

3. Results

3.1 Determinations of Anions with IonPac AS 4 A Column

3.1.1 Investigation of retention times of ions of interest

The most common anions in water 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 drinking water samples. The retention times of these anions found in the investigated water samples are given in **Table 3.1**.

Table 3.1 Retention times of anions obtained with IonPac AS 4 A column using 1.80 mM Na_2CO_3 /1.70 mM $NaHCO_3$ as eluent, at flow rate 2 ml/min.

Ion	Retention time (min)
F^-	0.95
Cl^-	1.51
NO_2^-	1.82
Br^-	2.79
NO_3^-	3.24
PO_4^{3-}	5.30
SO_4^{2-}	6.82

3.1.2 Optimization of IC conditions

3.1.2.1 Results of effect of eluent concentration

Table 3.2 Effect of eluent concentration on

(a) Retention time

Anions	RT (min) at Na ₂ CO ₃ /NaHCO ₃ (mM)				
	1.44/1.36	1.62/1.53	1.80/1.70	1.98/1.89	2.16/2.07
F ⁻	0.98	0.97	0.95	0.94	0.92
Cl ⁻	1.69	1.61	1.57	1.53	1.51
NO ₂ ⁻	2.10	2.01	1.96	1.89	1.85
Br ⁻	3.32	3.17	3.07	2.98	2.92
NO ₃ ⁻	3.93	3.73	3.62	3.49	3.43
PO ₄ ³⁻	7.45	6.43	5.67	5.14	4.67
SO ₄ ²⁻	9.67	8.43	7.47	6.77	6.23

(b) Peak area

Anions	Peak area (1×10^5) at $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ (mM)				
	1.44/1.36	1.62/1.53	1.80/1.70	1.98/1.89	2.16/2.07
F ⁻	2.79	2.76	2.33	2.08	2.01
Cl ⁻	1.85	1.75	2.21	1.86	1.80
NO ₂ ⁻	1.17	1.14	1.04	1.10	1.13
Br ⁻	0.53	0.53	1.12	0.52	0.50
NO ₃ ⁻	0.93	0.97	2.16	0.91	1.90
PO ₄ ³⁻	0.32	0.34	1.21	0.33	0.37
SO ₄ ²⁻	1.25	1.45	1.53	1.73	1.50

(c) Resolution

Anions pair	Resolution of each anion pair at $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ (mM)				
	1.44/1.36	1.62/1.53	1.80/1.70	1.98/1.89	2.16/2.07
F ⁻ & Cl ⁻	7.28	6.46	5.64	6.11	5.73
Cl ⁻ & NO ₂ ⁻	3.94	3.94	3.25	3.61	3.46
NO ₂ ⁻ & Br ⁻	10.21	10.13	8.64	9.77	9.23
Br ⁻ & NO ₃ ⁻	4.45	4.24	3.52	3.98	4.08
NO ₃ ⁻ & PO ₄ ³⁻	17.51	14.67	11.76	10.18	7.97
PO ₄ ³⁻ & SO ₄ ²⁻	8.04	7.97	6.96	7.84	7.95

3.1.2.2 Results of effect of eluent flow rate

Table 3.3 Effect of eluent flow rate on

(a) Retention time

Anions	RT (min) at eluent flow rate (ml/min)				
	1.80	1.90	2.00	2.10	2.20
F ⁻	1.10	1.03	0.95	0.88	0.78
Cl ⁻	1.65	1.55	1.50	1.40	1.28
NO ₂ ⁻	2.00	1.88	1.83	1.72	1.57
Br ⁻	3.03	2.85	2.82	2.62	2.43
NO ₃ ⁻	3.53	3.33	3.28	3.05	2.83
PO ₄ ³⁻	5.90	5.58	5.28	5.03	4.77
SO ₄ ²⁻	7.65	7.23	6.85	6.52	6.20

(b) Peak area

Anions	Peak area (1x10 ⁵) at eluent flow rate (ml/min)				
	1.80	1.90	2.00	2.10	2.20
F ⁻	3.14	3.07	3.10	3.10	3.01
Cl ⁻	2.59	2.69	2.10	2.02	2.00
NO ₂ ⁻	1.38	1.28	1.30	1.24	1.21
Br ⁻	0.98	0.91	0.93	0.84	0.83
NO ₃ ⁻	1.11	1.07	1.09	1.00	0.96
PO ₄ ³⁻	0.55	0.56	0.56	0.57	0.54
SO ₄ ²⁻	2.04	2.04	1.96	1.87	1.82

(c) Theoretical plates

Anions	N at eluent flow rate (ml/min)				
	1.80	1.90	2.00	2.10	2.20
F ⁻	1975	1804	1534	1372	1125
Cl ⁻	4186	4002	3748	3402	2904
NO ₂ ⁻	5590	5032	4860	4293	3790
Br ⁻	9107	8317	8275	7755	7143
NO ₃ ⁻	10172	9452	9171	8673	8333
PO ₄ ³⁻	12392	11189	10824	10325	10191
SO ₄ ²⁻	13640	12564	12206	11808	11728

(d) Resolution

Anions	Resolution of each anion pair at eluent flow rate (ml/min)				
	1.80	1.90	2.00	2.10	2.20
F ⁻ & Cl ⁻	5.47	5.33	5.64	5.44	5.31
Cl ⁻ & NO ₂ ⁻	3.35	3.24	3.25	3.18	2.94
NO ₂ ⁻ & Br ⁻	8.80	8.40	8.64	8.04	7.92
Br ⁻ & NO ₃ ⁻	3.74	3.66	3.52	3.44	3.35
NO ₃ ⁻ & PO ₄ ³⁻	13.46	12.93	11.76	12.04	12.40
PO ₄ ³⁻ & SO ₄ ²⁻	7.38	7.04	6.96	6.80	6.84

3.1.2.3 Summary of optimized IC conditions

The optimized IC conditions obtained with IonPac AS 4 A column established in this work are listed in **Table 3.4**.

Table 3.4 Optimized IC conditions yielding high sensitivity and good resolution of analysis obtained with IonPac AS 4 A.

Operation	Optimal conditions
o Eluent	1.80 mM Na ₂ CO ₃ /1.70 mM NaHCO ₃
o Eluent flow rate	2.00 ml/min
o Detector	conductivity
o Detector temperature compensation	1.7%/ °C
o Background conductivity	3 μS
o Sample loop volume	25 μl

3.1.3 Results of determination of linearity

Table 3.5 Relationship between peak areas and concentrations of anions for determination of linearity obtained with IonPac AS 4 A and 1.80 mM Na₂CO₃/1.70 mM NaHCO₃ as eluent at flow rate 2.00 ml/min, using a conductivity detector.

concentration ng/ μ l	Peak area (1×10^5) (arbitrary unit)						
	F ⁻	Cl ⁻	NO ₂ ⁻	Br ⁻	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻
0.2	0.52	0.65	0.23	0.20	0.25	0.15	0.47
0.4	1.22	1.00	0.51	0.44	0.49	0.25	0.75
0.6	2.03	1.40	0.85	0.59	0.70	0.34	1.10
0.8	2.84	1.84	1.10	0.71	0.92	0.40	1.48
1.0	3.58	2.34	1.41	0.92	1.11	0.48	1.91
2.0	7.08	4.32	2.71	1.93	2.14	0.99	3.50
4.0	14.21	8.66	5.51	3.76	4.15	2.28	6.79
6.0	21.57	13.08	8.34	5.53	6.18	3.32	10.36
8.0	28.54	17.65	11.16	7.60	8.12	4.70	13.47
10.0	35.53	22.29	14.21	9.51	10.26	5.23	17.01
20.0	74.19	51.23	28.45	19.94	23.10	11.90	33.27
40.0	148.47	110.58	66.28	41.19	51.56	25.44	69.30
60.0	214.66	160.09	92.44	69.94	78.51	39.36	103.49
80.0	272.76	225.01	120.48	95.95	113.89	56.12	152.46
100.0	342.92	290.09	149.61	122.67	142.14	72.76	194.64
200.0	672.72	591.88	291.79	265.53	287.72	152.24	405.51
400.0	1345.24	1181.37	583.42	530.35	520.61	320.86	847.84

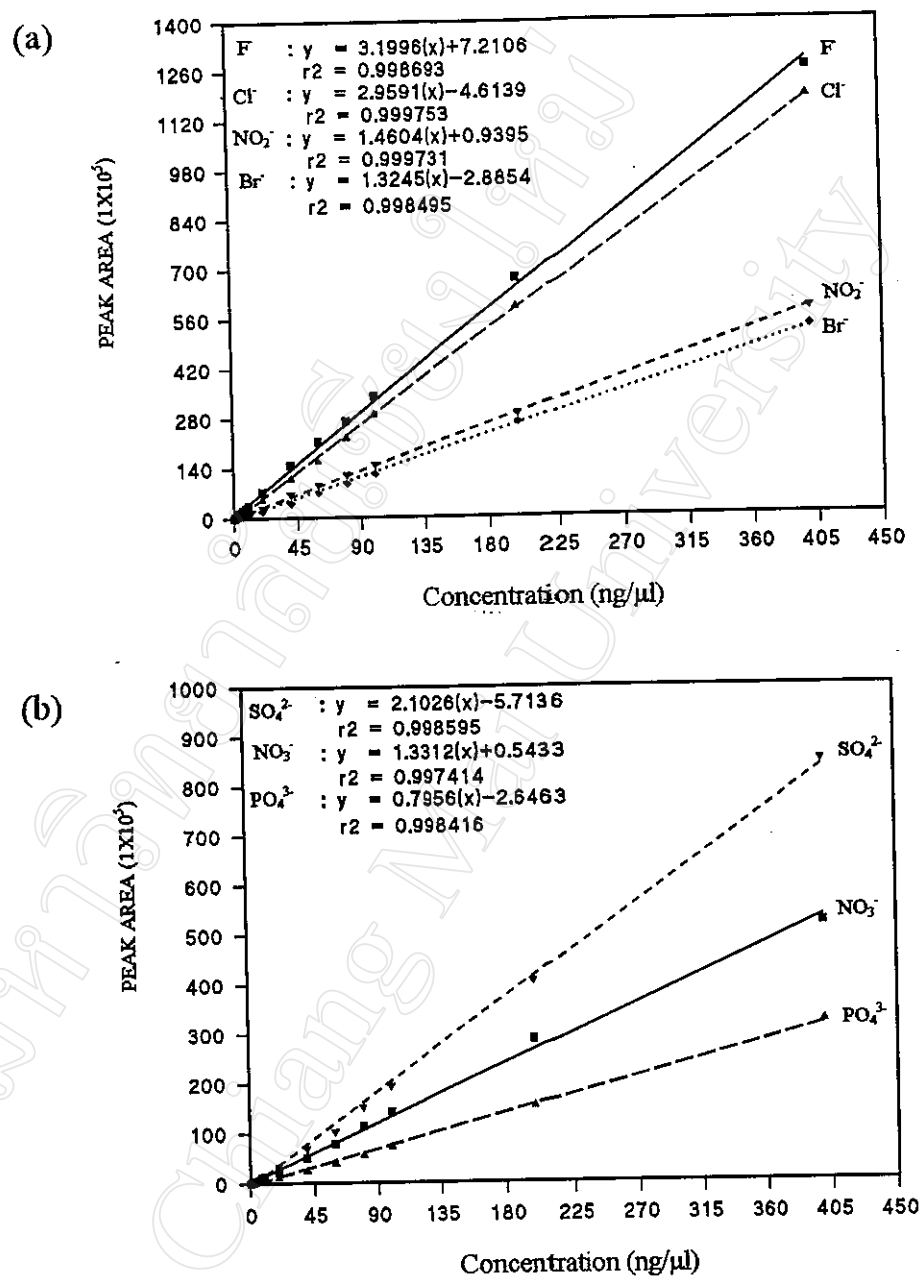
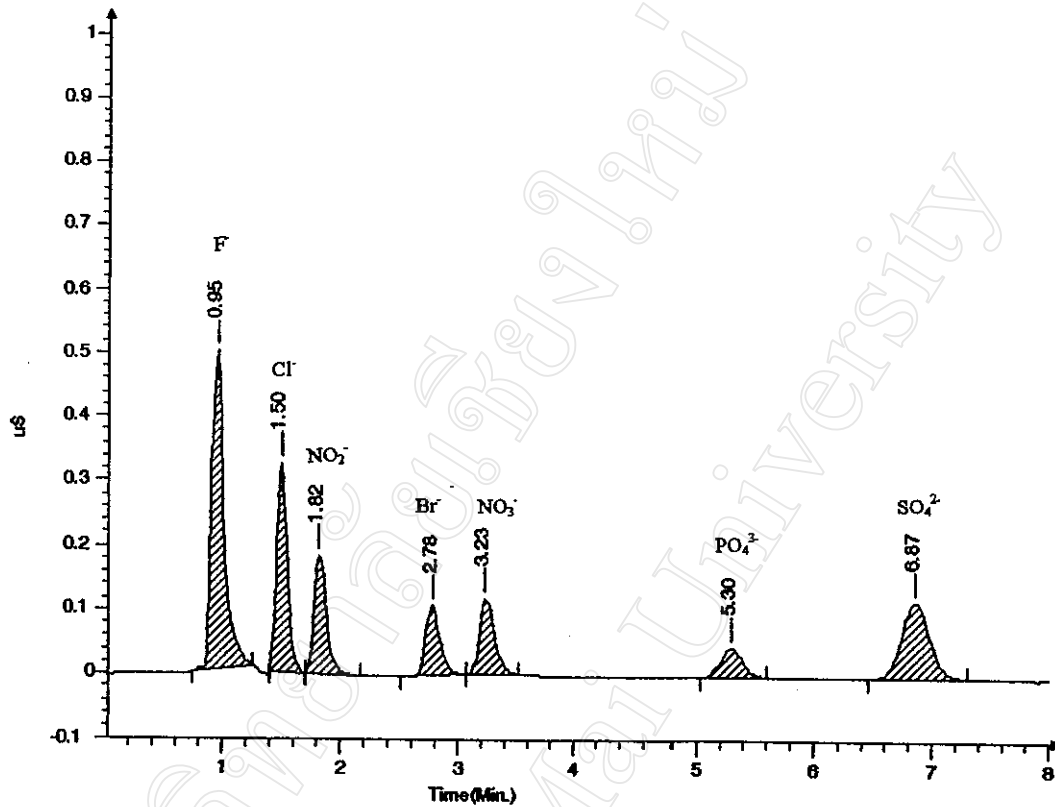


Figure 3.1 Linearity curve for anions obtained with IonPac AS 4 A column and 1.80 mM Na₂CO₃/1.70 mM NaHCO₃ as eluent at flow rate 2.0 ml/min, using a conductivity detector:

(a) for F⁻, Cl⁻, NO₂⁻ and Br⁻

(b) for SO₄²⁻, NO₃⁻ and PO₄³⁻.



