	83.1	92.1	116.3	111.3	155.8	218.17
Mn^{2+}	3.8	22.8	10.2	21.9	18.1	21.7	18.2
Noise level	8813	3511	3416	2926	2884	1763	1111

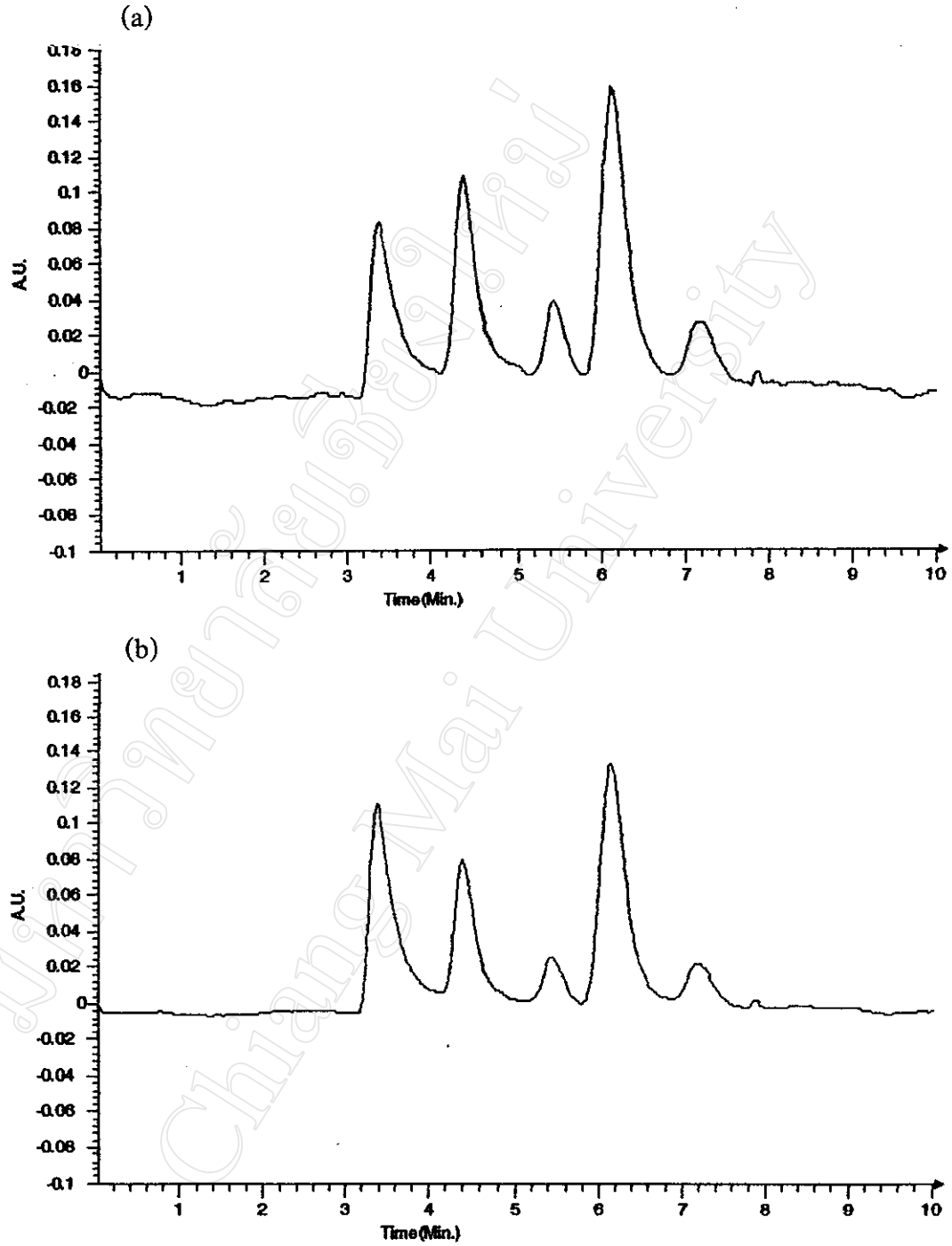


Figure 3.31 Chromatograms of Fe^{3+}, Cu^{2+}, Zn^{2+}, Co^{2+} and Mn^{2+} obtained with IonPac CS5 using 7.5 mM PDCA pH 4.1 as eluent, 0.36 mM PAR in 3.52 M NH_4OH/ 1.0 M CH_3COOH as post-column reagent, at wavelength; (a) 510 nm and (b) 530 nm.

3.3.2.5 Results of effect of PAR concentration

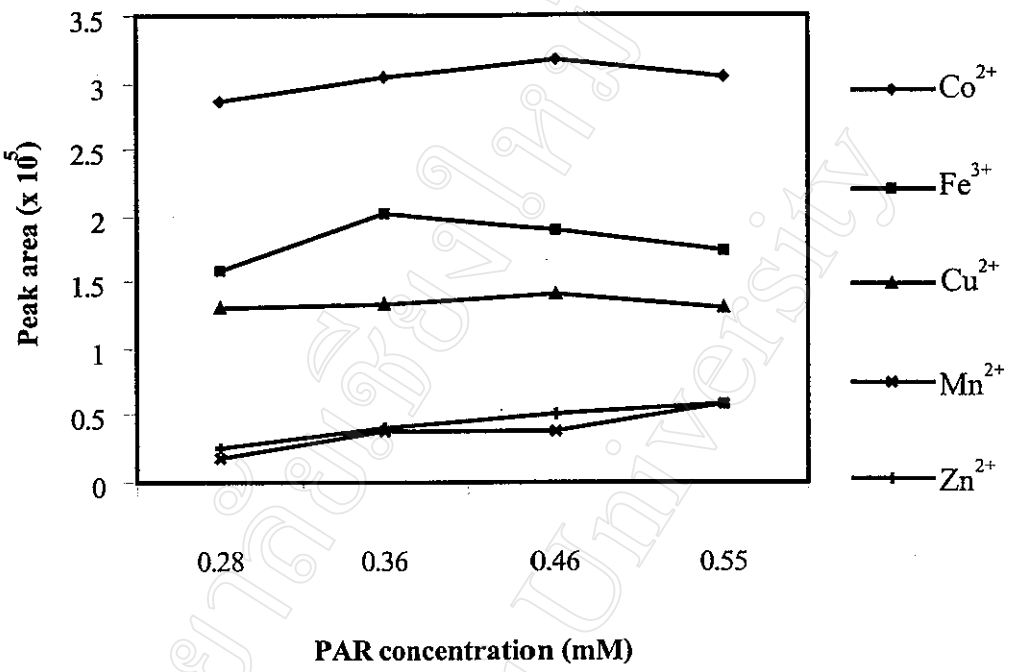


Figure 3.32 Plot of each metal ion peak area against PAR concentration (mM).

3.3.2.6 Results of effect of PAR pH

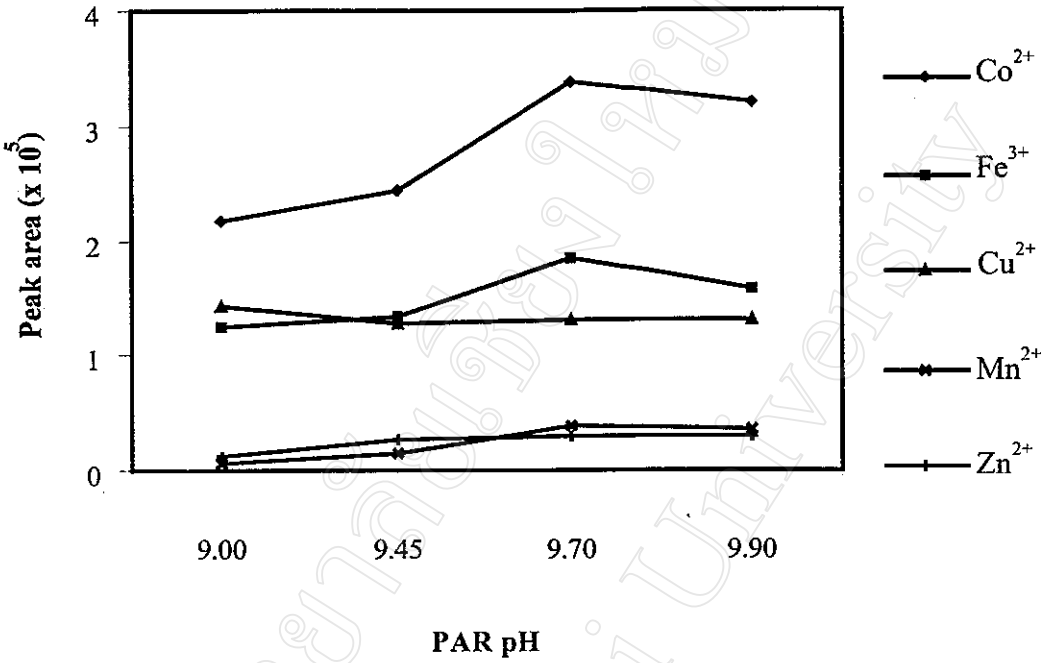


Figure 3.33 Plot of each metal ion peak area against PAR pH.

