APPENDIX A

Table A-1 Values of F at the 95% confidence level*

ν_2 \ ν_1	2	3	4	5	6	7	8	9	10	15	20	30
2	19.0	19.2	19.2	19.3	19.4	19.4	19.4	19.4	19.4	19.4	19.4	19.5
3	9.55	9.28	9.12	9.01	8.94	8.89	8.85	8.81	8.79	8.70	8.66	8.62
4	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.86	5.80	5.75
5	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.62	4.56	4.50
6	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	3.94	3.87	3.81
7	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.51	3.44	3.38
8	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.22	3.15	3.08
9	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.01	2.94	2.86
10	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.85	2.77	2.70
15	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.40	2.33	2.25
20	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.20	2.12	2.04
30	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.01	1.93	1.84

* G.D. Christian, Analytical Chemistry, 3rd ed., John Wiley & Sons, New York, 1980.

Table A-2 Values of t for degrees of freedom (ν) for various confidence levels*

Degree of freedom (ν)	Confidence Level			
	90%	95%	99%	99.5%
1	6.314	12.706	63.657	127.32
2	2.920	4.303	9.925	14.089
3	2.353	3.182	5.841	7.453
4	2.132	2.776	4.604	5.598
5	2.015	2.571	4.032	4.773
6	1.943	2.447	3.707	4.317
7	1.895	2.306	3.500	4.029
8	1.860	2.306	3.355	3.832
9	1.833	2.262	3.250	3.690
10	1.812	2.228	3.169	3.581
15	1.753	2.131	2.947	3.252
20	1.725	2.086	2.845	3.153
25	1.708	2.060	2.787	3.078
∞	1.645	1.960	2.576	2.807

* G.D. Christian, Analytical Chemistry, 3rd ed., John Wiley & Sons, New York, 1980.

APPENDIX B

Table B-1 The conductivity values of eluents were obtained from the experiment using a conductivity detector by ion chromatographic system

Eluent	Conductivity value (μS)
10 mM sodium hydroxide	3.5
10 mM sodium borate	7.7
0.3 mM sodium benzoate	39
1 mM sodium benzoate	86
3 mM sodium benzoate	153
0.5 mM sodium oxalate	220
1 mM phthalic acid	234
2.5 mM phthalic acid	667
1 mM potassium H-phthalate	231
3 mM sodium bicarbonate	12
2 mM sodium carbonate	20
6 mM sodium carbonate	21
12.8 mM sodium carbonate	28
1 mM citric acid	223
0.59 mM sodium citrate	153
1 mM sodium citrate	224
2 mM sodium citrate	330
1 mM potassium chromate	374
acetonitrile	1.6 (External mode)

APPENDIX C

Determination of Common Anions in Water Samples Using Ion Chromatography

C.1 The investigation of retention times of common anions of interest

The most common anions in water samples are generally F^-, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-} that are likely to be found as contaminating common anions in water samples. An IonPac AS4A anion-exchange column was employed for the separation of common anions using 1.80 mM sodium carbonate/1.70 mM sodium bicatbonate as eluent at flow rate of 2.00 ml/min. The retention times, peak areas and resolutions of these anions were found in the investigated in Table C-1.

Table C-1 The retention times, peak areas and resolutions of common anions obtained with an IonPac AS4A column and a conductivity detector using 1.80 mM sodium carbonate /1.70 mM sodium bicarbonate as eluent, at flow rate of 2.00 ml/min

Common anion	Average retention time (min)	Average peak area ($*10^5$)(arbitrary unit)
F^-	0.88	2.14
Cl^-	1.28	1.73
NO_3^-	2.48	0.99
PO_4^{3-}	4.10	0.45
SO_4^{2-}	5.20	1.34
Anion pair	Average resolution	
F^- - Cl^-	2.39	
Cl^- - NO_3^-	6.54	
NO_3^- - PO_4^{3-}	6.11	
PO_4^{3-} - SO_4^{2-}	3.12	

C.2 The conditions obtained with an IonPac AS4A column for analysis of common anions in the water samples

The conditions for analysis of common anions, obtained with an IonPac AS4A anion-exchange column can be summarized in Table C-2 and the chromatogram of mixed standard solution is presented in Figure C-1.