Barspec Data System File : C:\BDS\DATA\ANI\ANI2596.BDS

PEAK REPORT

#	RT	Height	Width	Type	Area	%Area	Conc.	Name	Plate N
1	0.95	0.4974	0.097	BB	349304	30.70			526
2	1.50	0.3259	0.097	BB	203680	17.90			1337
3	1.82	0.1841	0.106	BB	132246	11.62			1621
4	2.78	0.1103	0.125	BB	93061	8.18			2742
5	3.23	0.1182	0.136	BB	105253	9.25			3151
6	5.30	0.0448	0.206	BB	58786	5.17			3682
7	6.87	0.1194	0.251	BB	195449	17.18			4154

Figure 3.2 Chromatogram of F^- , Cl^- , NO_2^- , Br^- , NO_3^- , PO_4^{3-} and SO_4^{2-} obtained with IonPac AS 4 A 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.

3.1.4 Results of detection limit and minimum detectable quantity

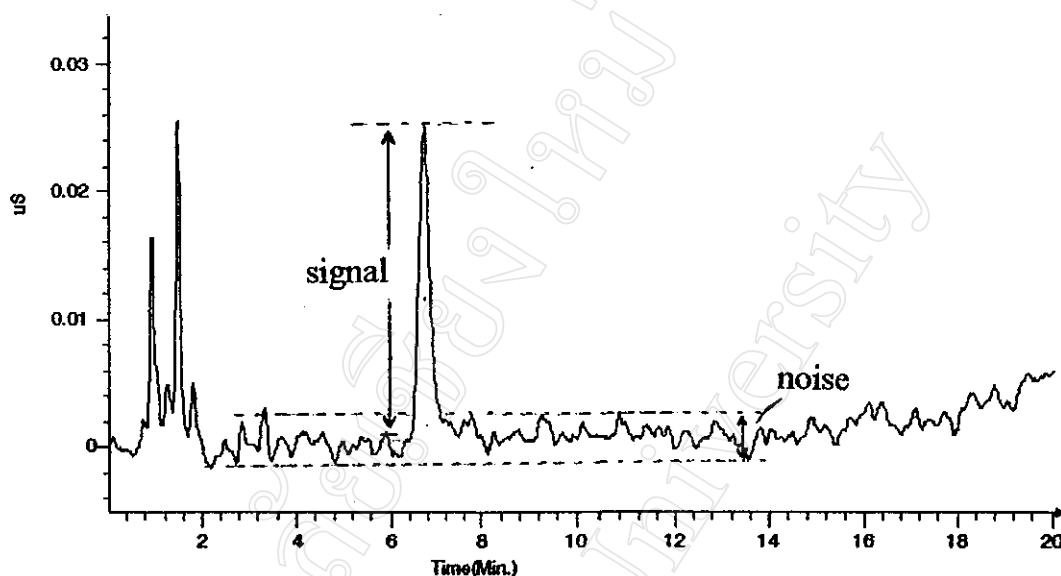


Figure 3.3 Chromatogram illustrating peak height, peak-half width and noise level.

Table 3.6 Detection limits and minimum detectable quantities of anions obtained with IonPac AS 4 A column and 1.80 mM Na_2CO_3 /1.70 mM NaHCO_3 as eluent at flow rate 2 ml/min, using a conductivity detector.

Anions	Concentration, m_x (ng/ μ l)	Noise signal, n (cm)	Peak height, R (cm)	$w_{1/2}$ (min)	L (ng)	MDQ (ng.sec)
F^-	0.02	0.65	2.50	0.05	0.26	0.75
Cl^-	0.02	0.65	3.90	0.05	0.17	0.49
NO_2^-	0.02	0.40	0.70	0.05	0.57	1.74
Br^-	0.02	0.35	0.60	0.07	0.58	2.44
NO_3^-	0.02	0.35	0.40	0.07	0.88	3.91
PO_4^{3-}	0.02	0.30	0.40	0.09	0.75	4.05
SO_4^{2-}	0.02	0.80	4.00	0.13	0.20	1.54

3.1.5 Reproducibility of results

Table 3.7 Reproducibility of results obtained with IonPac AS 4 A column, 1.80 mM Na₂CO₃/1.70 mM NaHCO₃, 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	RT (min)							
	F ⁻ 1.0 ng/μl	Cl ⁻ 1.0 ng/μl	NO ₂ ⁻ 1.0 ng/μl	Br ⁻ 1.0 ng/μl	NO ₃ ⁻ 1.0 ng/μl	PO ₄ ³⁻ 1.0 ng/μl	SO ₄ ²⁻ 1.0 ng/μl	
1	0.95	1.50	1.83	2.82	3.28	5.28	6.85	
2	0.95	1.50	1.83	2.78	3.25	5.30	6.25	
3	0.96	1.51	1.82	2.78	3.23	5.30	6.87	
4	0.95	1.50	1.81	2.79	3.24	5.29	6.86	
5	0.95	1.53	1.80	2.80	3.22	5.31	6.85	
mean	0.95	1.51	1.82	2.79	3.24	5.30	6.86	
SD	0.005	0.013	0.013	0.017	0.023	0.021	0.010	
%RSD	0.53	0.86	0.71	0.61	0.71	0.23	0.14	

Table 3.7 (continued)

(b) Peak areas of each anion investigated

Run	Peak area (1×10^5) (arbitrary unit)							
	F 1.0 ng/ μ l	Cl ⁻ 1.0 ng/ μ l	NO ₂ ⁻ 1.0 ng/ μ l	Br ⁻ 1.0 ng/ μ l	NO ₃ ⁻ 1.0 ng/ μ l	PO ₄ ³⁻ 1.0 ng/ μ l	SO ₄ ²⁻ 1.0 ng/ μ l	
1	3.25	2.13	1.30	0.93	1.08	0.56	1.96	
2	3.10	1.93	1.32	0.92	1.02	0.55	1.93	
3	3.29	2.04	1.32	0.93	1.05	0.59	1.95	
4	3.10	2.08	1.31	0.94	1.06	0.60	1.94	
5	3.16	2.19	1.32	0.95	1.08	0.59	1.98	
mean	3.18	2.07	1.31	0.93	1.06	0.58	1.95	
SD	0.087	0.098	0.01	0.012	0.025	0.022	0.019	
% RSD	2.74	4.73	0.76	1.29	2.36	3.79	0.98	

3.2 Determination of Anions in Drinking Water Samples by IC

From the investigation described in Section 2.3.1, it was found that IonPac AS 4 A 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 drinking water samples. The conditions obtained were applied to determine the amounts of anions in some potable drinking water and some well water samples.

3.2.1 Standard calibration curves of F^- , Cl^- , NO_3^- , PO_4^{3-} and SO_4^{2-}

Analysis for these anions in drinking water samples were constructed from the data in Tables 3.8-3.12. The resultant calibration curves are shown in Figures 3.4-3.8.

Table 3.8 The data used for construction of the standard calibration curve of F^- .

Concentration (ng/ μ l)	Peak area (arbitrary unit)
0.2	52078
0.4	122546
0.6	203487
0.8	284554
1.0	358201
2.0	708489

Table 3.9 The data used for construction of the standard calibration curve of Cl⁻.

Concentration (ng/ μ l)	Peak area (arbitrary unit)
0.6	14045
1.0	234286
4.0	866721
8.0	1765348
20.0	5123014
60.0	16009290

Table 3.10 The data used for construction of the standard calibration curve of NO₃⁻.

Concentration (ng/ μ l)	Peak area (arbitrary unit)
0.2	25487
0.6	70285
1.0	111548
4.0	415476
10.0	1026551
20.0	2310084

Table 3.11 The data used for construction of the standard calibration curve of PO_4^{3-} .

Concentration (ng/ μl)	Peak area (arbitrary unit)
0.05	3809
0.2	15108
0.6	34371
1.0	48269
2.0	99081
4.0	228562

Table 3.12 The data used for construction of the standard calibration curve of SO_4^{2-} .

Concentration (ng/ μl)	Peak area (arbitrary unit)
0.4	75482
1.0	191286
6.0	1036574
10.0	1701459
40.0	6930826
80.0	15246297

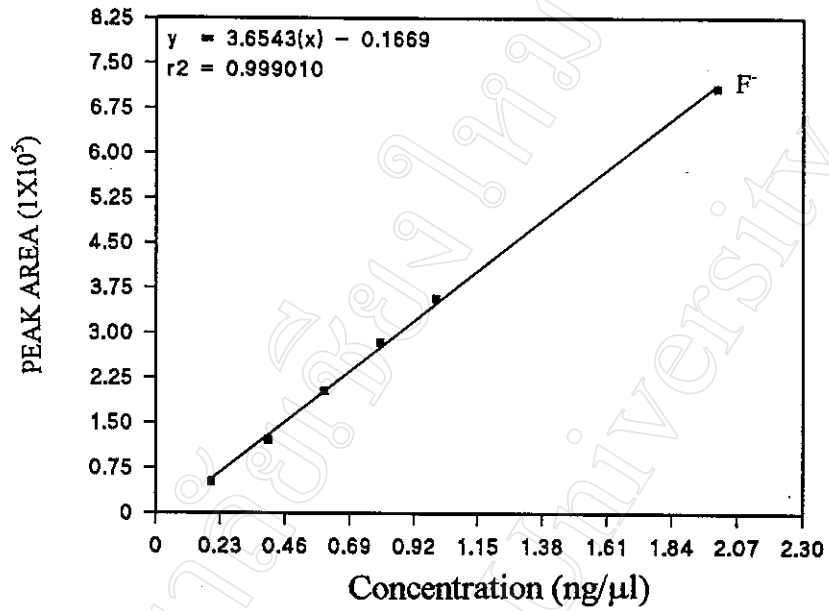


Figure 3.4 Calibration curve of F⁻.

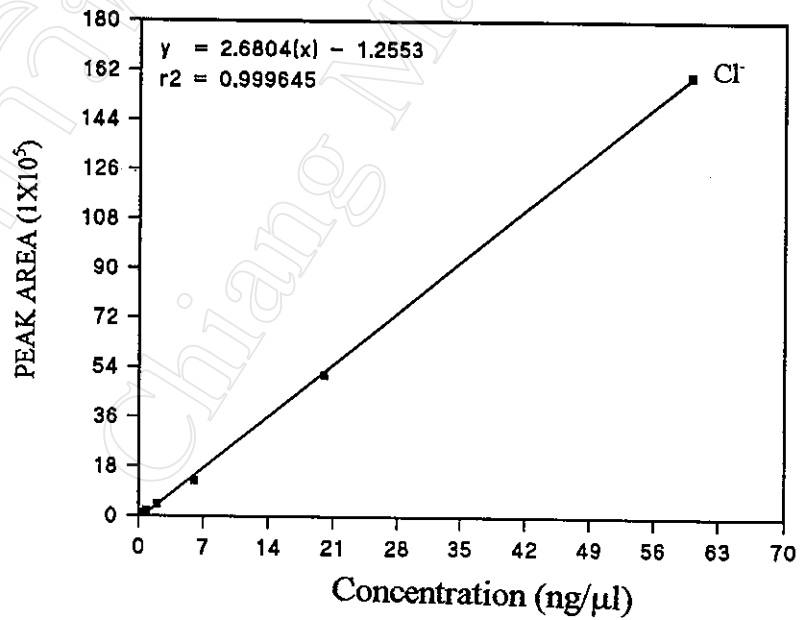


Figure 3.5 Calibration curve of Cl⁻.

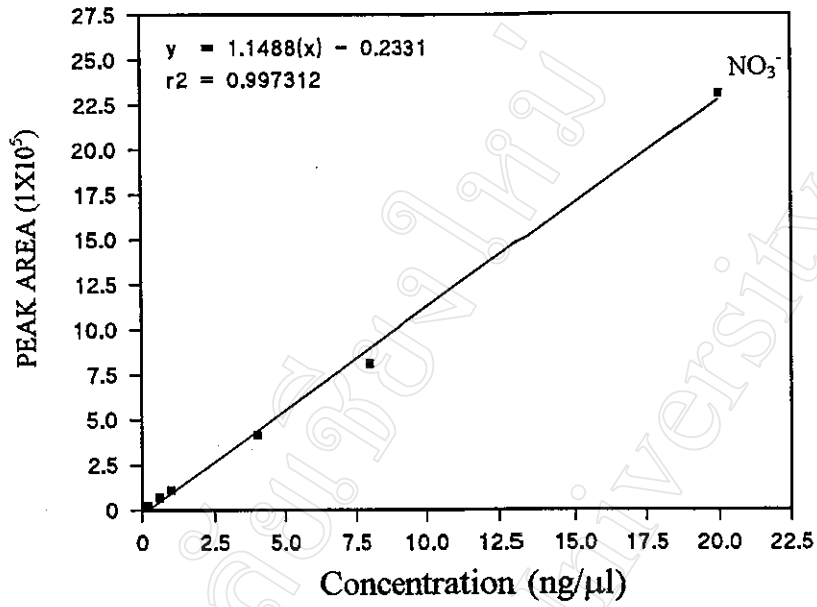


Figure 3.6 Calibration curve of NO_3^- .