3.3.2.7 Results of effect of PAR flow rate

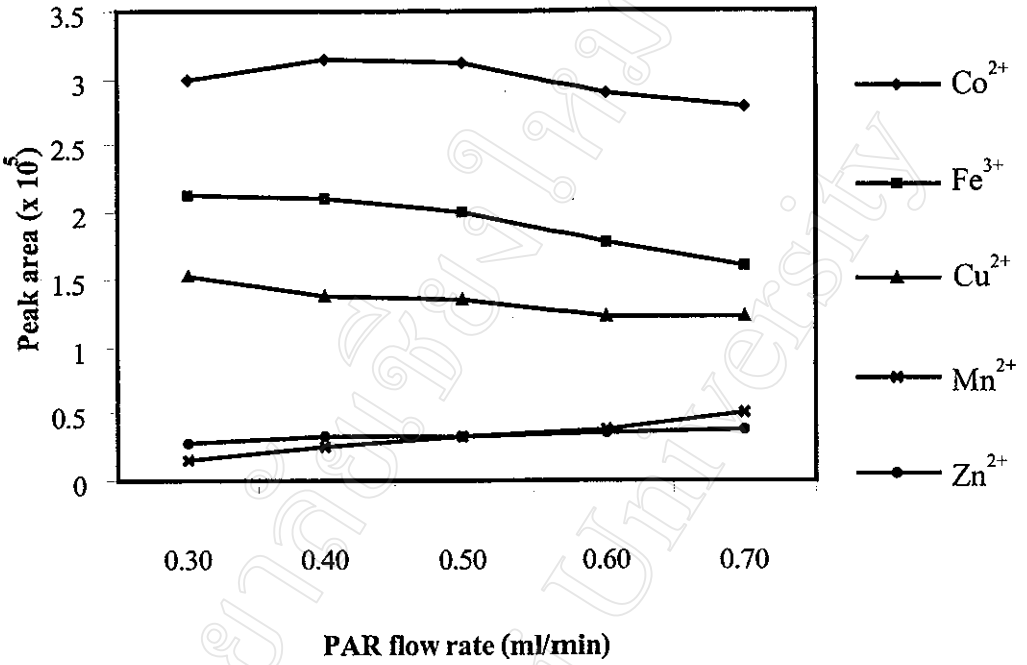


Figure 3.34 Plot of each metal ion peak area against PAR flow rate (ml/min).

3.3.2.8 Summary of optimized ion chromatographic conditions

The optimized ion chromatographic conditions obtained with IonPac CS5 column in this work are listed in **Table 3.45.**

Table 3.45 Optimized ion chromatographic conditions obtains with IonPac CS5 column and the post-column derivatization detection system for analysis metal ions in this work.

Operation	Optimal conditions
Eluent	7.5 mM PDCA pH 4.1
The post column reagent	0.36 mM PAR in 3.52 M NH_4OH/ 1.0 M CH_3COOH
Flow rate	1.0 ml/min (of eluent) 0.5 ml/min (of the post column reagent)
Detector	UV/vis spectrophotometric
Wavelength	530 nm
Absorbance unit (AU.) range	0.2 unit
Sample loop volume	25 µl

3.3.3 Repeatability and reproducibility of results

The precision of results was reported in term of standard deviation and the data are shown in **Tables 3.46 and 3.47.**

3.3.3.1 Repeatability

Table 3.46 The repeatability of results obtained with IonPac CS5 column, 7.5 mM PDCA pH 4.1 at flow rate 1.0 ml/min as eluent and 0.36 mM PAR in 3.52 M NH_4OH/ 1.0 M CH_3COOH at flow rate 0.5 ml/min as the post-column reagent at wavelength 530 nm.

(a) Retention times of various metal ions investigated.

Run	t_r (min)				
	Fe^{3+} 1.0 ng/µl	Cu^{2+} 1.0 ng/µl	Zn^{2+} 1.0 ng/µl	Co^{2+} 1.0 ng/µl	Mn^{2+} 1.0 ng/µl
1	3.30	4.18	5.17	5.80	6.80
2	3.30	4.20	5.17	5.82	6.82
3	3.28	4.18	5.17	5.80	6.80
4	3.28	4.18	5.17	5.80	6.82
5	3.28	4.18	5.17	5.80	6.80
mean	3.29	4.18	5.17	5.80	6.81
SD	0.01	0.00	0.00	0.00	0.01
%RSD	0.30	0.00	0.00	0.00	0.15

Table 3.46 (continued)

(b) Peak area of various metal ions investigated.

Run	Peak area ($1x10^5$) (arbitrary unit)				
	Fe^{3+} 1.0 ng/µl	Cu^{2+} 1.0 ng/µl	Zn^{2+} 1.0 ng/µl	Co^{2+} 1.0 ng/µl	Mn^{2+} 1.0 ng/µl
1	1.65	1.29	0.40	3.45	0.41
2	1.67	1.27	0.39	3.47	0.44
3	1.67	1.27	0.38	3.47	0.43
4	1.68	1.29	0.39	3.48	0.43
5	16.0	1.28	0.38	3.44	0.44
Mean	1.65	1.28	0.39	3.46	0.43
SD	0.03	0.01	0.01	0.02	0.01
%RSD	1.82	0.78	2.56	0.58	2.32

3.3.3.2 Reproducibility

Table 3.47 The reproducibility of results obtained with IonPac CS5 column, 7.5 mM PDCA pH 4.1 at flow rate 1.0 ml/min as eluent and 0.36 mM PAR in 3.52 M NH_4OH / 1.0 M CH_3COOH at flow rate 0.5 ml/min as the post-column reagent at wavelength 530 nm.

(a) Retention times of various metal ions investigated.

Run	t_r (min)				
	Fe^{3+} 1.0 ng/µl	Cu^{2+} 1.0 ng/µl	Zn^{2+} 1.0 ng/µl	Co^{2+} 1.0 ng/µl	Mn^{2+} 1.0 ng/µl
1	3.27	4.18	5.15	5.80	6.80
2	3.32	4.22	5.18	5.83	6.83
3	3.28	4.18	5.15	5.82	6.82
4	3.30	4.18	5.17	5.82	6.82
5	3.30	4.22	5.17	5.82	6.82
mean	3.29	4.20	5.16	5.82	6.82
SD	0.02	0.02	0.01	0.01	0.01
%RSD	0.61	0.48	0.27	0.19	0.15

Table 3.47 (continued)

(b) Peak area of various metal ions investigated.

Run	Peak area ($1x10^5$) (arbitrary unit)				
	Fe^{3+} 1.0 ng/µl	Cu^{2+} 1.0 ng/µl	Zn^{2+} 1.0 ng/µl	Co^{2+} 1.0 ng/µl	Mn^{2+} 1.0 ng/µl
1	1.68	1.29	0.39	3.44	0.42
2	1.68	1.24	0.38	3.42	0.44
3	1.67	1.29	0.38	3.42	0.43
4	1.64	1.27	0.36	3.41	0.41
5	1.67	1.29	0.37	3.43	0.44
Mean	1.67	1.28	0.38	3.42	0.43
SD	0.02	0.02	0.01	0.01	0.01
%RSD	1.20	1.56	2.63	0.29	2.32

3.3.4 Results of determination of linearity

Table 3.48 Relationship between peak area and concentration of metal ions for determination of linearity obtained with IonPac CS5 column, 7.5 mM PDCA pH 4.1 at flow rate 1.0 ml/min as eluent and 0.36 mM PAR in 3.52 M NH_4OH/ 1.0 M CH_3COOH at flow rate 0.5 ml/min as the post-column reagent at wavelength 530 nm.