Table C-2 The conditions obtained with an IonPac AS4A anion-exchange column

Operation	Conditions
Eluent	1.80 mM sodium carbonate and 1.70 mM sodium bicarbonate
Eluent flow rate	2.00 ml/min
Injection volume	25 µl
Detector	conductivity
Suppression	anion self-regenerating suppressor (autosuppression recycle mode)
Background conductivity	20 µS
Detector temperature compensation	1.7 %/^{o}C

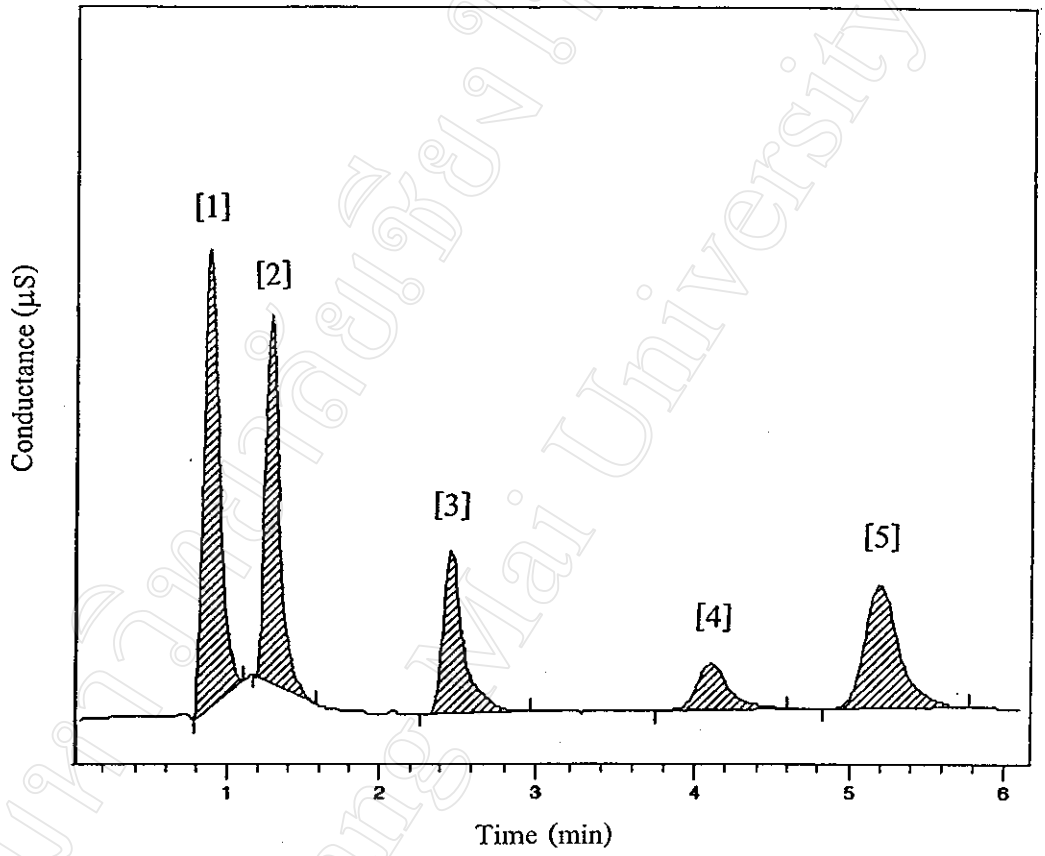

Figure C-1 Chromatogram of common anions obtained with an IonPac AS4A column and a conductivity detector using 1.80 mM sodium carbonate/1.70 mM sodium bicarbonate as eluent, at flow rate of 2.00 ml/min : [1] fluoride, [2] chloride, [3] nitrate, [4] phosphate and [5] sulphate.

C.3 Determination of common anions in the water samples

In this investigation, an IonPac AS4A anion-exchange column could be used to separate common anions, F^-, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-} with the isocratic condition in less than 6.0 minutes. So this column was used for the determination of common anions in the water samples. The condition obtained with the eluents consisting of 1.80 mM sodium carbonate/1.70 mM sodium bicarbonate at flow rate of 2.00 ml/min and detection was achieved using a conductivity detector. This condition was applied to determine the amounts of common anions in the water samples.