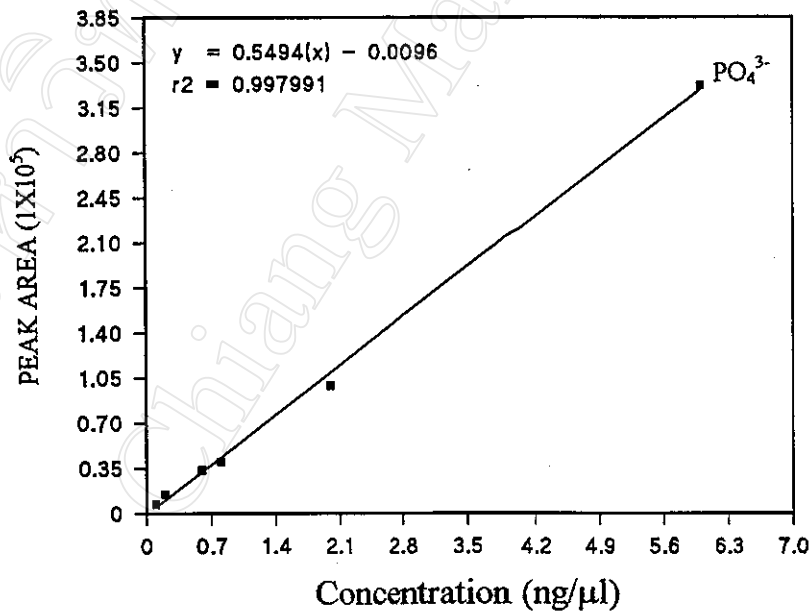


Figure 3.7 Calibration curve of PO_4^{3-} .

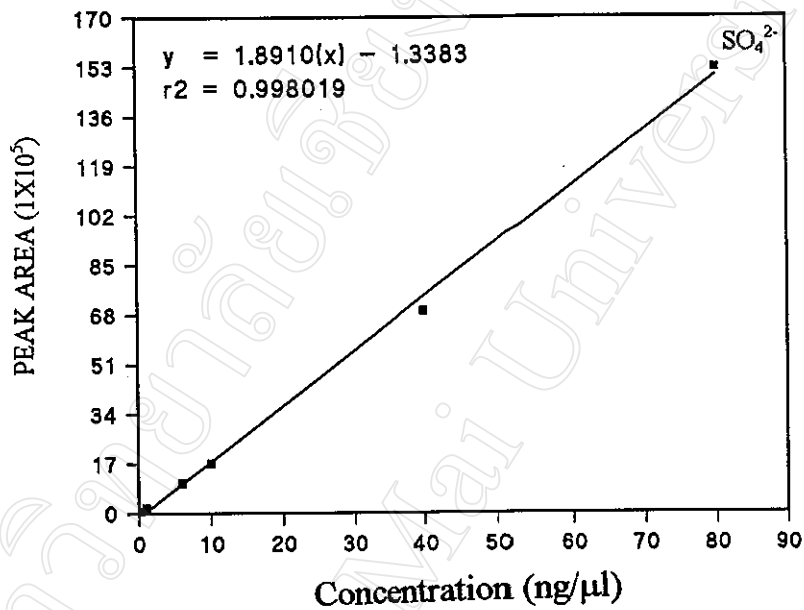


Figure 3.8 Calibration curve of SO_4^{2-} .

3.2.2 The amounts of F^- , Cl^- , NO_3^- , PO_4^{3-} and SO_4^{2-}

The amounts of F^- , Cl^- , NO_3^- , PO_4^{3-} and SO_4^{2-} in drinking water samples were obtained with IonPac AS 4 A. The results of analysis are shown in **Tables 3.13 and 3.14**. The chromatograms of some bottled drinking water sample and some well water samples are shown in **Figures 3.9 and 3.10**.

Table 3.13 Peak areas of anions in bottled drinking water samples (b.w.) and well water samples (w.w.) obtained with IonPac AS 4 A column.

Sample	Peak area (arbitrary unit)*				
	F ⁻	Cl ⁻	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻
b.w. ₁	316275	5238521	NF.	NF.	4924520
b.w. ₂	NF.	185477	11357	7720	9541
b.w. ₃	297081	4455728	18289	48510	9180201
b.w. ₄	NF.	10002484	260256	NF.	3032824
b.w. ₅	NF.	251997	17479	NF.	9748
b.w. ₆	NF.	203449	11458	NF.	8202
b.w. ₇	387261	660827	104872	NF.	11766729
b.w. ₈	NF.	1691756	30126	NF.	3628
b.w. ₉	104576	5349078	NF.	NF.	504046
b.w. ₁₀	NF.	50993281	692481	NF.	1548402
w.w. ₁	NF.	1525502	1410465	321826	7877720
w.w. ₂	NF.	6560208	352880	268704	4143427
w.w. ₃	154896	14250177	134570	NF.	9303751
w.w. ₄	119028	4425485	1312762	NF.	5546806
w.w. ₅	NF.	10136570	1148965	122779	4074227
w.w. ₆	NF.	11643284	230186	228670	9866708
w.w. ₇	120479	10703281	2384721	174896	9399004
w.w. ₈	NF.	1492751	238855	238880	4944660
w.w. ₉	123451	14201620	656961	177981	3311798
w.w. ₁₀	130908	7025488	136880	NF.	2458721

* averaged from 3 runs.

Table 3.14 Concentrations of analyte anions in bottled drinking water samples (b.w.) and well water samples (w.w.) obtained with IonPac AS 4 A column.

Sample	Concentration (ng/ μ l)*				
	F ⁻	Cl ⁻	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻
b.w. ₁	0.95	20.01	NF.	NF.	28.65
b.w. ₂	NF.	0.78	0.10	0.12	0.51
b.w. ₃	0.79	16.63	0.17	0.77	51.00
b.w. ₄	NF.	37.34	2.52	NF.	18.19
b.w. ₅	NF.	1.15	0.16	NF.	0.52
b.w. ₆	NF.	0.87	0.10	NF.	0.44
b.w. ₇	1.10	3.06	1.01	NF.	64.71
b.w. ₈	NF.	7.66	0.28	NF.	0.19
b.w. ₉	0.31	19.97	NF.	NF.	29.32
b.w. ₁₀	NF.	173.38	6.82	NF.	9.08
w.w. ₁	NF.	56.13	12.34	5.79	44.31
w.w. ₂	NF.	24.27	3.44	4.84	24.09
w.w. ₃	1.55	53.44	1.25	NF.	51.69
w.w. ₄	1.19	17.40	11.49	NF.	35.52
w.w. ₅	NF.	40.54	10.05	2.21	23.67
w.w. ₆	NF.	42.71	2.23	4.12	54.82
w.w. ₇	1.20	39.25	19.88	3.15	52.22
w.w. ₈	NF.	55.04	2.32	4.30	28.77
w.w. ₉	1.23	53.76	6.48	3.20	19.23
w.w. ₁₀	1.31	26.23	1.28	NF.	14.23

* averaged from 3 runs. However, actual concentration ranges in ng/ μ l for F⁻, Cl⁻, NO₃⁻, PO₄³⁻ and SO₄²⁻ were NF.-1.55, 0.78-173.38, NF.-19.88, NF.-5.79 and 0.19-54.82, respectively.

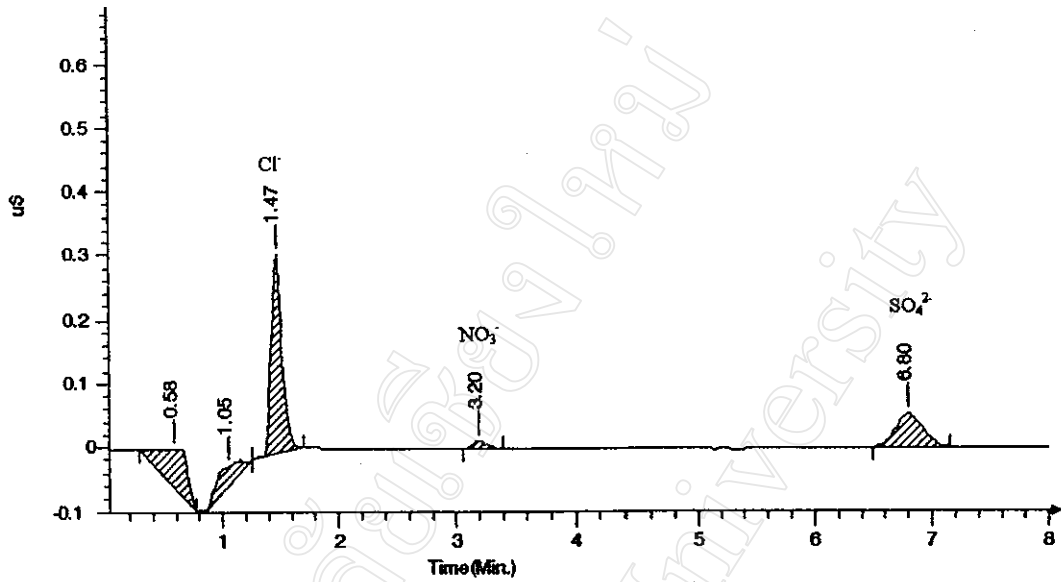


Figure 3.9 Typical chromatogram of b.w.₆ water sample obtained with IonPac AS 4 A column.

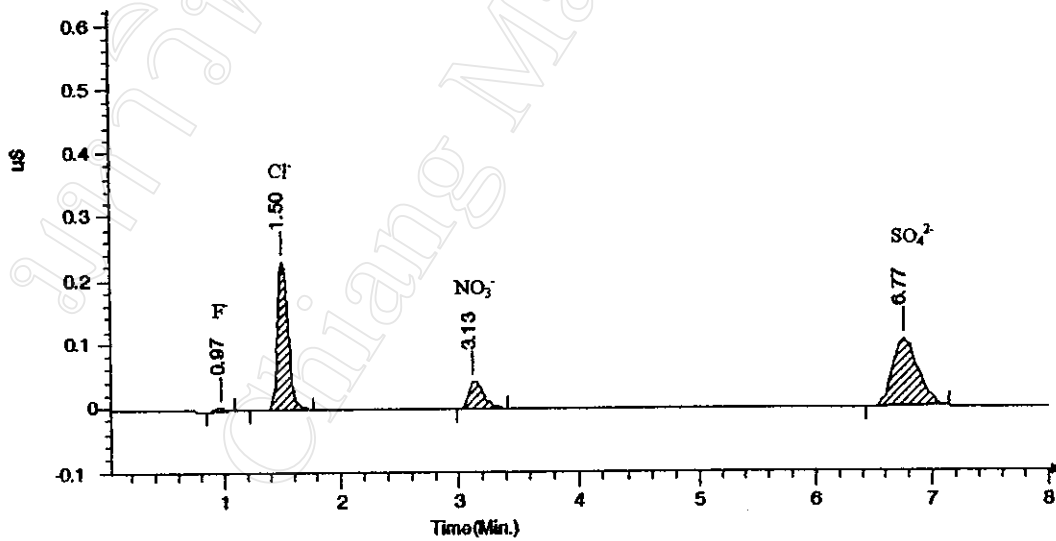


Figure 3.10 Typical chromatogram of w.w.₄ sample obtained with IonPac AS 4 A column.

3.2.3 % Recovery of each anion in drinking water samples

Reliability of the % recovery obtained from drinking water samples was confirmed using the “spike” method. The results are shown in **Table 3.15-3.19** and confirmation of analyte peaks in bottled drinking water samples is shown in **Figure 3.11-3.13**.

Table 3.15 % Recovery of F⁻ in b.w.₃ sample when spiked with standard F⁻ at various concentration (ng/μl).

Spiked standard F ⁻ (ng/μl)	Peak area (arbitrary unit)	Concentration (ng/μl)	% Recovery
b.w. ₃	235489	0.70	
b.w. ₃ + 1 ng/μl	594537	1.69	99.00
b.w. ₃ + 2 ng/μl	920278	2.63	96.50
b.w. ₃ + 3 ng/μl	1321565	3.69	99.67
b.w. ₃ + 4 ng/μl	1658271	4.64	98.50
		mean	98.42

Table 3.16 % Recovery of Cl^- in b.w.₆ sample when spiked with standard Cl^- at various concentration (ng/ μl).

Spiked standard Cl^- (ng/ μl)	Peak area (arbitrary unit)	Concentration (ng/ μl)	% Recovery
b.w. ₆	179473	0.82	
b.w. ₆ + 1 ng/ μl	390528	1.78	96.00
b.w. ₆ + 2 ng/ μl	598174	2.76	97.00
b.w. ₆ + 3 ng/ μl	808265	3.74	97.33
b.w. ₆ + 4 ng/ μl	1018488	4.71	97.25
		mean	96.90

Table 3.17 % Recovery of NO_3^- in b.w.₆ sample when spiked with standard NO_3^- at various concentration (ng/ μl).

Spiked standard NO_3^- (ng/ μl)	Peak area (arbitrary unit)	Concentration (ng/ μl)	% Recovery
b.w. ₆	11480	0.10	
b.w. ₆ + 1 ng/ μl	109354	1.05	95.00
b.w. ₆ + 2 ng/ μl	217329	2.08	99.00
b.w. ₆ + 3 ng/ μl	320175	3.07	99.00
b.w. ₆ + 4 ng/ μl	441426	4.05	98.75
		mean	97.94

Table 3.18 % Recovery of PO_4^{3-} in b.w.₂ sample when spiked with standard PO_4^{3-} at various concentration (ng/ μl).

Spiked standard PO_4^{3-} (ng/ μl)	Peak area (arbitrary unit)	Concentration (ng/ μl)	% Recovery
b.w. ₂	8511	0.12	
b.w. ₂ + 1 ng/ μl	77138	1.09	97.00
b.w. ₂ + 2 ng/ μl	117275	2.11	99.50
b.w. ₂ + 3 ng/ μl	168426	3.02	96.67
b.w. ₂ + 4 ng/ μl	228548	4.10	99.50
		mean	98.17

Table 3.19 % Recovery of SO_4^{2-} in b.w.₆ sample when spiked with standard SO_4^{2-} at various concentration (ng/ μl).