Concentration (ng/µl)	Peak area ($1x10^5$) (arbitrary unit)				
	Fe^{3+} 1.0 ng/µl	Cu^{2+} 1.0 ng/µl	Zn^{2+} 1.0 ng/µl	Co^{2+} 1.0 ng/µl	Mn^{2+} 1.0 ng/µl
0.08	0.12	0.08	0.04	0.24	0.02
0.10	0.14	0.11	0.05	0.32	0.03
0.20	0.30	0.25	0.08	0.71	0.07
0.40	0.50	0.52	0.20	1.41	0.18
0.60	0.83	0.77	0.22	2.05	0.24
0.80	1.23	1.02	0.30	2.70	0.36
1.00	1.67	1.25	0.35	3.45	0.44
2.00	3.74	2.55	0.70	6.92	0.88
4.00	8.22	5.35	1.39	13.69	1.79
6.00	12.77	7.83	2.05	20.11	2.64
8.00	17.34	10.68	2.80	26.51	3.67

* averaged from 3 runs

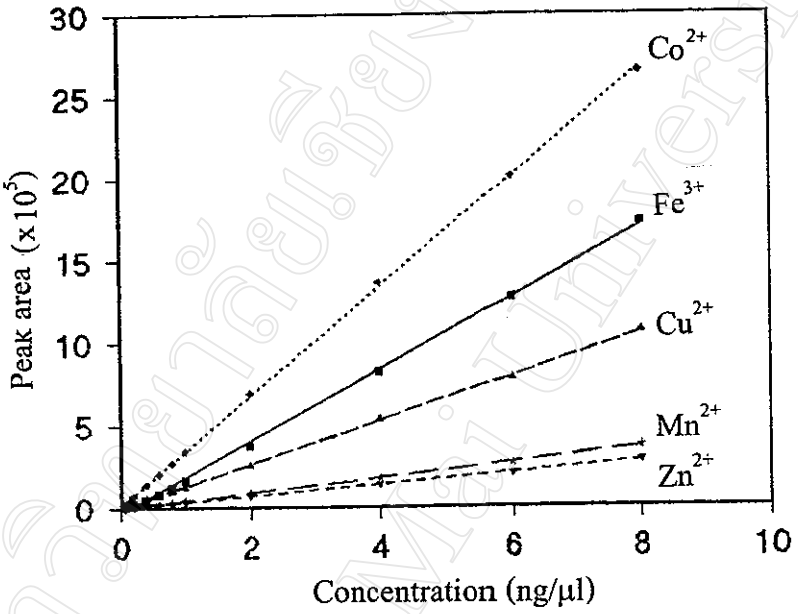


Figure 3.35 Lineaity curves for Fe^{3+}, Cu^{2+}, Zn^{2+}, Co^{2+} and Mn^{2+} obtained with IonPac CS 5 column using 7.5 mM PDCA pH 4.1 as eluent and 0.36 mM PAR in 3.52 M NH_4OH/ 1,0 M CH_3COOH as post-column reagent at 530 nm.

3.3.5 Results of detection limit (L) and minimum detectable quantity (MDQ)

The example of noise level of mixed standard solution in shown in **Figure 3.36**.

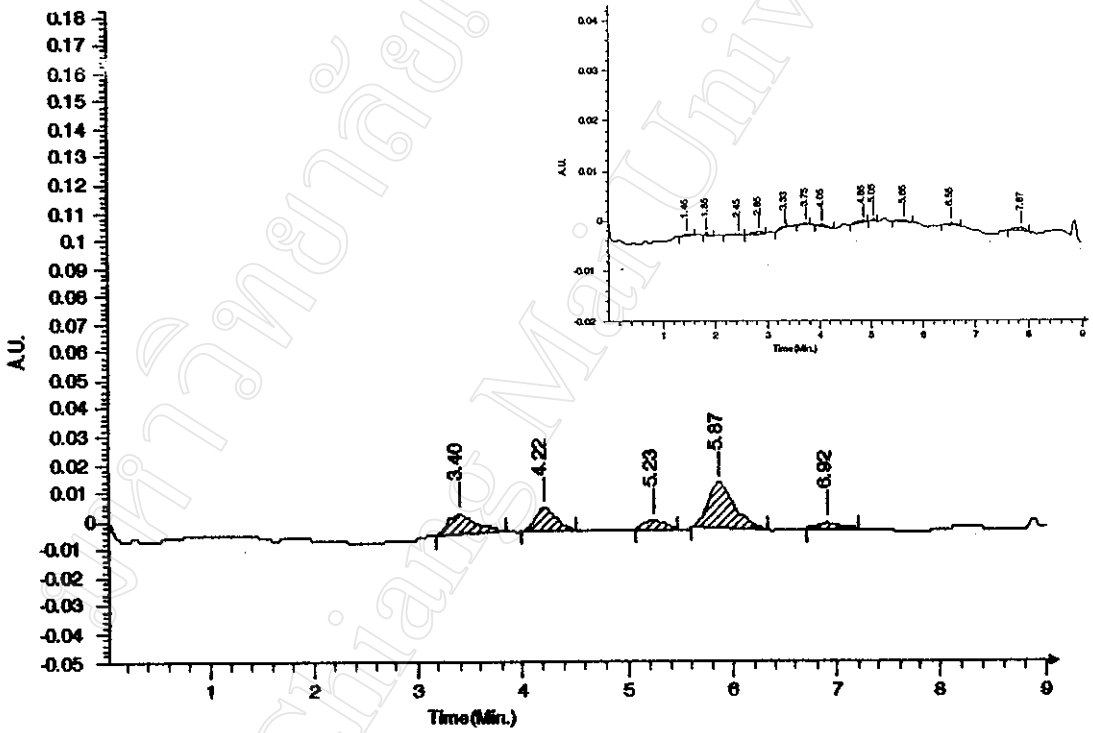


Figure 3.36 The noise level of mixed standard solution obtained at output range 0.2 AU.

Table 3.49 Results of determination of the detection limit (L) and the minimum detectable quantity (MDQ)

Metal ion	Concentration m_x (ng/μl)	Noise level (n)	Peak area R (arbitrary unit)	$W_{1/2}$ (min)	L (ng)	MDQ (ng . sec)
Fe^{3+}	0.1	526	13440	0.14	0.008	0.057
Cu^{2+}	0.1	526	10481	0.10	0.010	0.100
Zn^{2+}	0.1	526	4272	0.12	0.025	0.208
Co^{2+}	0.1	526	29578	0.14	0.004	0.029
Mn^{2+}	0.1	526	2830	0.12	0.037	0.310