C.3.1 The calibration curves of F^-, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-}

The external standard method was used in the investigation by calibration curves of common anions, constructed from average peak area and concentration of standard common anions in the range of 0.2-1.0 ng/μl, as shown in Figure C-2.

C.3.2 Analysis of common anions, F^-, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-}

The filtered water (No.1) and raw water (No.2) samples were determined of the amount of common anions F^-, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-} by ion chromatographic method using an IonPac AS4A with 1.80 mM sodium carbonate/1.70 mM sodium bicarbonate at a flow rate of 2.0 ml/min. The detection of commom anions was achieved using a conductivity detector. The results obtained are shown in Tables C-3 and C-4 and the chromatograms of water samples are shown in Figures C-3 – C-6.

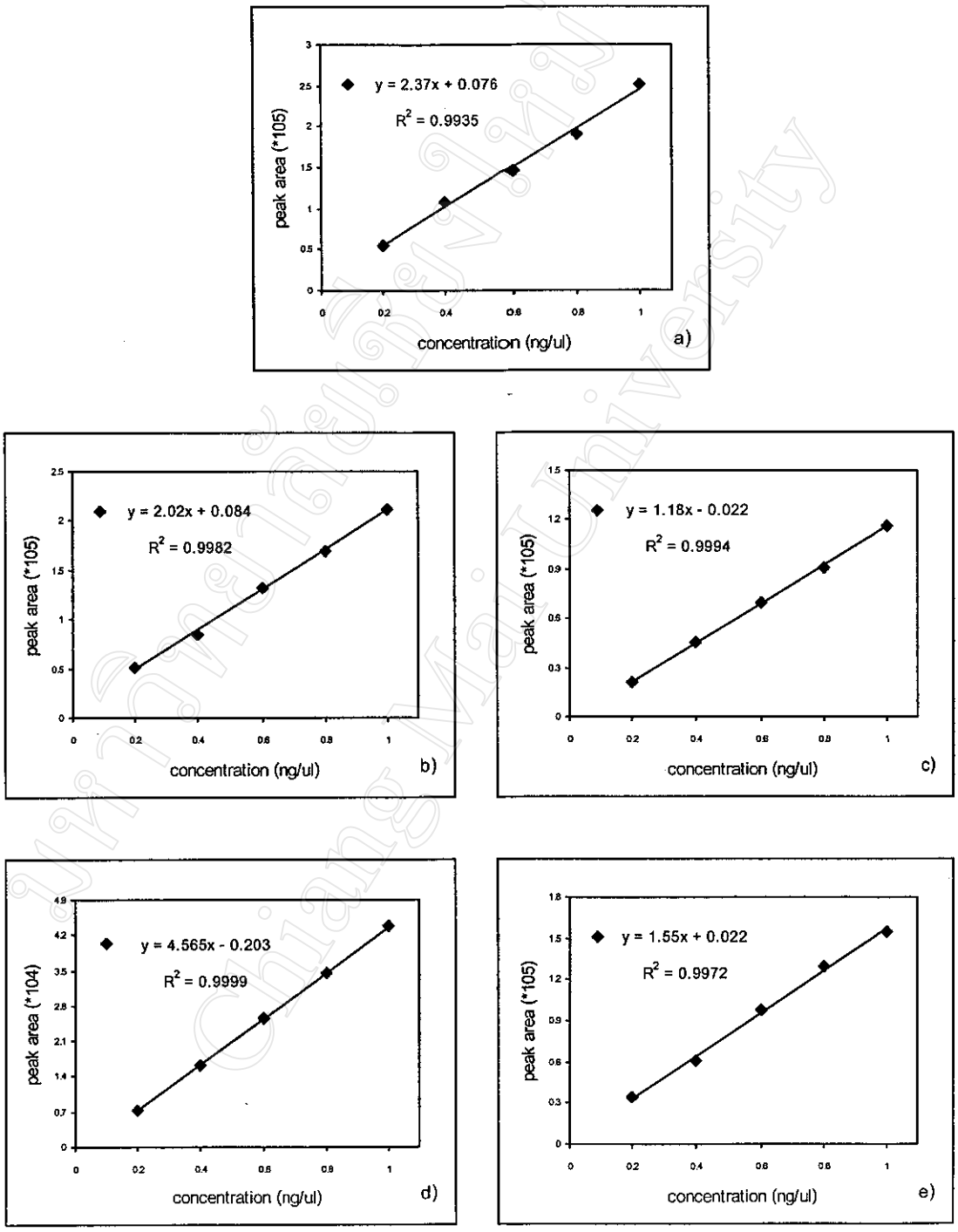

Figure C-2 Calibration curves of common anions

a) fluoride, b) chloride, c) nitrate, d) phosphate and e) sulphate.