Spiked standard SO_4^{2-} (ng/ μl)	Peak area (arbitrary unit)	Concentration (ng/ μl)	% Recovery
b.w. ₆	8281	0.44	
b.w. ₆ + 1 ng/ μl	27007	1.43	99.00
b.w. ₆ + 2 ng/ μl	44657	2.37	96.50
b.w. ₆ + 3 ng/ μl	62770	3.34	96.67
b.w. ₆ + 4 ng/ μl	81780	4.34	97.50
		mean	97.42

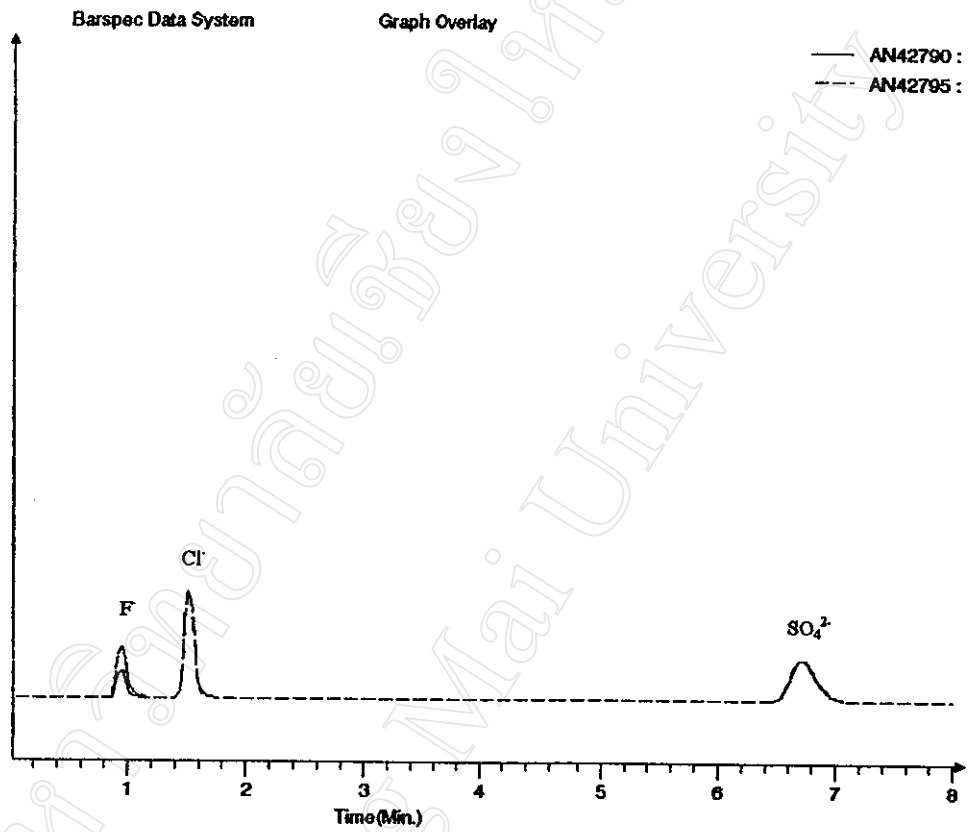


Figure 3.11 Chromatograms of b.w.₉ sample (AN 42790) and b.w.₉ sample with spiked F⁻ (AN 42795) in comparison.

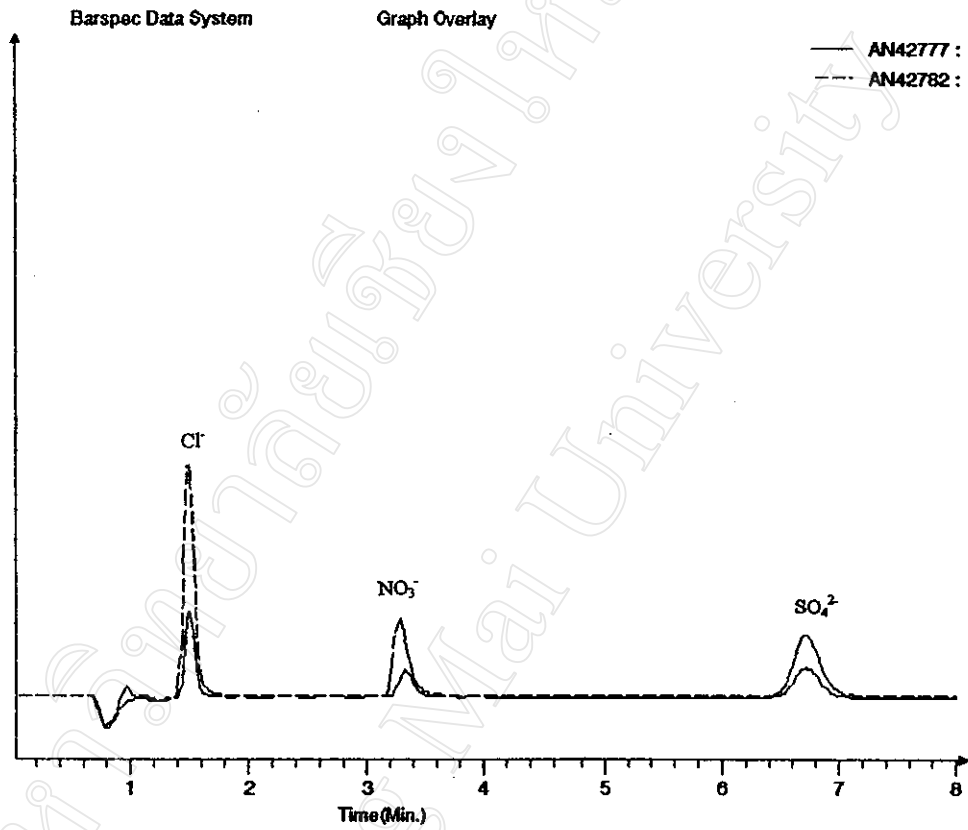


Figure 3.12 Chromatograms of b.w.₆ sample (AN 42777) and b.w.₆ sample with spiked Cl⁻, NO₃⁻ and SO₄²⁻ (AN 42782) in comparison.

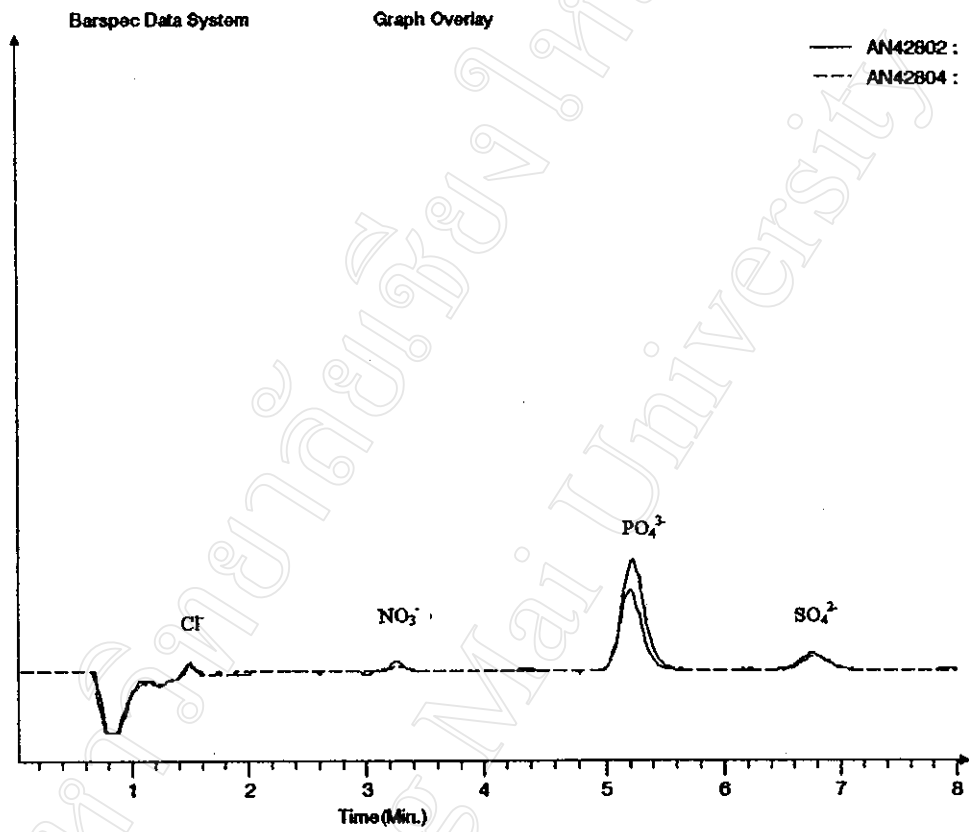


Figure 3.13 Chromatograms of b.w.₂ sample (AN 42802) and b.w.₂ sample with spiked PO₄³⁻ (AN 42804) in comparison.

3.2.4 Analysis for F^- , Cl^- , NO_3^- , PO_4^{3-} and SO_4^{2-} by ion selective electrode method and spectrophotometric method

3.2.4.1 The amounts of F^- in bottled drinking water samples and well water samples were determined by ion-selective electrode method (ISE method). The results of analysis were compared with the results of IC technique in Table 3.20.

Table 3.20 Comparison of the results of F^- analysis in bottled drinking water samples and well water samples by IC technique and by ISE technique.

Sample	IC technique (ng/ μ l)	ISE technique (ng/ μ l)	D_i	$(D_i - \bar{D})$	$(D_i - \bar{D})^2$
b.w. ₃	0.79	0.70	0.09	0.04	0.002
b.w. ₇	1.10	0.98	0.12	0.07	0.005
b.w. ₉	0.31	0.32	-0.01	0.04	0.002
w.w. ₃	1.55	1.51	0.04	0.01	0.0001
w.w. ₄	1.19	1.17	0.02	0.03	0.0009
w.w. ₉	1.23	1.18	0.05	0.00	0.000
			Σ 0.31		Σ 0.01
\bar{D}					0.05
S_d					0.04
$t_{calc.}$					3.06

3.2.4.2 The amounts of Cl^- , NO_3^- , PO_4^{3-} and SO_4^{2-} in bottled drinking water samples and well water samples were determined by spectroanalytical method. The results of analysis were compared with the results of IC technique in Tables 3.21-3.24.

Table 3.21 Comparison of the results of Cl^- analysis in bottled drinking water samples and well water samples by IC technique and by Mercury (II) thiocyanate method.

Sample	IC technique (ng/ μl)	Spectro. technique (ng/ μl)	D_i	$(D_i - \bar{D})$	$(D_i - \bar{D})^2$
b.w. ₁	20.01	19.57	0.44	0.45	0.20
b.w. ₇	3.06	2.61	0.45	0.44	0.19
b.w. ₉	19.97	18.85	1.12	0.23	0.05
w.w. ₄	17.40	16.65	0.75	0.14	0.02
w.w. ₉	53.76	51.89	1.89	1.00	1.00
w.w. ₁₀	26.23	25.56	0.67	0.22	0.05
			Σ 5.32		Σ 1.51
\bar{D}					0.89
S_d					0.55
$t_{\text{calc.}}$					3.96

Table 3.22 Comparison of the results of NO_3^- analysis in bottled drinking water samples and well water samples by IC technique and by ultraviolet spectrophotometric screening method.

Sample	IC technique (ng/ μl)	Spectro. technique (ng/ μl)	D_i	$(D_i - \bar{D})$	$(D_i - \bar{D})^2$
b.w. ₁₀	6.82	6.73	0.09	0.09	0.008
w.w. ₁	12.34	12.29	0.05	0.13	0.017
w.w. ₄	11.49	11.23	0.26	0.08	0.006
w.w. ₆	2.23	2.52	-0.29	0.11	0.012
w.w. ₈	2.32	2.17	0.15	0.03	0.0009
w.w. ₁₀	1.28	1.01	0.27	0.09	0.008
			Σ 1.11	Σ 0.05	
\bar{D}					0.18
S_d					0.10
t_{calc}					4.41

Table 3.23 Comparison of the results of PO_4^{3-} analysis in bottled drinking water samples and well water samples by IC technique and by ascorbic acid method.

Sample	IC technique (ng/ μl)	Spectro. technique (ng/ μl)	D_i	$(D_i - \bar{D})$	$(D_i - \bar{D})^2$
b.w. ₃	0.77	0.62	0.15	0.06	0.004
w.w. ₁	5.79	5.62	0.17	0.04	0.002
w.w. ₂	4.84	4.41	0.43	0.15	0.022
w.w. ₅	2.21	1.99	0.22	0.04	0.002
w.w. ₈	4.30	4.06	0.24	0.03	0.0009
w.w. ₉	3.20	3.25	-0.05	0.16	0.025
			Σ 1.26		Σ 0.06
\bar{D}					0.21
S_d					0.11
$t_{\text{calc.}}$					4.68

Table 3.24 Comparison of the results of SO_4^{2-} analysis in bottled drinking water samples and well water samples by IC technique and by turbidimetric method.

Sample	IC technique (ng/ μl)	Spectro. technique (ng/ μl)	D_i	$(D_i - \bar{D})$	$(D_i - \bar{D})^2$
b.w. ₁	28.65	26.40	2.25	0.01	0.0001
b.w. ₇	64.71	61.02	3.69	1.43	2.040
w.w. ₁	44.31	40.66	3.65	1.39	1.930
w.w. ₃	51.69	53.67	-1.98	-4.24	17.970
w.w. ₈	28.77	26.20	2.57	0.31	0.096
w.w. ₁₀	14.23	10.80	3.43	1.17	1.369
			Σ 13.62		Σ 23.40
\bar{D}					2.27
S_d					2.16
$t_{\text{calc.}}$					2.58

3.3 Determination of Alkaline Earth Metal Ions with IonPac CS 12 Column

3.3.1 Investigation of retention times of ions of interest

The ions of interest in this work were Mg^{2+} , Ca^{2+} and Sr^{2+} which could have been contaminating metal ions in drinking water samples. The retention times of these metal ions are given in Table 3.25.

Table 3.25 Retention times of cations obtained with IonPac CS 12 column using 20 mM MSA as eluent at flow rate 1.0 ml/min and 25 mM TBAOH as regenerant at flow rate 6.0 ml/min .