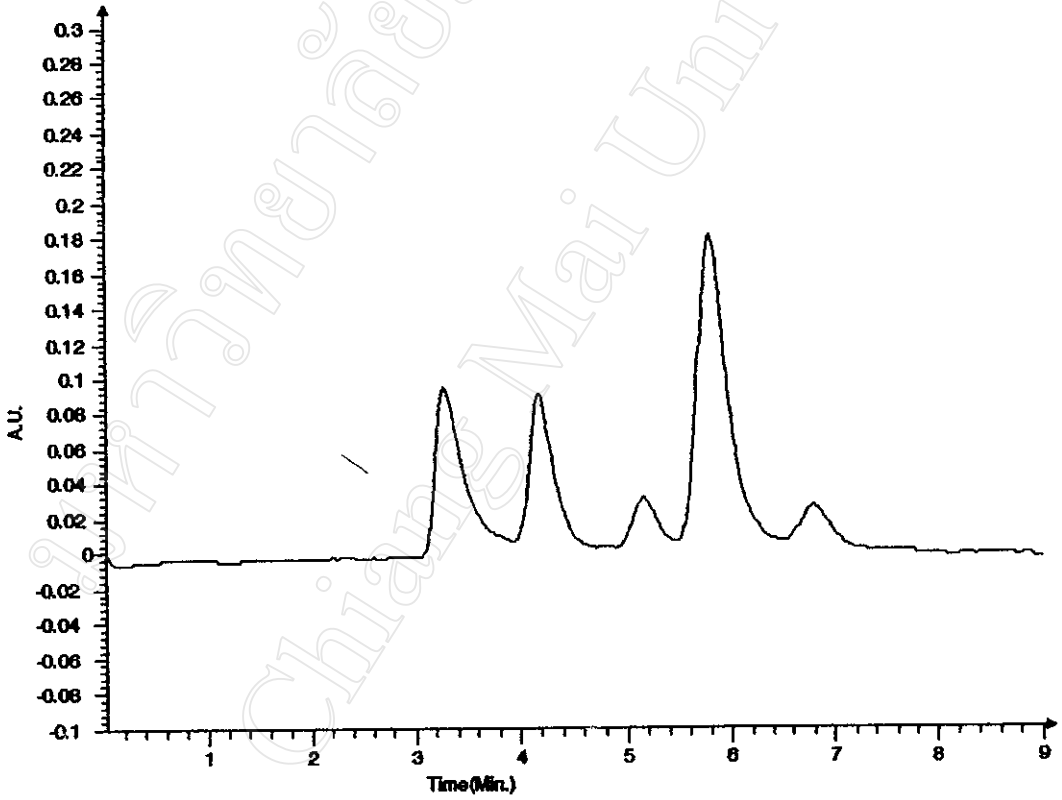


Figure 3.37 Chromatogram of 1.0 ppm Fe^{3+}, 1.0 ppm Cu^{2+}, 1.0 ppm Zn^{2+}, 1.0 ppm Co^{2+} and 1.0 ppm Mn^{2+} obtained with IonPac CS5 using 7.5 mM PDCA pH 4.1 as eluent, 0.36 mM PAR in 3.52 M NH_4OH/ 1.0 M CH_3COOH as post-column reagent, at 530 nm.

3.3.6 Determination of heavy metal ions in geological samples by IC

The amount of metal ions in geological samples, namely Fe^{3+}, Cu^{2+}, Zn^{2+}, $Co^{2+}$and Mn^{2+} were determined by the IC technique.

3.3.6.1 Standard calibration curves of Fe^{3+}, Cu^{2+}, Zn^{2+}, $Co^{2+}$and Mn^{2+}

Calibration curve of these metal ions in geological samples were constructed from the data in **Tables 3.50-3.54** and calibration curve are shown in **Figures 3.38-3.42.**

Table 3.50 The data used for construction of the standard calibration curve of Fe^{3+}

Concentration(ng/μl)	Peak area (1x 10^5)(arbitrary unit)
0.10	0.14
0.20	0.30
0.40	0.61
0.60	0.83
0.80	1.23

Table 3.51 The data used for construction of the standard calibration curve of Cu^{2+}

Concentration(ng/μl)	Peak area (1x 10^5)(arbitrary unit)
0.10	0.08
0.20	0.25
0.40	0.50
0.60	0.77
0.80	1.02

Table 3.52 The data used for construction of the standard calibration curve of Zn^{2+}

Concentration(ng/μl)	Peak area (1x10^5)(arbitrary unit)
0.10	0.05
0.20	0.08
0.40	0.14
0.60	0.22
0.80	0.30

Table 3.53 The data used for construction of the standard calibration curve of Co^{2+}

Concentration(ng/μl)	Peak area ($1x10^5$)(arbitrary unit)
0.10	0.32
0.20	0.71
0.40	1.41
0.60	2.05
0.80	2.70

Table 3.54 The data used for construction of the standard calibration curve of Mn^{2+}

Concentration(ng/μl)	Peak area ($1x10^5$)(arbitrary unit)
0.10	0.03
0.20	0.07
0.40	0.18
0.60	0.24
0.80	0.36

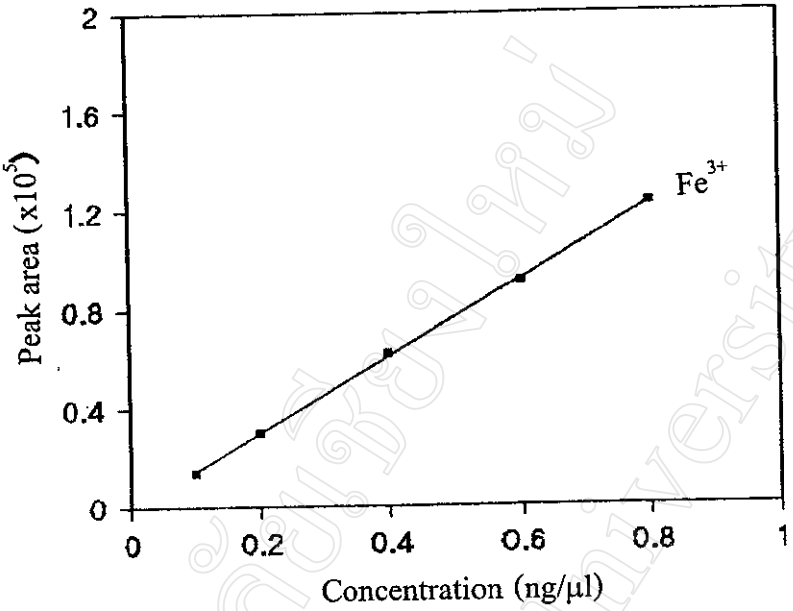


Figure 3.38 Calibration curve of Fe^{3+}.

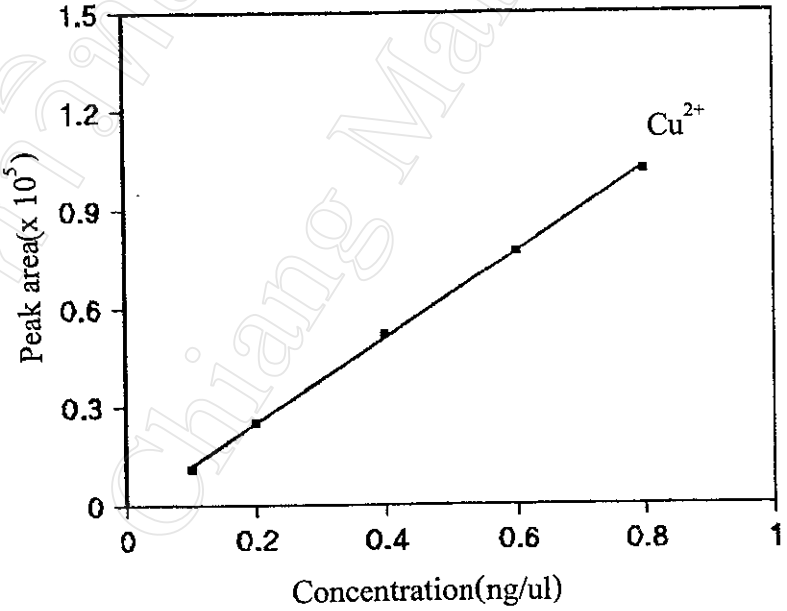


Figure 3.39 Calibration curve of Cu^{2+}.

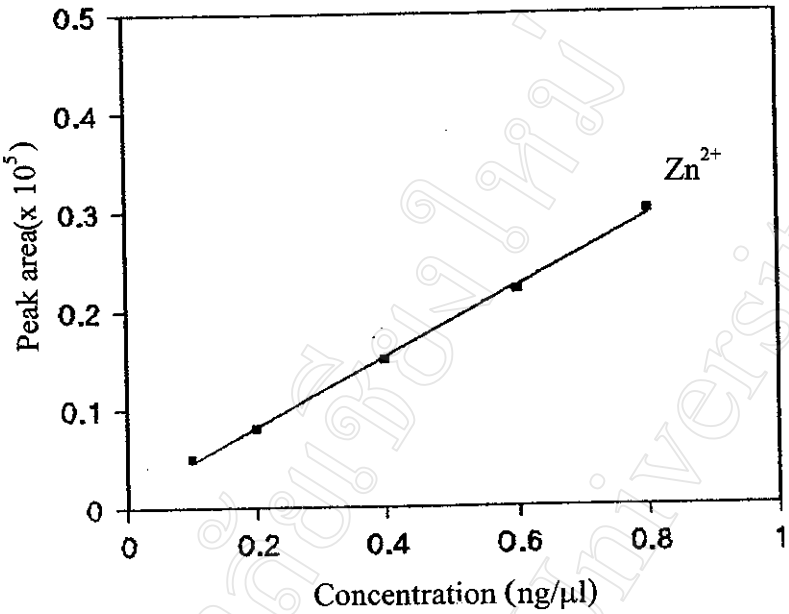


Figure 3.40 Calibration curve of Zn^{2+}.