Table C-3 The results of water samples No.1 obtained with an IonPac AS4A column and a conductivity detector using 1.80 mM sodium carbonate/1.70 mM sodium bicarbonate as eluent, at flow rate of 2.0 ml/min

Result	Common anion				
	F^-	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
Average peak area (arbitrary unit)	NF	160844	79850	NF	70809
	NF	155971	78632	NF	70006
	NF	154458	84800	NF	64129
Original concentration (ng/ul)	NF	47.30	0.81	NF	26.00
	NF	45.76	0.80	NF	25.71
	NF	45.29	0.86	NF	23.56
Mean concentration (ng/ul)	-	46.12	0.82	-	25.09
SD	-	1.05	0.04	-	1.33
%RSD	-	2.28	3.66	-	5.30

Table C-4 The results of water samples No.2 obtained with an IonPac AS4A column and a conductivity detector using 1.80 mM sodium carbonate/1.70 mM sodium bicarbonate as eluent, at flow rate of 2.0 ml/min

Result	Common anion				
	F^-	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
Average peak area (arbitrary unit)	NF	161476	NF	NF	76166
	NF	161618	NF	NF	68780
	NF	160037	NF	NF	69061
Original concentration (ng/ul)	NF	37.86	NF	NF	23.85
	NF	37.90	NF	NF	21.46
	NF	37.51	NF	NF	21.55
Mean concentration (ng/ul)	-	37.76	-	-	22.29
SD	-	0.21	-	-	1.35
%RSD	-	0.56	-	-	6.06

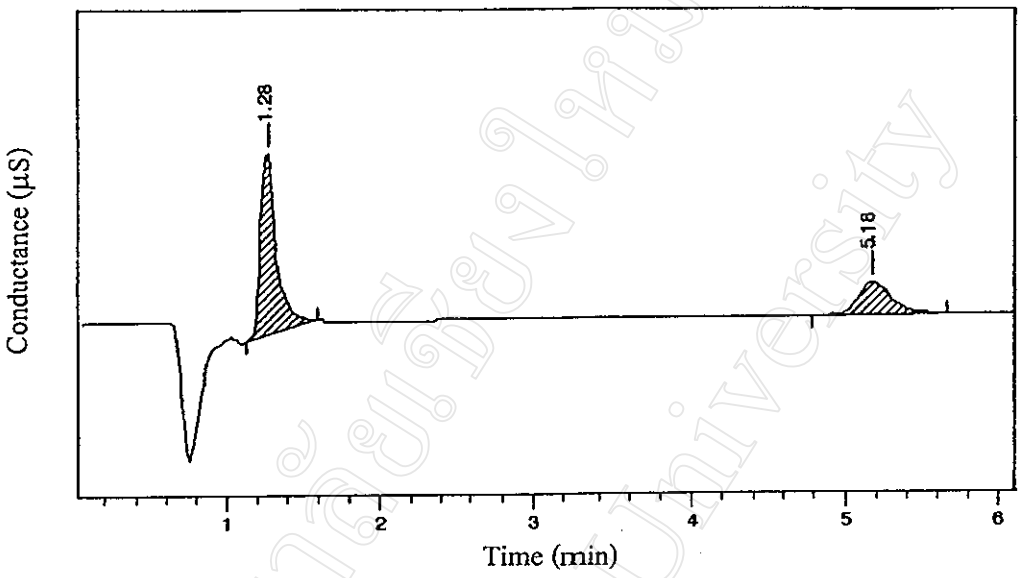

Figure C-3 Typical chromatogram of water sample No.1 (50 fold dilution) obtained with an IonPac AS4A column using 1.80 mM sodium carbonate/1.70 mM sodium bicarbonate at flow rate of 2.00 ml/min.