Ion	Retention time (min)
Mg^{2+}	7.58
Ca^{2+}	9.55
Sr^{2+}	11.50

3.3.2 Optimization of IC conditions

3.3.2.1 Results of effect of eluent concentration

Table 3.26 Effect of eluent concentration on

(a) Retention time

Ions	RT (min) at MSA concentration (mM)			
	10	15	20	25
Mg ²⁺	24.05	11.70	7.58	5.67
Ca ²⁺	32.13	15.25	9.55	6.93
Sr ²⁺	40.23	18.88	11.50	8.18

(b) Peak area

Ions	Peak area (1x10 ⁵) at MSA concentration (mM)			
	10	15	20	25
Mg ²⁺	3.58	3.46	3.32	2.66
Ca ²⁺	3.42	3.33	3.05	1.46
Sr ²⁺	0.89	0.87	0.82	0.44

(c) Resolution

Ions	Resolution of each cation pair at MSA concentration (mM)			
	10	15	20	25
Mg ²⁺ & Ca ²⁺	8.17	6.69	5.52	5.74
Ca ²⁺ & Sr ²⁺	6.21	5.33	4.47	4.88

3.3.2.2 Results of eluent flow rate

Table 3.27 Effect of eluent flow rate

(a) Retention time

Ions	RT (min) at eluent flow rate (ml/min)			
	0.8	0.9	1.0	1.1
Mg ²⁺	9.51	8.43	7.58	6.93
Ca ²⁺	11.97	10.65	9.55	8.72
Sr ²⁺	14.40	12.83	11.57	10.48

(b) Peak area

Ions	Peak area (1x10 ⁵) at eluent flow rate (ml/min)			
	0.8	0.9	1.0	1.1
Mg ²⁺	4.61	3.84	3.20	2.26
Ca ²⁺	3.66	3.16	3.05	1.91
Sr ²⁺	1.09	0.97	0.80	0.41

(c) The resolution

Ions	Resolution of each cation pair at eluent flow rate (ml/min)			
	10	15	20	25
Mg ²⁺ & Ca ²⁺	5.73	5.72	5.52	5.61
Ca ²⁺ & Sr ²⁺	4.71	4.56	4.61	4.83

Table 3.27 (continued)

(d) The theoretical plates

Ions	N at eluent flow rate (ml/min)			
	0.8	0.9	1.0	1.1
Mg ²⁺	9813	9497	9090	9328
Ca ²⁺	10203	9860	9352	9875
Sr ²⁺	10708	9483	9216	12364

3.3.2.3 Summary of optimized IC conditions

The optimized IC conditions obtained with IonPac CS 12 column established in this work are listed in **Table 3.28**.

Table 3.28 Optimized ion chromatographic conditions obtained with IonPac CS 12 column.

Operation	Optimal conditions
o Eluent	20 mM methansulfonic acid (MSA)
o Regenerant	25 mM tetrabutyl ammonium hydroxide (TBAOH)
o Flow-rate	1.0 ml/min (of eluent) 6.0 ml/min (of regenerant)
o Detector	conductivity
o Detector temperature compensation	1.7%/ ° C
o Background conductivity	10 µS
o sample loop volume	25 µl

3.3.3 Results of determination of linearity

Table 3.29 Relationship between peak area and concentration of ions for determination of linearity obtained with IonPac CS 12 column, 20 mM MSA at flow rate 1.0 ml/min as eluent and 25 mM TBAOH at flow rate 6.0 ml/min as regenerant, using a conductivity detector.

Concentration ng/ μ l	Peak area (1×10^5) (arbitrary units)		
	Mg ²⁺	Ca ²⁺	Sr ²⁺
0.2	1.01	1.40	0.19
0.4	1.63	1.71	0.40
0.6	2.36	2.47	0.55
0.8	3.01	3.02	0.71
1.0	3.81	3.15	0.92
2.0	7.25	5.60	1.81
4.0	15.09	11.00	3.73
6.0	22.03	15.11	5.54
8.0	28.92	19.14	7.23
10.0	34.08	21.89	8.60
20.0	63.67	42.00	18.78
40.0	123.62	81.18	36.79
60.0	183.69	120.69	50.71
80.0	252.15	164.38	70.56
100.0	327.78	199.16	83.40
200.0	602.62	375.60	161.82
300.0	878.64	556.65	225.18

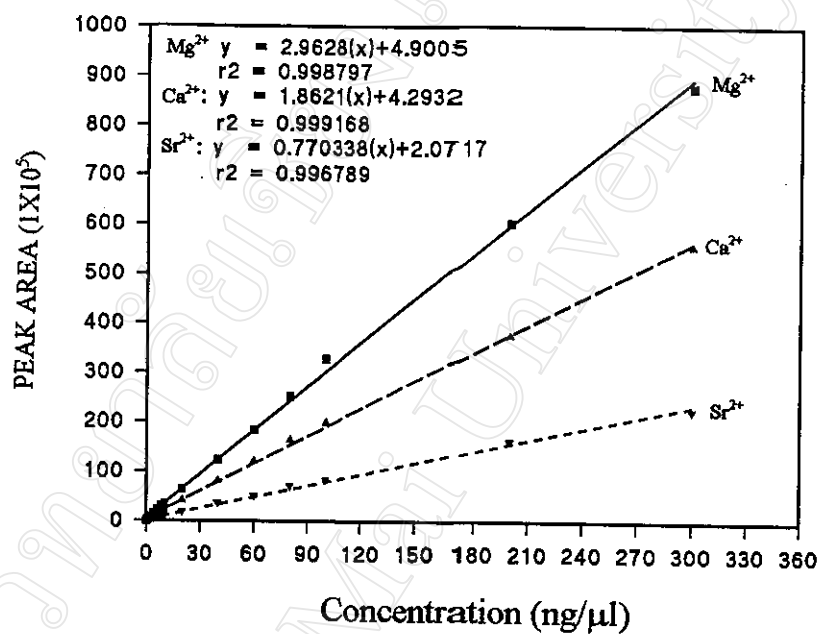
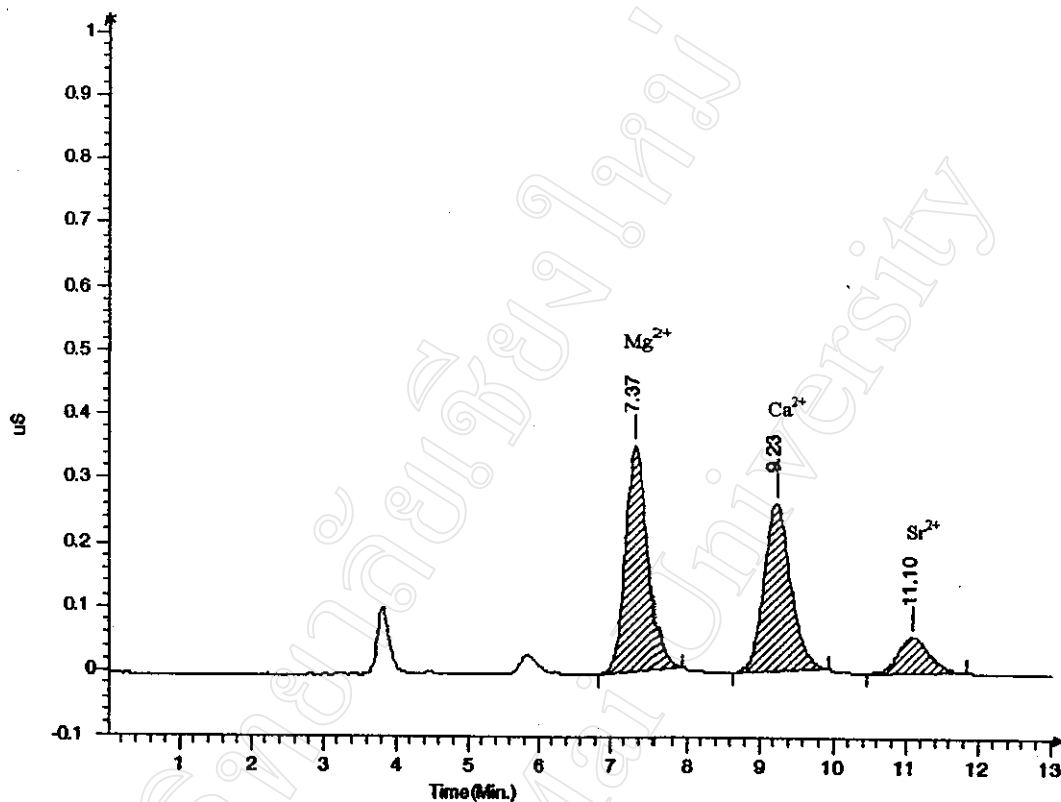


Figure 3.14 Linearity curve for cations obtained with IonPac CS 12 column, 20 mM MSA as eluent at flow rate 1.0 ml/min, 25 mM TBAOH as regenerant at flow rate 6.0 ml/min, using a conductivity detector.



BarSpec Data System File : C:\BDS\DATA\CAT5\CAT52887.BDS

PEAK REPORT

#	RT	Height	Width	Type	Area	%Area	Conc.	Name	Plate N
1	7.37	0.3515	0.315	BB	725462	46.61			3030
2	9.23	0.2603	0.365	BB	659299	42.36			3189
3	11.10	0.0559	0.475	BB	171670	11.03			3031

Figure 3.15 Chromatogram of Mg²⁺, Ca²⁺ and Sr²⁺ obtained with IonPac CS 12 column, 20 mM MSA as eluent at flow rate 1.0 ml/min, 25 mM TBAOH as regenerant at flow rate 6.0 ml/min using a conductivity detector.

3.3.4 Results of detection limit and minimum detectable quantity

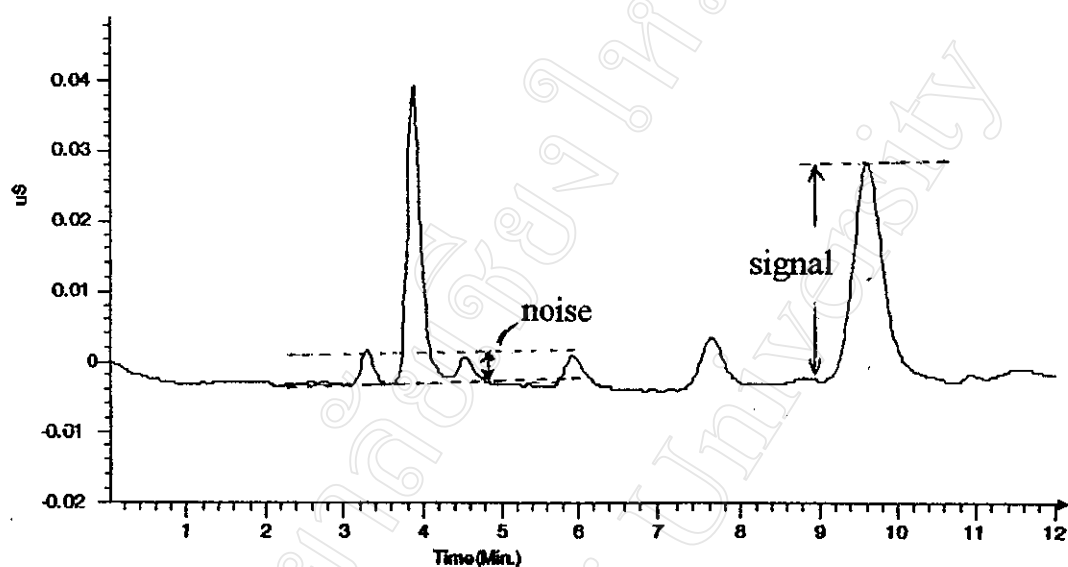


Figure 3.16 Chromatogram illustrating peak-height, peak-half width and noise level.

Table 3.30 Detection limits and minimum detectable quantities of ions obtained with IonPac CS 12 column, 20 mM MSA as eluent at flow rate 1.0 ml/min, 25 mM TBAOH as regenerant at flow rate 6.0 ml/min.

Ions	Concentration, mx (ng/ μ l)	Noise signal, n (cm)	Peak height, R (cm)	$W_{1/2}$ (min)	L (ng)	MDQ (ng.sec)
Mg ²⁺	0.01	0.23	0.65	0.16	0.18	1.73
Ca ²⁺	0.02	0.23	2.90	0.20	0.08	0.96
Sr ²⁺	0.05	0.19	0.10	0.19	4.75	53.01

3.3.5 Reproducibility of results

Table 3.31 Reproducibility of results obtained with IonPac CS 12 column, 20 mM MSA as eluent at flow rate 1.0 ml/min; 25 mM TBAOH as regenerant at flow rate 6.0 ml/min using a conductivity detector with temperature compensation 1.7%/ °C and output range 10 μ S.

(a) Retention times of the cations investigated.

Run	RT (min)		
	Mg ²⁺ 1.0 ng/ μ l	Ca ²⁺ 1.0 ng/ μ l	Sr ²⁺ 1.0 ng/ μ l
1	7.37	9.28	11.12
2	7.37	9.28	11.14
3	7.37	9.27	11.13
4	7.37	9.28	11.13
5	7.32	9.27	11.13
mean	7.36	9.28	11.13
SD	0.025	0.008	0.008
% RSD	0.340	0.086	0.072

Table 3.31 (continued)

(b) Peak areas of the cations investigated.

Run	Peak area (1×10^5)(arbitrary unit)		
	Mg ²⁺ 1.0 ng/ μ l	Ca ²⁺ 1.0 ng/ μ l	Sr ²⁺ 1.0 ng/ μ l
1	3.32	3.05	0.82
2	3.26	2.96	0.82
3	3.20	3.01	0.79
4	3.05	3.04	0.79
5	3.18	3.12	0.08
mean	3.20	3.04	0.80
SD	0.117	0.014	0.018
% RSD	3.656	0.460	2.25

3.4 Determination of Metal Ions in Drinking Water Samples by IC

The IonPac CS 12 analytical column, designed to separate Mg^{2+} , Ca^{2+} and Sr^{2+} with suppressed conductivity detection, was used for the analysis for Mg^{2+} , Ca^{2+} and Sr^{2+} in drinking water samples. The optimized conditions were applied to determine the amounts of cations in drinking water samples in this work.