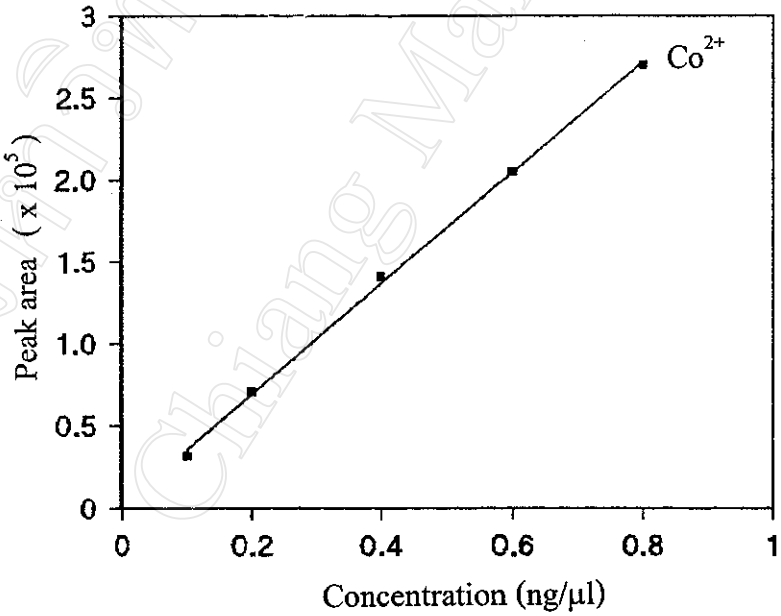


Figure 3.41 Calibration curve of Co^{2+}.

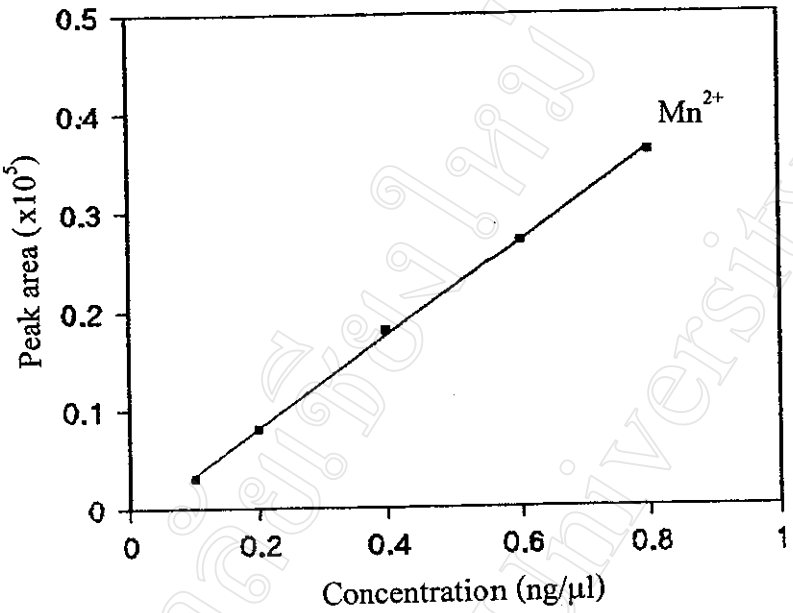


Figure 3.42 Calibration curve of Mn^{2+}.

3.3.6.2 The amounts of Fe^{3+}, Cu^{2+}, Zn^{2+}, Co^{2+} and Mn^{2+} in geological water samples

The amounts of Fe^{3+}, Cu^{2+}, Zn^{2+}, Co^{2+} and Mn^{2+} in geological samples were obtained with IonPac CS5. The results of analysis are shown in **Tables 3.55 and 3.56**. The chromatograms of some geological samples are shown in **Figures 3.43-3.46**.

Table 3.55 Peak area of metal ions in geological water samples obtained with IonPac CS5

Sample	Peak area ($1x10^5$)(arbitrary unit) *				
	Fe^{2+}	Cu^{2+}	Zn^{2+}	Co^{2+}	Mn^{2+}
1	NF.	NF.	NF.	NF.	NF.
2	NF.	NF.	NF.	NF.	NF.
3	15685	NF.	NF.	NF.	NF.
4	7354	2483	2295	3215	1652
5	NF.	NF.	NF.	NF.	NF.
6	NF.	NF.	NF.	NF.	NF.
7[a]	NF.	37434	66194	NF.	NF.
8	NF.	NF.	1792	NF.	NF.
9	NF.	NF.	NF.	NF.	NF.
10	4018	NF.	NF.	NF.	NF.
11	NF.	NF.	2661	NF.	NF.
12[a]	NF.	NF.	77117	NF.	NF.
13	NF.	NF.	NF.	NF.	NF.
14	NF.	NF.	NF.	NF.	NF.
15	NF.	NF.	NF.	NF.	NF.
16	NF.	NF.	NF.	NF.	NF.
17	NF.	NF.	NF.	NF.	NF.
18[a]	NF.	NF.	193464	NF.	NF.
19[a]	NF.	NF.	25950	NF.	NF.

* averaged from 3 runs

[a] from Archemica International Co., Ltd.

Table 3.56 Concentration of metal ions in geological water samples obtained with IonPac CS5

Sample	Concentration (ng/μl) *				
	Fe^{2+}	Cu^{2+}	Zn^{2+}	Co^{2+}	Mn^{2+}
1	NF.	NF.	NF.	NF.	NF.
2	NF.	NF.	NF.	NF.	NF.
3	0.12	NF.	NF.	NF.	NF.
4	0.04	0.03	0.03	0.02	0.07
5	NF.	NF.	NF.	NF.	NF.
6	NF.	NF.	NF.	NF.	NF.
7[a]	NF.	0.04	0.06	NF.	NF.
8	NF.	NF.	NF.	NF.	NF.
9	NF.	NF.	0.01	NF.	NF.
10	0.01	NF.	NF.	NF.	NF.
11	NF.	NF.	0.05	NF.	NF.
12[a]	NF.	NF.	0.07	NF.	NF.
13	NF.	NF.	NF.	NF.	NF.
14	NF.	NF.	NF.	NF.	NF.
15	NF.	NF.	NF.	NF.	NF.
16	NF.	NF.	NF.	NF.	NF.
17[a]	NF.	NF.	NF.	NF.	NF.
18[a]	NF.	NF.	0.18	NF.	NF.
19	NF.	NF.	0.02	NF.	NF.

* averaged from 3 runs

[a] from Archemica International Co., Ltd.