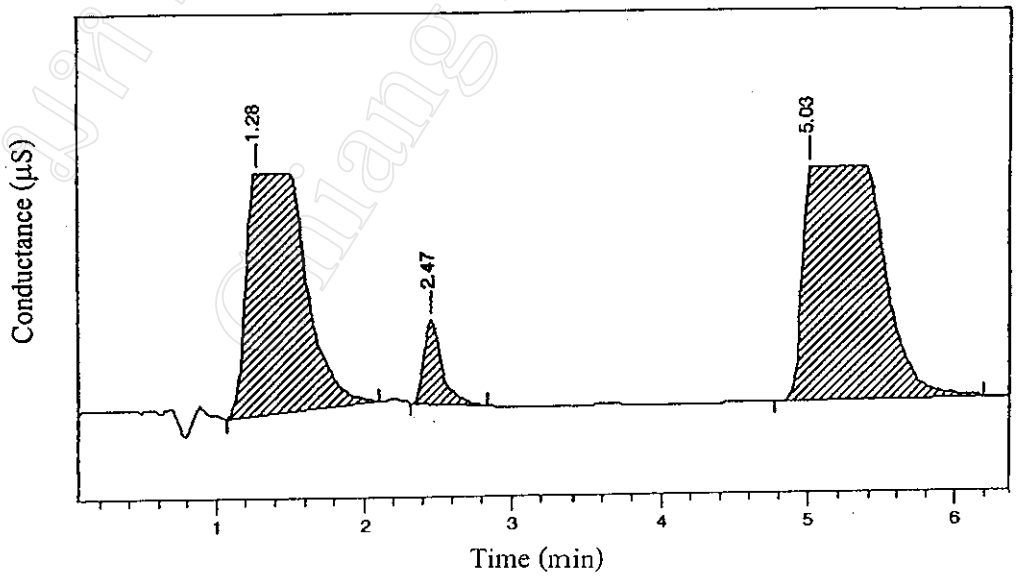

Figure C-4 Typical chromatogram of water sample No.1 obtained with an IonPac AS4A column using 1.80 mM sodium carbonate/1.70 mM sodium bicarbonate at flow rate of 2.00 ml/min.

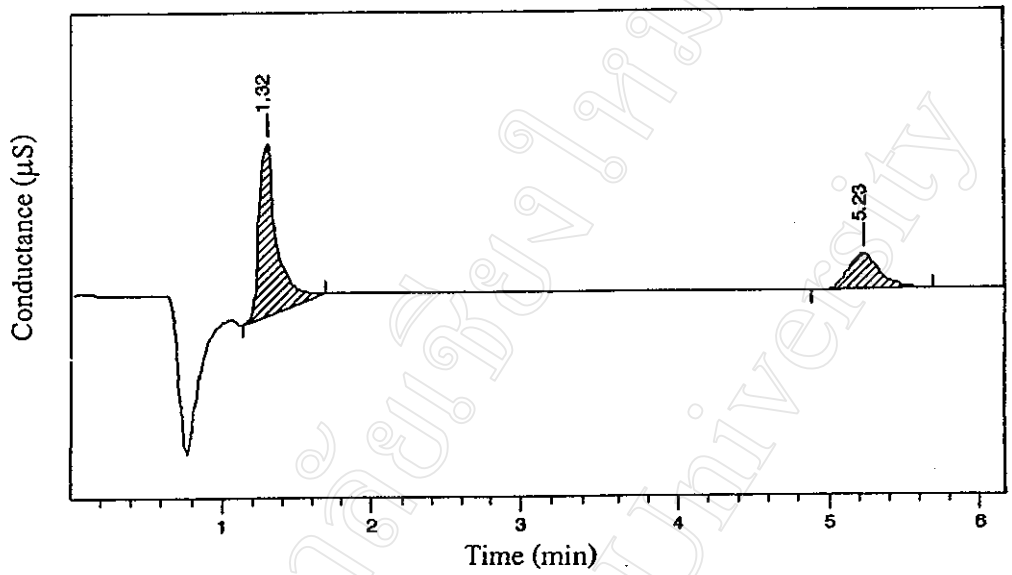

Figure C-5 Typical chromatogram of water sample No.2 (50 fold dilution) obtained with an IonPac AS4A column using 1.80 mM sodium carbonate/1.70 mM sodium bicarbonate at flow rate of 2.0 ml/min.