3.4.1 Standard calibration curves of Mg^{2+} , Ca^{2+} and Sr^{2+} were constructed from data in Tables 3.32-3.34 and the peak areas obtained are shown in Figures 3.17-3.19.

Table 3.32 The data used for construction of the standard calibration curve of Mg^{2+} .

Concentration (ng/ μ l)	Peak area (arbitrary unit)
0.02	101481
0.60	236375
1.00	381246
4.00	1509297
10.00	3408254
20.00	6367428

Table 3.33 The data used for construction of the standard calibration of Ca^{2+} .

Concentration (ng/ μl)	Peak area (arbitrary unit)
0.02	140298
0.80	302112
2.00	560725
8.00	1914238
20.00	4200755
60.00	12069237

Table 3.34 The data used for construction of the standard calibration of Sr^{2+} .

Concentration (ng/ μl)	Peak area (arbitrary unit)
0.05	5289
0.10	9455
0.20	19287
0.40	40527
0.60	55282
0.80	71286

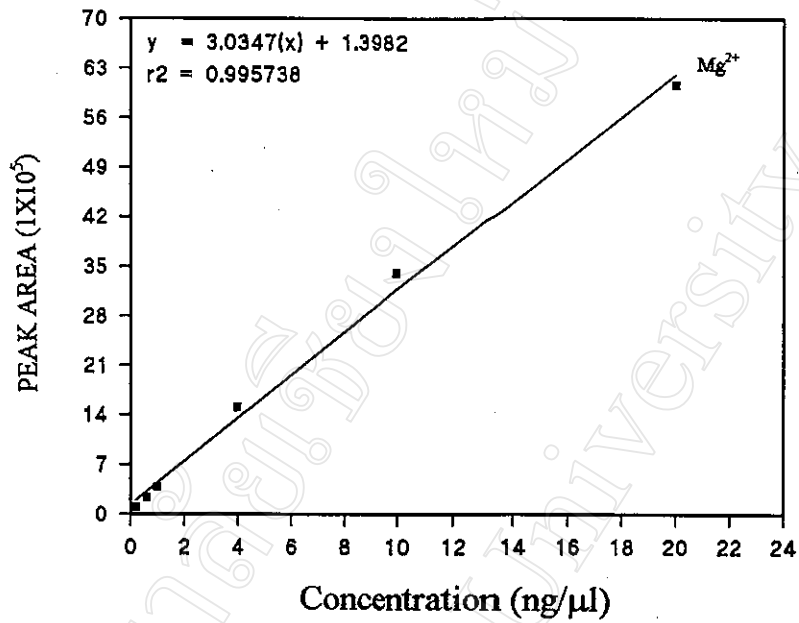


Figure 3.17 Calibration curve of Mg²⁺.

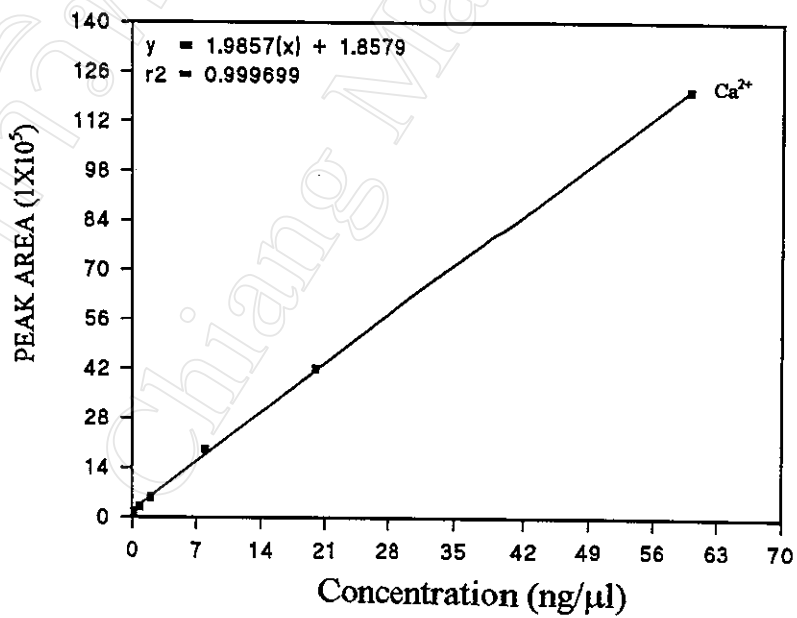


Figure 3.18 Calibration curve of Ca²⁺.

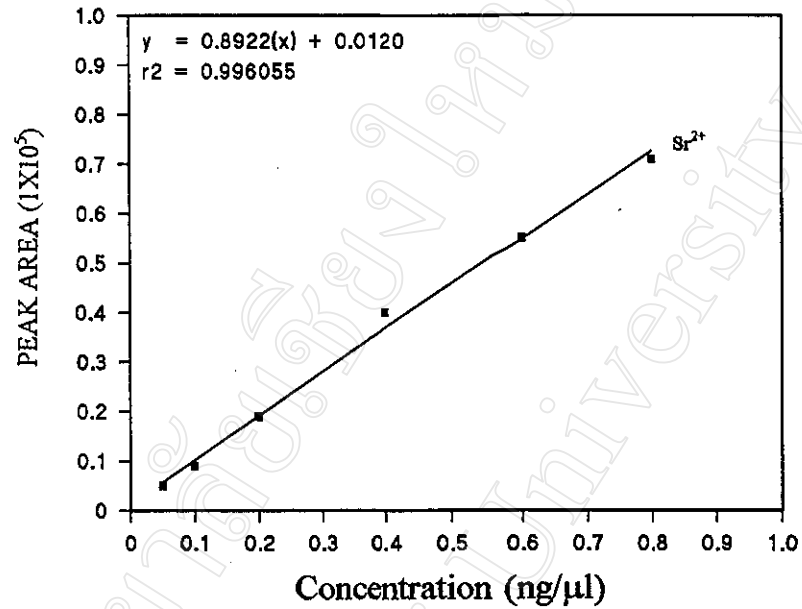


Figure 3.19 Calibration curve of Sr²⁺.

3.4.2 Analysis of cations in drinking water samples

The amounts of Mg²⁺, Ca²⁺ and Sr²⁺ in drinking water samples were obtained with IonPac CS12. The results of analysis are shown in Tables 3.35 and 3.36. Chromatograms of some bottled drinking water sample and some well water samples are shown in Figures 3.20 and 3.21.

Table 3.35 Peak areas and concentrations of cations in bottled drinking water samples (b.w.) and well water samples (w.w.) obtained with IonPac CS 12 column.

Sample	Mg ²⁺		Ca ²⁺		Sr ²⁺	
	Peak area (1x10 ⁵ unit)	Concentration (ng/μl)*	Peak area (1x10 ⁵ unit)	Concentration (ng/μl)*	Peak area (1x10 ⁵ unit)	Concentration (ng/μl)*
b.w. ₁	0.17	0.05	1.04	0.39	0.19	0.21
b.w. ₂	NF.	-	0.27	0.10	NF.	-
b.w. ₃	1.59	0.42	7.00	2.62	NF.	-
b.w. ₄	0.11	0.03	0.86	0.32	NF.	-
b.w. ₅	0.09	0.02	0.48	0.18	0.15	0.17
b.w. ₆	0.26	0.07	2.64	0.99	NF.	-
b.w. ₇	2.55	0.67	7.58	2.84	NF.	-
b.w. ₈	1.40	0.37	8.03	3.01	NF.	-
b.w. ₉	0.31	0.08	1.46	0.55	NF.	-
b.w. ₁₀	1.56	0.41	3.78	1.41	NF.	-
w.w. ₁	47.59	14.28	107.85	51.83	NF.	-
w.w. ₂	50.42	15.12	118.39	56.83	NF.	-
w.w. ₃	29.48	8.84	30.00	14.40	NF.	-
w.w. ₄	19.64	5.89	41.78	20.05	NF.	-
w.w. ₅	29.66	8.90	73.11	35.09	NF.	-
w.w. ₆	46.13	13.84	143.26	68.77	NF.	-
w.w. ₇	48.18	14.45	114.59	55.00	NF.	-
w.w. ₈	42.74	12.82	89.50	42.96	NF.	-
w.w. ₉	39.00	11.70	122.18	58.64	NF.	-
w.w. ₁₀	19.32	5.80	43.27	20.77	NF.	-

* averaged from 3 runs. However, actual concentration ranges in ng/μl for Mg²⁺, Ca²⁺ and Sr²⁺ were NF.-15.12, 0.10-68.77 and NF.-0.21, respectively

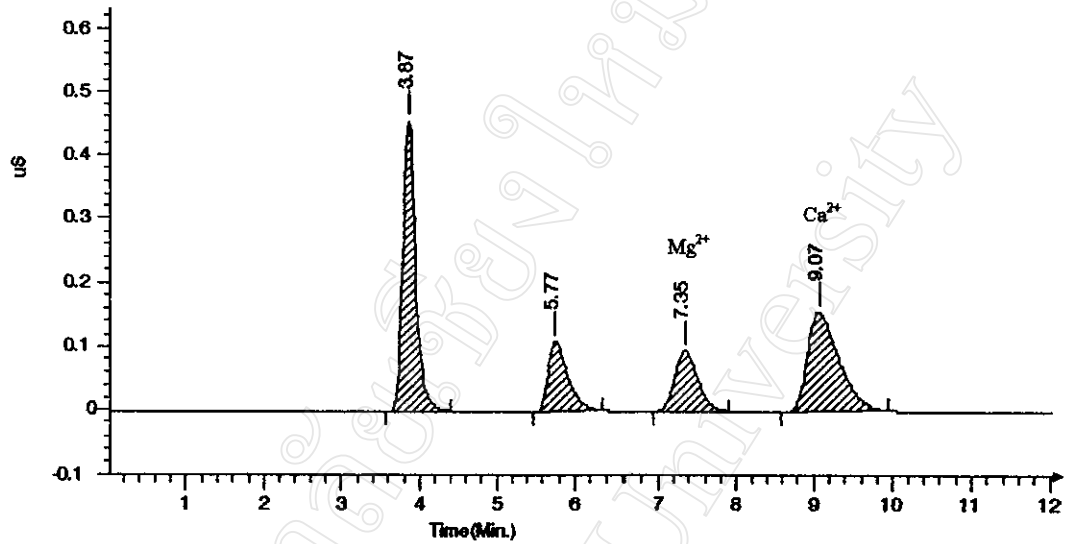


Figure 3.20 Typical chromatogram of b.w.₃ water sample obtained with IonPac CS 12 column.

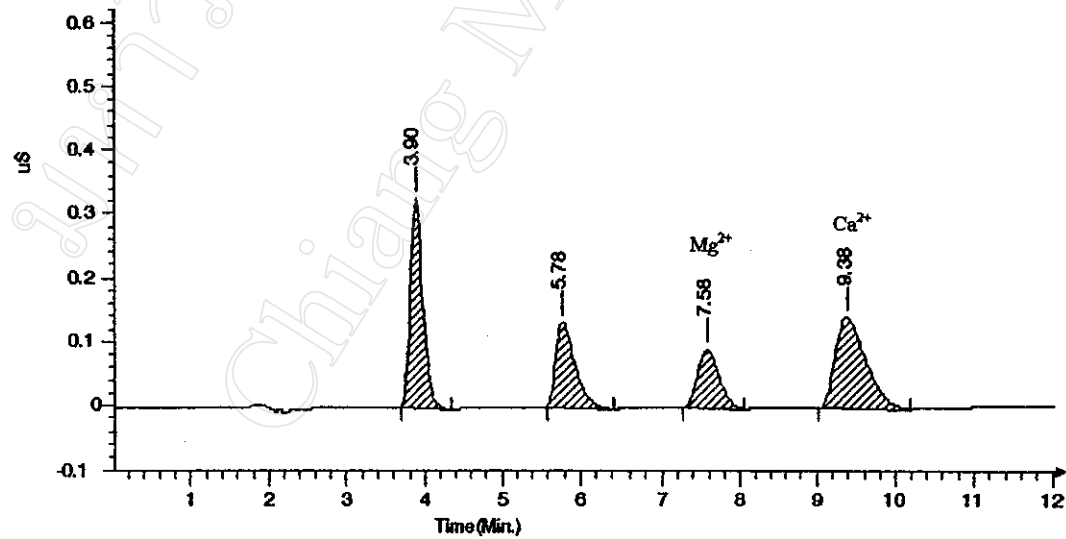


Figure 3.21 Typical chromatogram of w.w.₄ sample obtained with IonPac CS 12 column.

3.4.3 % Recovery of each cation in drinking water samples

Analyte cations were quantitatively confirmed via the % recovery of each cation. The results are shown in Tables 3.36-3.38 and confirmation of analyte peaks in drinking water samples is shown in Figure 3.22.

Table 3.36 % Recovery of Mg^{2+} in b.w.₁ sample when spiked with standard Mg^{2+} at various concentrations (ng/ μ l).

Spiked standard Mg^{2+} (ng/ μ l)	Peak area (arbitrary unit)	Concentration (ng/ μ l)	% Recovery
b.w. ₁	17501	0.5	
b.w. ₁ + 1 ng/ μ l	385072	1.01	96.00
b.w. ₁ + 2 ng/ μ l	756241	1.98	96.50
b.w. ₁ + 3 ng/ μ l	1128560	2.96	97.00
b.w. ₁ + 4 ng/ μ l	1498422	3.94	97.25
		mean	96.69

Table 3.37 % Recovery of Ca^{2+} in b.w.₁ sample when spiked with standard Ca^{2+} at various concentrations (ng/ μl).

Spiked standard Ca^{2+} (ng/ μl)	Peak area (arbitrary unit)	Concentration (ng/ μl)	% Recovery
b.w. ₁	104251	0.39	
b.w. ₁ + 1 ng/ μl	362152	1.36	97.00
b.w. ₁ + 2 ng/ μl	625657	2.34	97.50
b.w. ₁ + 3 ng/ μl	891934	3.34	98.33
b.w. ₁ + 4 ng/ μl	1125869	4.22	95.75
		mean	97.14

Table 3.38 % Recovery of Sr^{2+} in b.w.₁ sample when spiked with standard Sr^{2+} at various concentrations (ng/ μl).