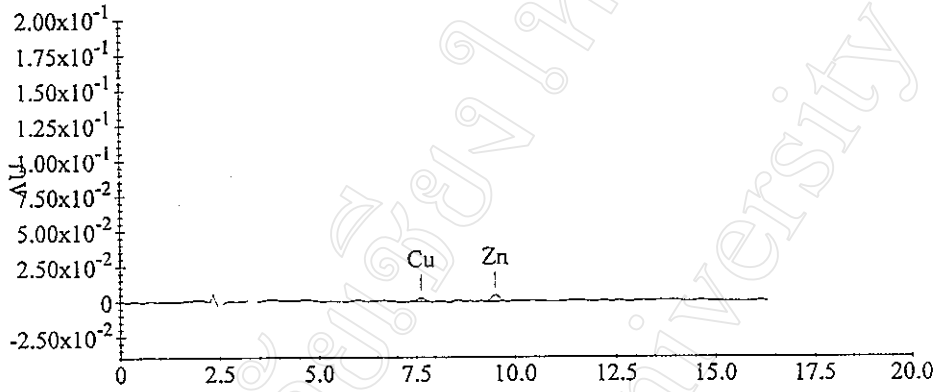


Figure 3.43 Typical chromatogram of sample #7 obtained with IonPac CS5 column

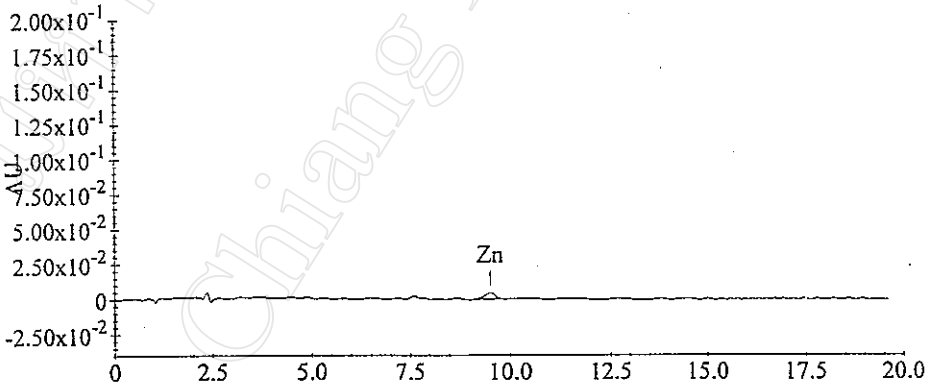


Figure 3.44 Typical chromatogram of sample #12 obtained with IonPac CS5 column

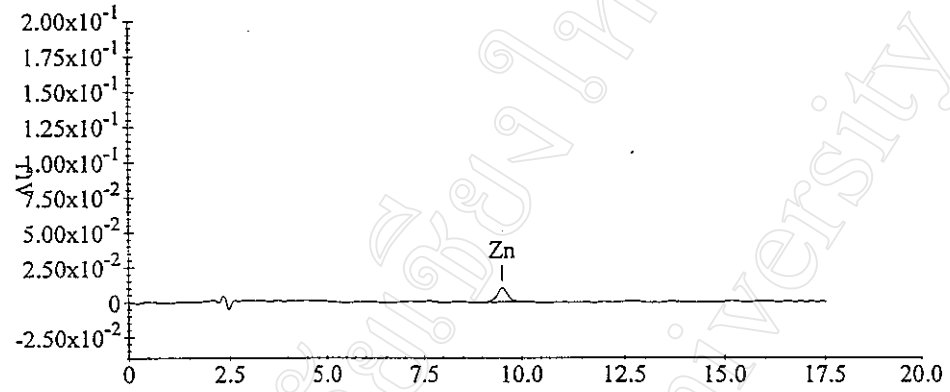


Figure 3.45 Typical chromatogram of sample #18 obtained with IonPac CS5 column

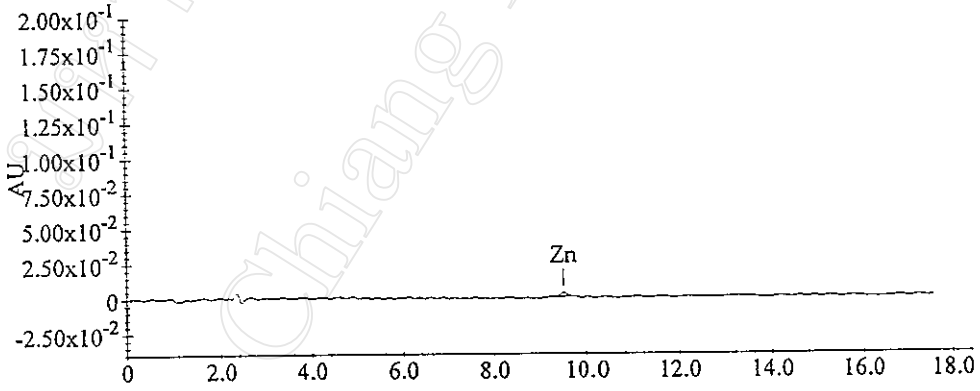


Figure 3.46 Typical chromatogram of sample #19 obtained with IonPac CS5 column

3.3.6.3 The amounts of Fe^{3+}, Cu^{2+}, Zn^{2+}, Co^{2+} and Mn^{2+} in geological reference materials

The amounts of Fe^{3+}, Cu^{2+}, Zn^{2+}, Co^{2+} and Mn^{2+} in geological reference materials were obtained with IonPac CS5. The results of analysis are shown in **Tables 3.57 and 3.58.** The chromatograms of some geological samples are shown in **Figures 3.47-3.50.**

Table 3.57 Concentration of metal ions in sample #22 obtained IonPac CS5 column.

Metal ions	Concentration (ng/μl) of metal ions *							
	Method #1		Method #2		Method #3		Method #4	
	A*	B**	A*	B**	A*	B**	A*	B**
Fe^{3+}	0.27	0.14	2.46	1.24	12.68	5.66	4.16	3.85
Cu^{2+}	0.03	0.02	0.07	0.06	0.01	0.004	NF.	NF.
Zn^{2+}	0.04	0.02	0.03	0.03	0.10	0.04	0.02	0.02
Co^{2+}	NF.	NF.	0.01	0.01	0.01	0.004	NF.	NF.
Mn^{2+}	0.07	0.04	0.25	0.23	0.17	0.08	0.13	0.12

* averaged from 3 runs

A* = from calibration curve (ng/μl)

B** = actual amount in original sample (%w/w)

Table 3.58 Concentration of metal ions in sample #23 obtained IonPac CS5 column.

Metal ions	Concentration (ng/µl) of metal ions *							
	Method #1		Method #2		Method #3		Method #4	
	A*	B**	A*	B**	A*	B**	A*	B**
Fe^{3+}	1.09	0.54	5.83	1.43	2.71	1.35	2.73	2.70
Cu^{2+}	0.03	0.01	0.14	0.03	0.11	0.05	0.02	0.02
Zn^{2+}	NF.	NF.	0.19	0.05	0.04	0.02	0.02	0.02
Co^{2+}	NF.	NF.	NF.	NF.	NF.	NF.	NF.	NF.
Mn^{2+}	0.04	0.02	NF.	NF.	0.16	0.08	0.08	0.08

* averaged from 3 runs

A* = from calibration curve (ng/µl)

B** = actual amount in original sample (%w/w)