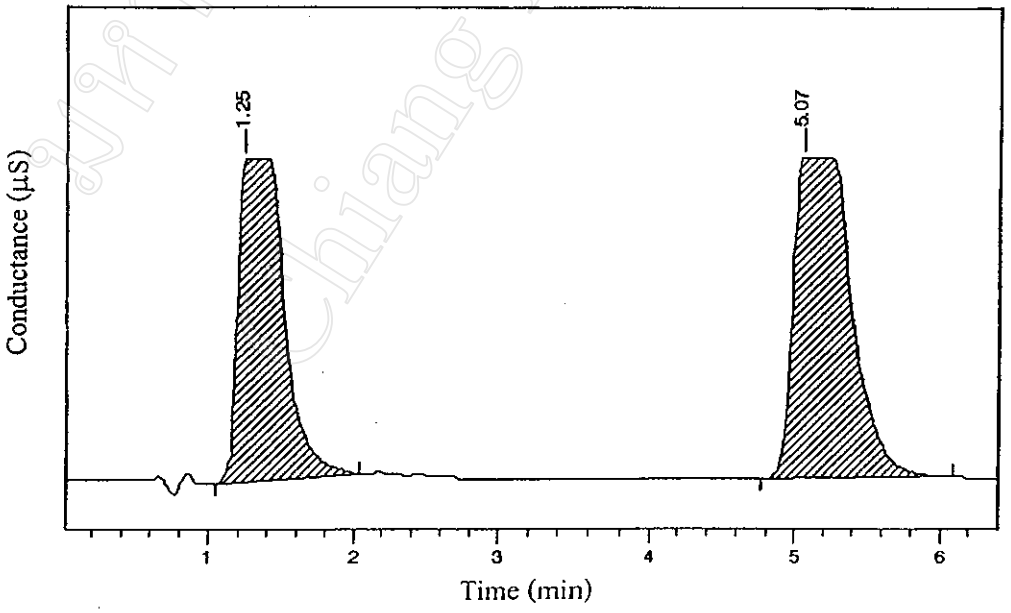

Figure C-6 Typical chromatogram of water sample No.2 obtained with an IonPac AS4A column using 1.80 mM sodium carbonate/1.70 mM sodium bicarbonate at flow rate of 2.0 ml/min.

The ion chromatographic condition reported in EPA method 300.0* was employed for the determination of common anions in the water samples. The optimum conditions are summarized in Table C-2. The retention times of the fluoride, chloride, nitrate, phosphate and sulphate peaks obtained with an IonPac AS4A column, 1.8 mM sodium carbonate/1.7 mM sodium bicarbonate at flow rate of 2.0 ml/min and detected the signal using a conductivity detector were 0.88, 1.28, 2.48, 4.10 and 5.20 minutes, respectively. The chromatogram obtained with this condition is presented in Figure C-1.

The condition was applied to determine the amounts of common anions in the water samples. The external standard method was employed for the quantitative analysis by the construction of the calibration curves, obtained from plotting the average peak area versus the concentration of each anion. The calibration curves are shown in Figure C-2. The results obtained for the filtered water (No.1) and raw water (No.2) samples are summarized in Tables C-3 and C-4, respectively. The chromatograms obtained with the water samples are presented in Figures C-3 – C-6, respectively. The common anions, which were found in the water samples, were the chloride, nitrate and sulphate ions.

* U.S. EPA Method 300.0, U.S. Environmental Protection Agency, Cincinnati, OH, 1993.

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Previous Works

1) K. Sa-nguanwong, N. Lenghor and S. Liawruangrath "Development of Flow Injection Turbidimetric Method for Determination of Chromium (lll) in Thornsmitt Metal" 26th Congress on Science and Technology of Thailand, 2000.
2) K. Sa-nguanwong, M. Rayanakorn and S. Wangkarn "Separation of Chlorine-containing Anions using Ion Chromatography" 27th Congress on Science and Technology of Thailand, 2001.
3) K. Sa-nguanwong, M. Rayanakorn and S. Wangkarn "Separation of Chlorine-containing Anions using Ion Chromatography" The First PERCH Annual Scientific Conference, 2002.
4) K. Sa-nguanwong, M. Rayanakorn and S. Wangkarn "Development of the Gradient Elution for Separation of Chlorine-containing Anions using Ion Chromatography with Conductivity Detection" 28th Congress on Science and Technology of Thailand, 2002.