Spiked standard Sr^{2+} (ng/ μl)	Peak area (arbitrary unit)	Concentration (ng/ μl)	% Recovery
b.w. ₁	2.002	0.21	
b.w. ₁ + 1 ng/ μl	11058	0.16	95.00
b.w. ₁ + 2 ng/ μl	19925	2.09	94.00
b.w. ₁ + 3 ng/ μl	29362	3.08	95.67
b.w. ₁ + 4 ng/ μl	39086	4.10	97.25
		mean	95.48

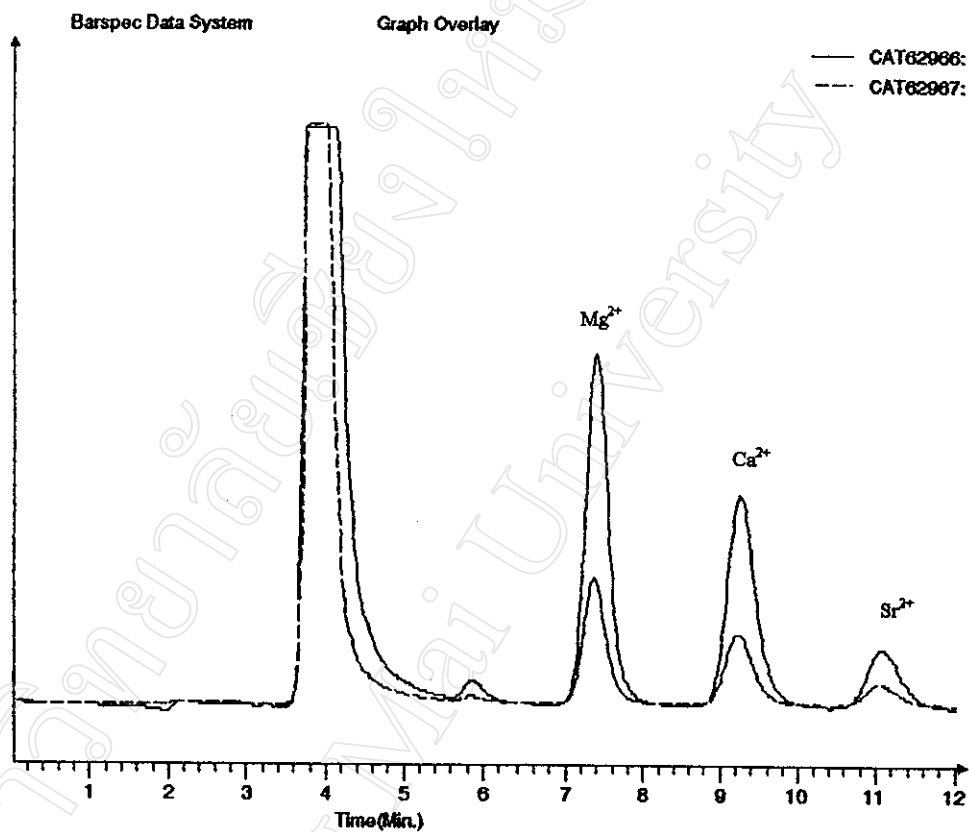


Figure 3.22 Chromatograms of b.w.₁ sample (CAT 62966) and b.w.₁ sample with spiked Mg²⁺, Ca²⁺ and Sr²⁺ (CAT 62967) in comparison.

3.4.4 Analysis for Mg²⁺, Ca²⁺ and Sr²⁺ by the AAS technique

The amounts of Mg²⁺, Ca²⁺ and Sr²⁺ in drinking samples were determined by the AAS technique. The results of analysis were compared with the results by the IC technique shown in Tables 3.39 and 3.40.

Table 3.39 Comparison of the results of Mg^{2+} determinations in bottled drinking water samples and well water samples by IC technique and by AAS technique.

Sample	IC technique (ng/ μ l)	AAS technique (ng/ μ l)	D_i	$(D_i - \bar{D})$	$(D_i - \bar{D})^2$
b.w. ₃	0.42	0.33	0.09	0.20	0.04
b.w. ₆	0.07	0.06	0.01	0.27	0.07
b.w. ₈	0.37	0.36	0.01	0.27	0.07
w.w. ₂	15.12	14.25	0.87	0.59	0.35
w.w. ₅	8.90	8.51	0.39	0.11	0.01
w.w. ₁₀	5.80	5.50	0.30	0.02	0.0004
			$\Sigma 1.67$		$\Sigma 0.54$
\bar{D}					0.28
s_d					0.33
$t_{calc.}$					2.09

Table 3.40 Comparison of the results of Ca^{2+} determinations in bottled drinking water samples and well water samples by IC technique and by AAS technique.

Sample	IC technique (ng/ μl)	AAS technique (ng/ μl)	D_i	$(D_i - \bar{D})$	$(D_i - \bar{D})^2$
b.w. ₁	0.39	0.31	0.08	0.03	0.0009
b.w. ₈	3.01	3.14	-0.13	-0.08	0.006
b.w. ₉	0.55	0.52	0.03	0.02	0.0004
w.w. ₃	14.40	14.90	-0.50	-0.55	0.302
w.w. ₄	20.05	20.20	-0.15	0.20	0.04
w.w. ₈	42.96	42.00	0.96	0.91	0.828
			$\Sigma 0.29$		$\Sigma 1.18$
\bar{D}					0.05
S_d					0.48
$t_{\text{calc.}}$					0.26

3.5 Determination of Metal Ions with IonPac CS 5 Column

3.5.1 Results of investigation of color-forming reagent

Table 3.41 Absorption maximum wavelength (λ max) and absorbance value of metal-PAR complexes in deionized water.

Metal ion	λ max (nm)	Absorbance
Pb ²⁺	523.0	2.182
Cu ²⁺	513.2	2.756
Mn ²⁺	504.0	2.776
Zn ²⁺	508.6	2.702
Ni ²⁺	513.4	2.712

Table 3.42 Absorption maximum wavelength (λ max) and absorbance value of metal-PAR complexes in 50 mM oxalic acid pH 5.3 (eluent).

Metal ion	λ max (nm)	Absorbance
Pb ²⁺	515.0	2.357
Cu ²⁺	512.6	2.909
Mn ²⁺	499.2	2.981
Zn ²⁺	504.4	2.896
Ni ²⁺	508.6	2.862

3.5.2 Investigation of retention times of metal ions of interest

The ions of interest in this work were Pb^{2+} , Cu^{2+} , Mn^{2+} , Zn^{2+} and Ni^{2+} in drinking water samples. The retention time of these mixture standard cations solutions from Section 2.5.3 are given in Table 3.43.

Table 3.43 Retention times of the mixture standard cations solution obtained with IonPac CS 5 column using 50 mM oxalic acid pH 5.3 at flow rate 1.0 ml/min as eluent, 4×10^{-4} M PAR in 3.0 M $\text{NH}_4\text{OH}/1.0$ M CH_3COOH at flow rate 0.5 ml/min as the post-column reagent and λ_{max} at 510 nm.

Ion	Retention time (min)
Pb^{2+}	2.18
Cu^{2+}	2.85
Mn^{2+}	4.04
Zn^{2+}	10.05
Ni^{2+}	13.31

3.5.3 Optimization of ion chromatographic conditions

3.5.3.1 Results of effect of eluent pH

Table 3.44 Resolution of each metal ion pair at various eluent pH.

Metal ion pair	Resolution of various eluent pH					
	3.8	4.3	4.8	5.3	5.8	6.3
Pb ²⁺ & Cu ²⁺	8.24	3.01	3.24	3.15	3.01	3.24
Cu ²⁺ & Mn ²⁺	9.12	6.86	5.40	4.80	4.05	3.53
Mn ²⁺ & Zn ²⁺	6.69	14.52	16.25	17.08	16.84	16.67
Zn ²⁺ & Ni ²⁺	5.11	3.80	3.32	3.23	2.74	2.59

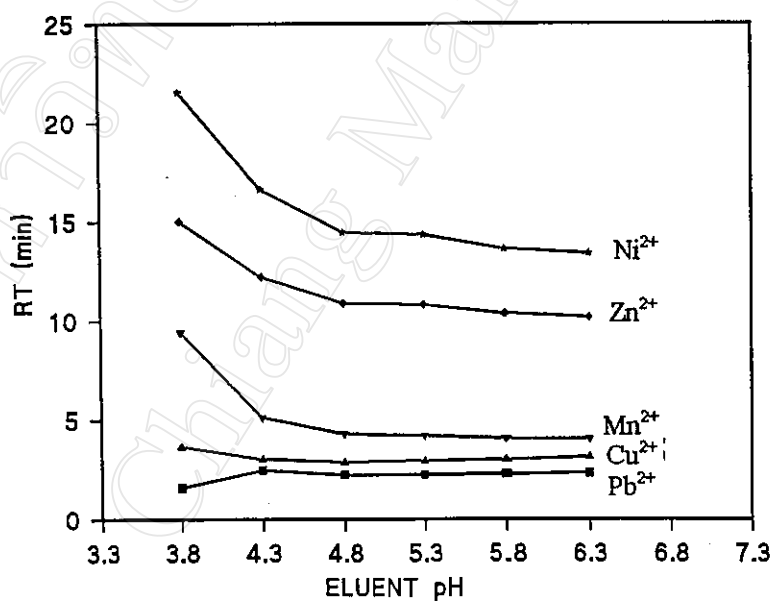


Figure 3.23 Plot of metal ion pairs at various eluent pH.

3.5.3.2 Optimum detection wavelength

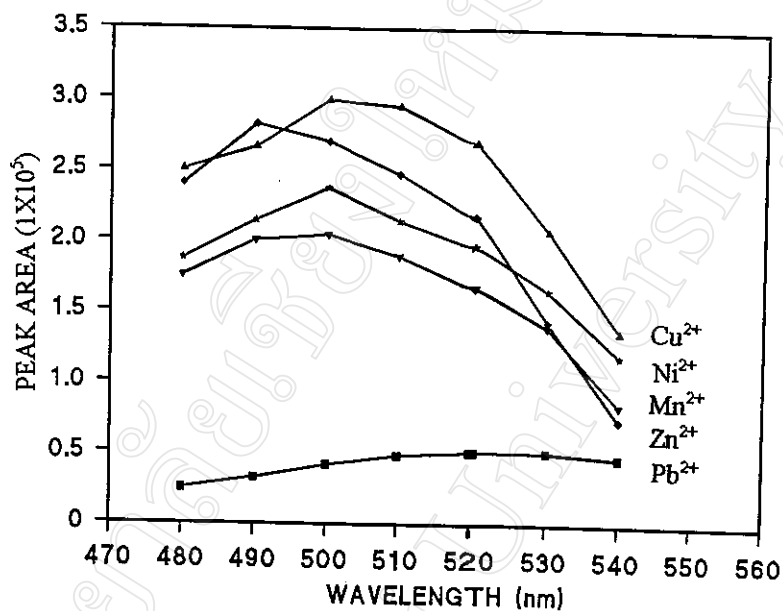


Figure 3.24 Relationship between each metal peak area and the wavelength employed.

3.5.3.3 Results of effect of eluent flow rate

Table 3.45 Resolution of each metal ion pair at various eluent flow rates.

Metal ion pair	Resolution at various eluent flow rate (ml/min)				
	0.9	1.0	1.1	1.2	1.3
Pb ²⁺ & Cu ²⁺	3.24	3.18	3.09	2.98	2.89
Cu ²⁺ & Mn ²⁺	4.92	4.76	4.70	4.67	4.56
Mn ²⁺ & Zn ²⁺	17.29	17.10	16.89	16.60	16.09
Zn ²⁺ & Ni ²⁺	3.44	3.18	3.13	3.10	3.02

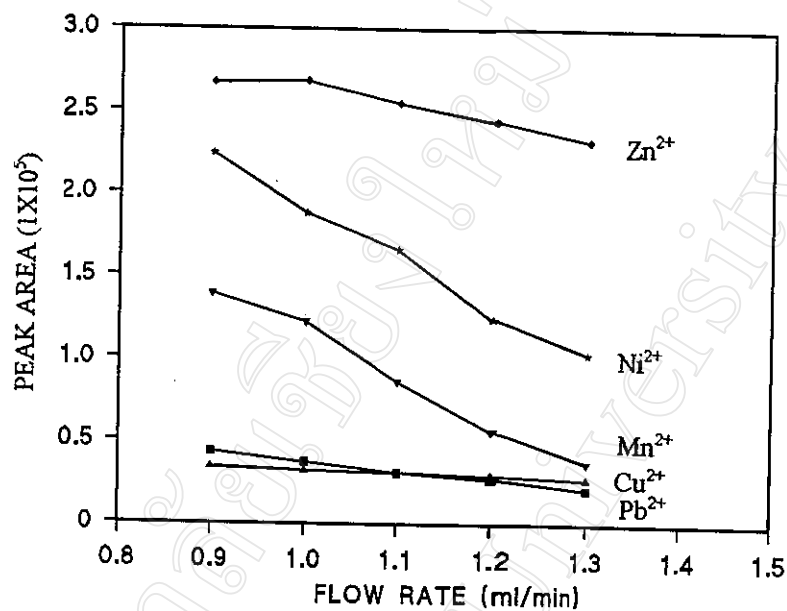


Figure 3.25 Plot of each metal ion peak area against the eluent flow rate.

Table 3.46 The number of theoretical plates (N) of each metal ion at various eluent flow rates.