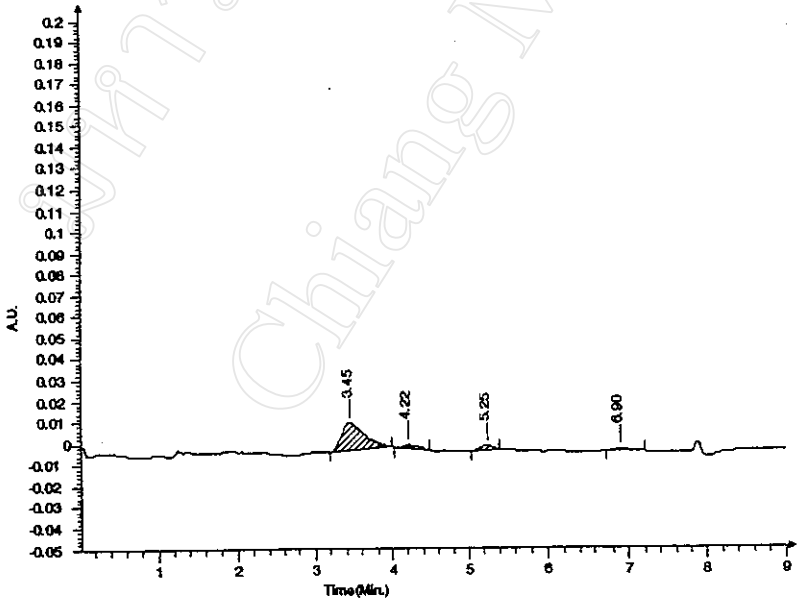


Figure 3.47 Typical chromatogram of sample #22 obtained by method #1

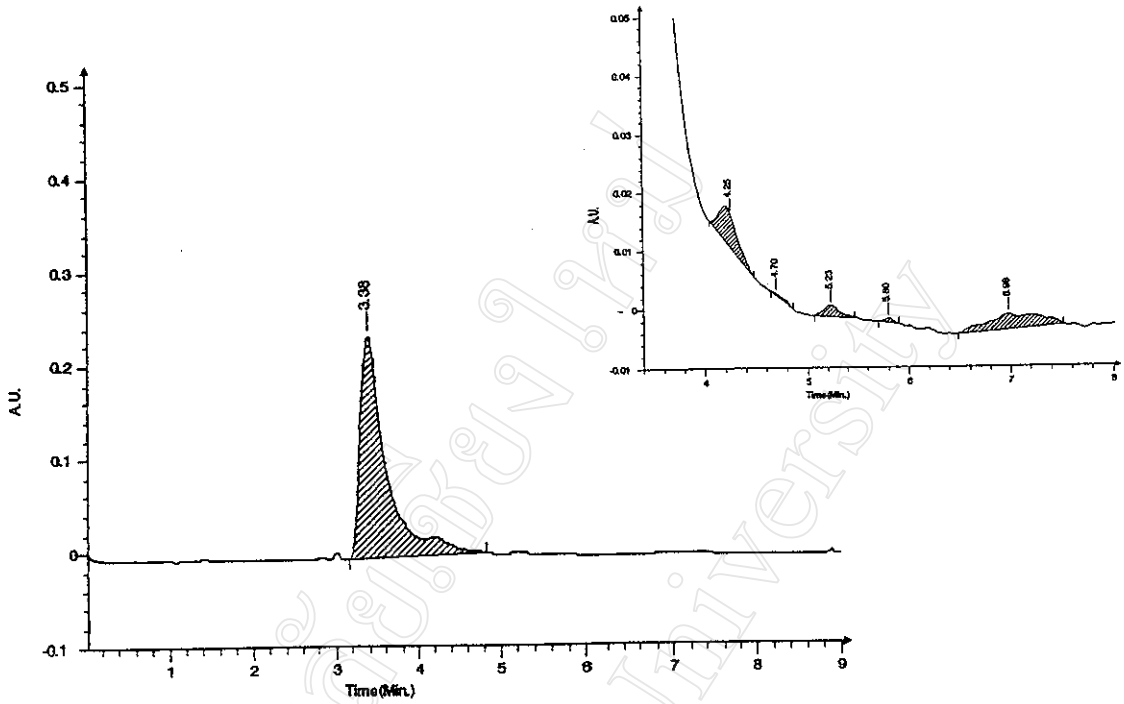


Figure 3.48 Typical chromatogram of sample #22 obtained by method #2

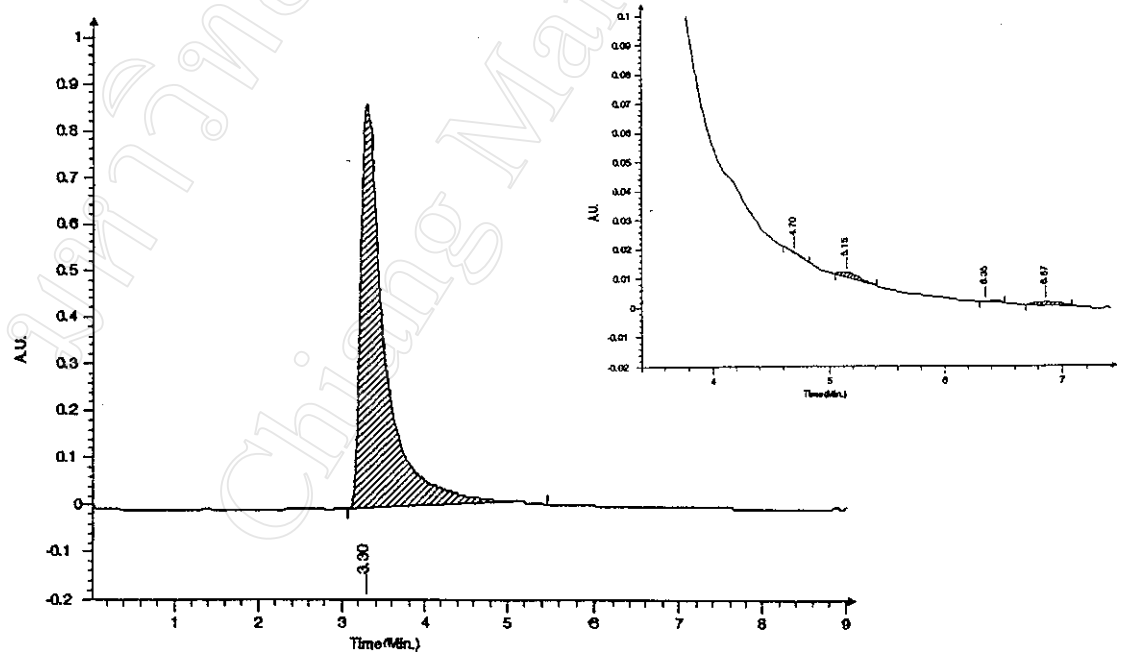


Figure 3.49 Typical chromatogram of sample #23 obtained by method #3

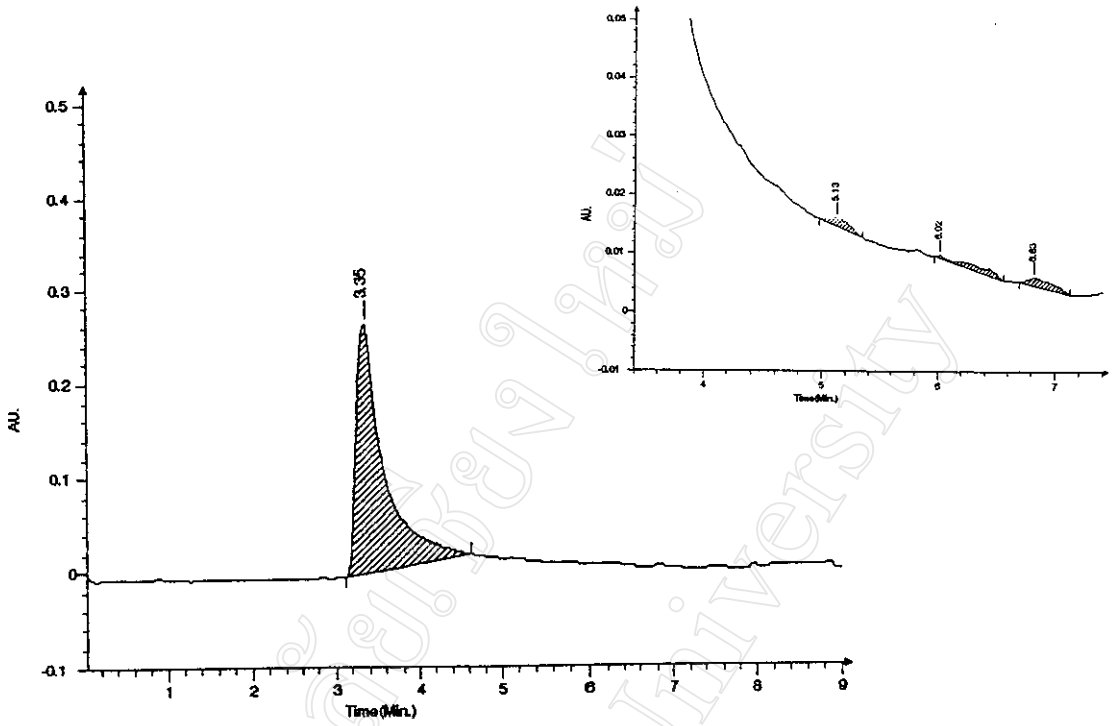


Figure 3.50 Typical chromatogram of sample #23 obtained by method #4

3.3.7 % Recovery of each metal ion in IC technique

% Recovery obtained from standards was confirmed using the "spike" method

Table 3.59 % Recovery of Fe^{3+} in 0.2 ng/µl mixed standard

Spike standard Fe^{3+} (ng/µl)	Peak area (arbitrary unit)	Concentration	% Recovery
0.2 ng/µl mixed std.	30400	0.200	-
0.2 ng/µl mixed std. + 0.1 ng/µl	33696	0.296	96.0 %
0.2 ng/µl mixed std. + 0.2 ng/µl	55647	0.397	98.5 %
0.2 ng/µl mixed std. + 0.3 ng/µl	77523	0.496	98.7 %
0.2 ng/µl mixed std. + 0.4 ng/µl	99012	0.595	98.8 %
		Mean	98.5 %

Table 3.60 % Recovery of Cu^{2+} in 0.2 ng/µl mixed standard

Spike standard Cu^{2+} (ng/µl)	Peak area (arbitrary unit)	Concentration	% Recovery
0.2 ng/µl mixed std.	25857	0.200	-
0.2 ng/µl mixed std. + 0.1 ng/µl	36294	0.300	100.0 %
0.2 ng/µl mixed std. + 0.2 ng/µl	48631	0.396	98.0 %
0.2 ng/µl mixed std. + 0.3 ng/µl	62049	0.494	98.0 %
0.2 ng/µl mixed std. + 0.4 ng/µl	75088	0.592	98.0 %
		Mean	98.5 %

Table 3.61 % Recovery of Zn^{2+} in 0.2 ng/µl mixed standard

Spike standard Zn^{2+} (ng/µl)	Peak area (arbitrary unit)	Concentration	% Recovery
0.2 ng/µl mixed std.	7700	0.200	-
0.2 ng/µl mixed std. + 0.1 ng/µl	12103	0.298	98.0 %
0.2 ng/µl mixed std. + 0.2 ng/µl	15527	0.397	98.5 %
0.2 ng/µl mixed std. + 0.3 ng/µl	19045	0.498	99.3 %
0.2 ng/µl mixed std. + 0.4 ng/µl	22303	0.594	98.5 %
		Mean	98.6 %

Table 3.62 % Recovery of Co^{2+} in 0.2 ng/µl mixed standard

Spike standard Co^{2+} (ng/µl)	Peak area (arbitrary unit)	Concentration	% Recovery
0.2 ng/µl mixed std.	71078	0.200	-
0.2 ng/µl mixed std. + 0.1 ng/µl	105371	0.297	97.0 %
0.2 ng/µl mixed std. + 0.2 ng/µl	139412	0.397	98.5 %
0.2 ng/µl mixed std. + 0.3 ng/µl	170683	0.492	97.3 %
0.2 ng/µl mixed std. + 0.4 ng/µl	204793	0.594	98.5 %
		Mean	97.8 %

Table 3.63 % Recovery of Mn^{2+} in 0.2 ng/µl mixed standard

Spike standard Mn^{2+} (ng/µl)	Peak area (arbitrary unit)	Concentration	% Recovery
0.2 ng/µl mixed std.	7066	0.200	-
0.2 ng/µl mixed std. + 0.1 ng/µl	11717	0.300	100.0 %
0.2 ng/µl mixed std. + 0.2 ng/µl	16130	0.397	98.5 %
0.2 ng/µl mixed std. + 0.3 ng/µl	20359	0.494	98.0 %
0.2 ng/µl mixed std. + 0.4 ng/µl	24988	0.593	98.3 %
		Mean	98.7 %

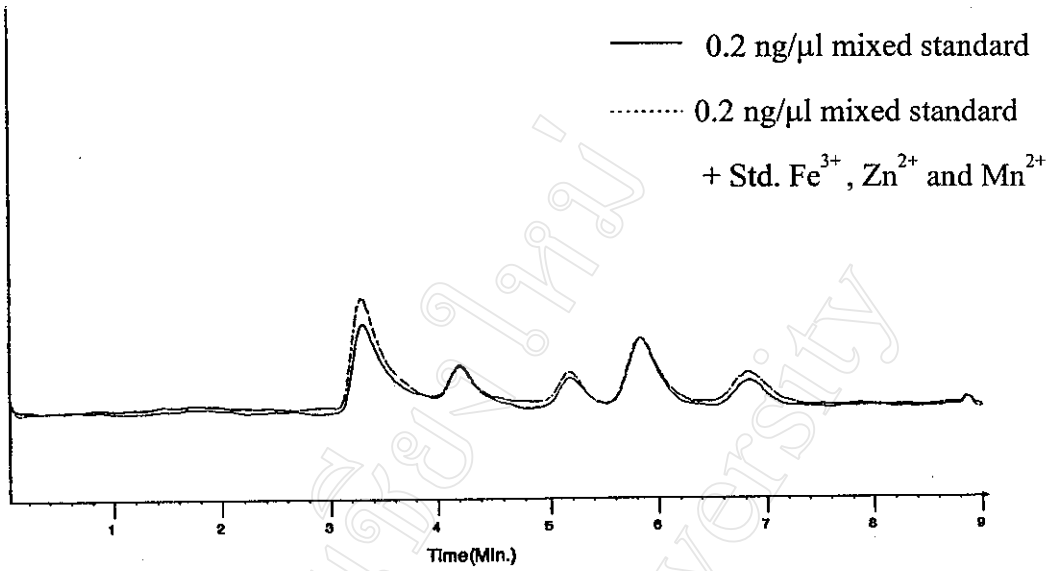


Figure 3.51 Chromatogram of 0.2 ng/µl mixed standard (——) and chromatogram of 0.2 ng/µl mixed standard spiked with standard of Fe^{3+}, Zn^{2+} and Mn^{2+} (·····)

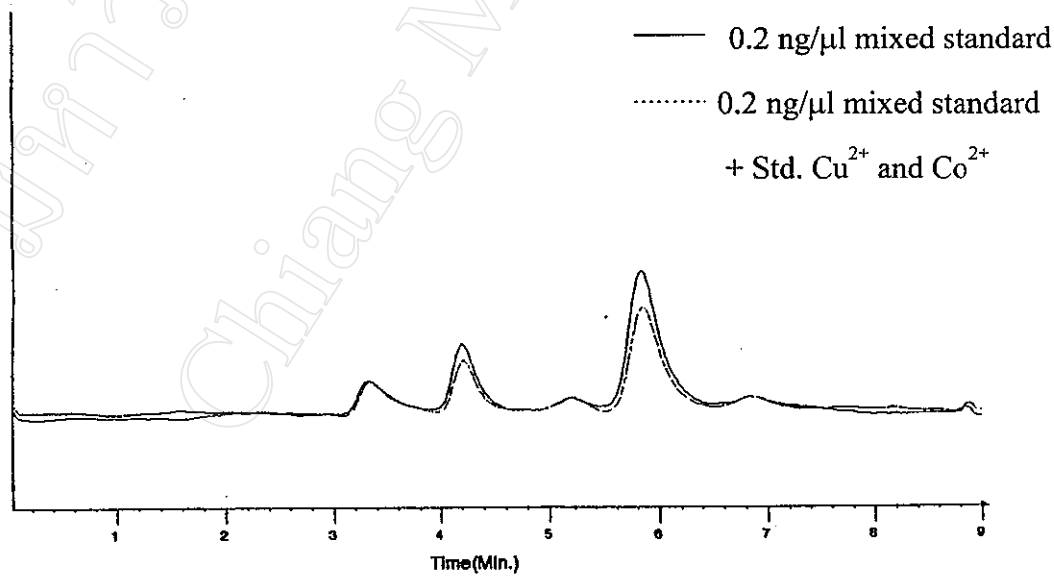


Figure 3.52 Chromatogram of 0.2 ng/µl mixed standard (——) and chromatogram of 0.2 ng/µl mixed standard spiked with standard of Cu^{2+} and Co^{2+} (·····)

3.3.8 Analysis of metal ions in geological water samples by atomic absorption spectrophotometry (AAS) and inductively coupled plasma spectrophotometry (ICP)

The amounts of Fe^{3+}, Cu^{2+}, Zn^{2+}, Co^{2+} and Mn^{2+} in geological water samples were determined again by the AAS technique and ICP technique using external standard method. In this work was determined only the Zn^{2+}. For other metal ions could not compared because they were found in a few sample. The results are shown in **Table 3.64**.

Table 3.64 Concentration of Zn^{2+} in geological water samples by IC and AAS techniques

Sample #	Concentration of metal ions (ng/μl) obtained by	
	IC technique	AAS technique
4	0.03	0.02
7	0.06	0.04
11	0.05	0.04
12	0.07	0.04
18	0.18	0.04
Σ Di		0.21
$\bar{D}$		0.04
SD		0.06
t_{calc}		1.69

Table 3.65 Concentration of Zn^{2+} in geological water samples by IC and ICP techniques

Sample #	Concentration of metal ions (ng/μl) obtained by	
	IC technique	ICP technique
4	0.03	0.55
7	0.06	0.02
11	0.05	0.03
12	0.07	0.03
18	0.18	0.11
Σ Di		0.69
$\bar{D}$		0.14
SD		0.21
t_{calc}		1.44