Metal ion	N at eluent flow rate (ml/min)				
	0.9	1.0	1.1	1.2	1.3
Pb ²⁺	1842	1673	1664	1600	1546
Cu ²⁺	2897	2877	2802	2695	2562
Mn ²⁺	3218	2970	2864	2839	2680
Zn ²⁺	8884	8679	8693	8473	8075
Ni ²⁺	1320	1082	1080	1061	1040

3.5.3.4 Results of effect of eluent concentration

Table 3.47 Effects of eluent concentration on

(a) Retention time

Metal ion	RT (min) at eluent concentration (mM)						
	35	40	45	50	55	60	65
Pb ²⁺	3.05	2.67	2.39	2.26	2.13	2.00	1.96
Cu ²⁺	3.48	3.28	3.01	2.93	2.79	2.63	2.58
Mn ²⁺	6.56	5.26	4.52	4.17	3.78	3.43	3.32
Zn ²⁺	14.50	12.57	11.12	10.62	9.61	8.55	8.15
Ni ²⁺	20.17	17.13	14.91	13.99	12.46	10.92	10.31

(b) Peak area

Metal ion	Peak area (1x10 ⁵) at eluent concentration (mM)						
	35	40	45	50	55	60	65
Pb ²⁺	0.86	1.44	1.79	2.45	1.85	2.09	2.13
Cu ²⁺	2.34	2.85	3.16	3.34	3.32	3.27	3.24
Mn ²⁺	11.46	10.19	11.25	9.65	6.39	5.31	5.13
Zn ²⁺	2.74	2.81	2.85	2.80	2.70	2.62	2.57
Ni ²⁺	2.06	2.04	2.01	2.02	1.80	1.76	1.69

Table 3.47 (continued)

(c) Resolution

Metal ion	Resolution at eluent concentration (mM)						
	35	40	45	50	55	60	65
Pb ²⁺ & Cu ²⁺	1.88	2.42	2.63	2.24	3.10	3.25	3.32
Cu ²⁺ & Mn ²⁺	7.46	5.71	5.07	4.63	4.19	3.86	3.76
Mn ²⁺ & Zn ²⁺	13.18	14.84	15.46	16.67	17.27	17.18	17.10
Zn ²⁺ & Ni ²⁺	4.03	3.59	3.42	3.60	3.19	2.80	2.75

3.3.3.5 Summary of optimized ion chromatographic conditions

The optimized ion chromatographic conditions obtained with IonPac CS 5 column in this work are listed in **Table 3.48**.

Table 3.48 Optimized ion chromatographic conditions obtained with IonPac CS5 column and the post column derivatization detection system for analysis metal ions in this work.

Operation	Optimal conditions
o Eluent	50 mM oxalic acid pH 5.30
o The post-column reagent	4.0x10 ⁻⁴ M PAR in 3.0 M NH ₄ OH/1.0 M CH ₃ COOH
o Flow rate	1.0 ml/min (of eluent) 0.5 ml/min (of the post column reagent)
o Detector	uv-vis spectrophotometric
o Wavelength	510 nm
o Absorbance unit (AU.) range	0.05 unit
o Sample loop volume	25 µl

3.5.4 Results of determination of linearity

Table 3.49 Relationship between peak area and concentration of metal ions for determination of linearity obtained with IonPac CS 5 column, 50 mM oxalic acid pH 5.3 at flow rate 1.0 ml/min as eluent and 4×10^{-4} M PAR in 3.0 M NH_4OH /1.0 M CH_3COOH at flow rate 0.5 ml/min as the post-column reagent, at λ 510 nm.

Concentration (ng/ μ l)	Peak area (1×10^5) (arbitrary unit)				
	Pb^{2+}	Cu^{2+}	Mn^{2+}	Zn^{2+}	Ni^{2+}
0.2	1.32	4.07	2.04	8.59	2.51
0.4	2.72	7.01	3.45	16.45	5.24
0.6	3.20	11.97	6.59	22.47	7.88
0.8	4.56	15.38	9.09	29.12	10.35
1.0	5.05	19.03	11.43	36.71	13.27
2.0	10.31	40.00	25.64	73.92	26.46
4.0	19.63	81.00	45.19	140.31	54.14
6.0	29.24	120.51	65.56	206.44	83.10
8.0	38.47	158.18	85.85	268.36	110.31
10.0	42.99	209.71	105.21	334.43	138.56
20.0	82.79	378.94	217.10	691.46	200.36
40.0	164.90	707.16	373.20	1219.91	400.42
60.0	200.15	1048.40	456.85	1704.48	600.21
80.0	159.83	1494.66	623.27	2158.00	780.43
100.0	131.92	1769.17	855.60	2500.73	921.00
200.0	99.06	3508.34	1719.21	4981.46	1799.85

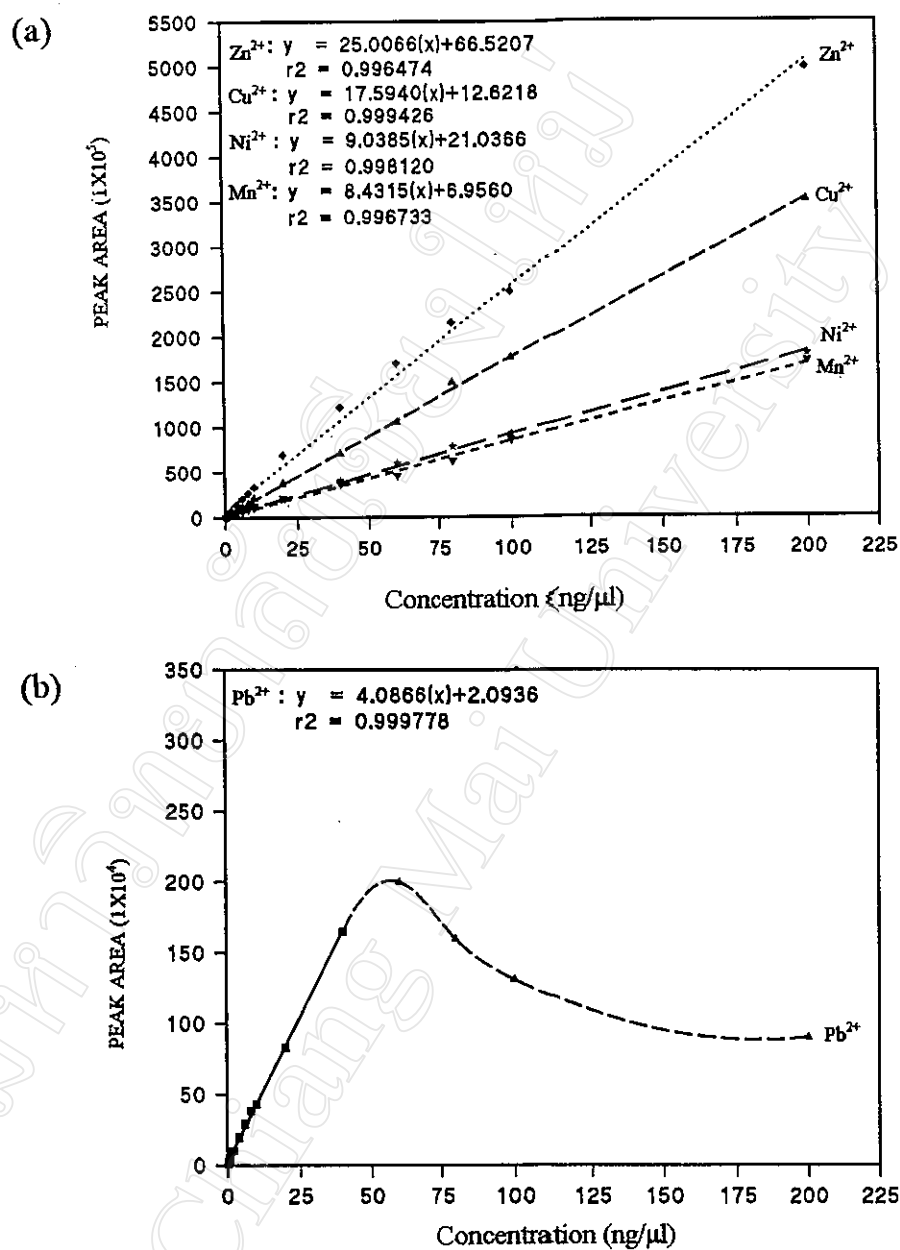
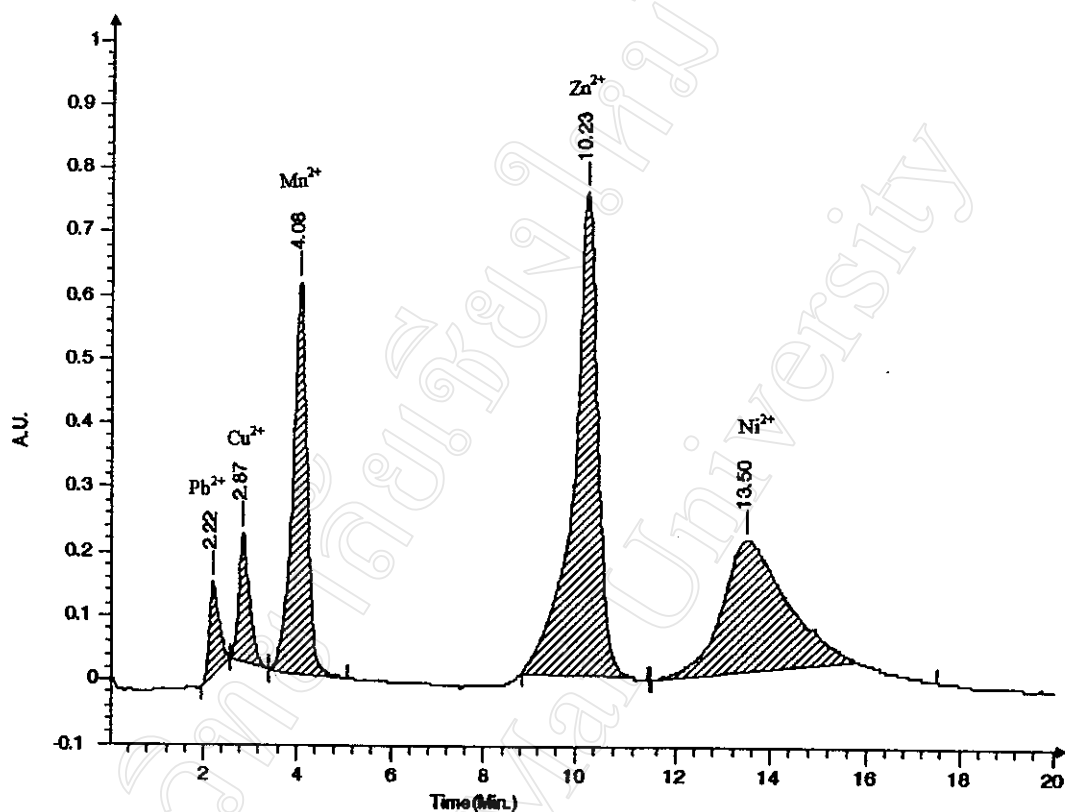


Figure 3.26 Linearity curve for metal ions obtained with IonPac CS 5 column, 50 mM oxalic acid pH 5.3 as eluent, 4.0×10^{-4} M PAR in 3.0 M $NH_4OH/1.0$ M CH_3COOH as the post-column reagent, at λ 510nm: (a) for Zn^{2+} , Cu^{2+} , Ni^{2+} and Mn^{2+}
(b) for Pb^{2+}



BarSpec Data System File : C:\BDS\DATA\CAT3\CAT31487.BDS

PEAK REPORT

#	RT	Height	Width	Type	Area	%Area	Conc.	Name	Plate N
1	2.22	0.1445	0.223	BB	2071.45	2.99			547
2	2.87	0.2010	0.220	BB	3081.03	4.45			937
3	4.08	0.6077	0.294	BB	12679.07	18.31			1066
4	10.23	0.7558	0.432	BB	26672.46	38.81			3103
5	13.50	0.2177	1.517	BB	24532.68	35.43			439

Figure 3.27 Chromatogram of Pb^{2+} , Cu^{2+} , Mn^{2+} , Zn^{2+} and Ni^{2+} obtained with IonPac CS 5 column, 50 mM oxalic acid pH 5.3 as eluent, 4×10^{-4} M PAR in 3.0 M $\text{NH}_4\text{OH}/1.0$ M CH_3COOH as the post-column reagent, at λ 510 nm.

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

The example of noise level of Mn^{2+} solution is shown in Figure 3.28.

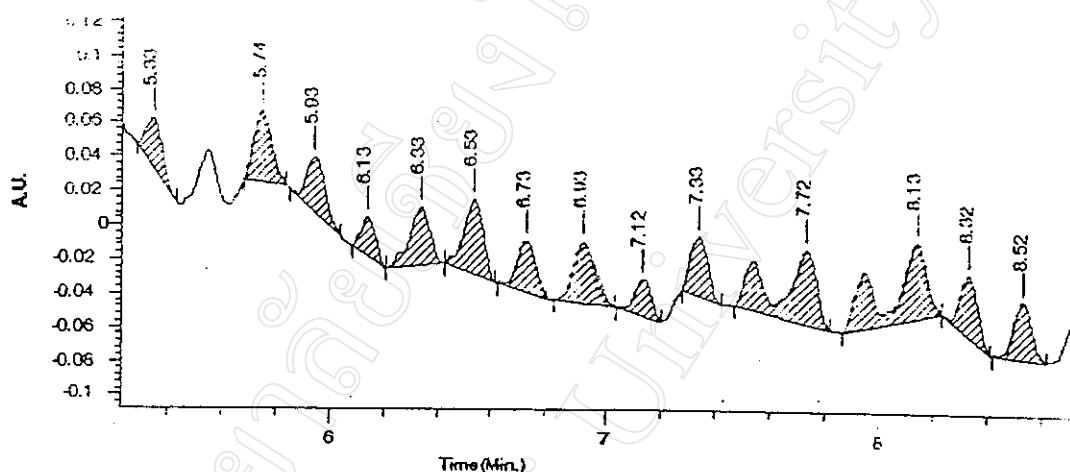


Figure 3.28 The noise level of Mn^{2+} solution obtained at the highest detection sensitivity, output range Mn^{2+} and detection sensitivity (1000).

Table 3.50 Results of determination of the detection limit (L) and the minimum detectable quantity (MDQ).

Metal ion	Concentration $m_x(\text{ng}/\mu\text{l})$	Noise signal (n)	Peak area (arbitrary unit)	$W_{1/2}$ (min)	L (ng)	MDQ (ng.sec)
Pb^{2+}	1.0	5158	815728	0.10	0.32	1.96
Cu^{2+}	0.1	37234	2337135	0.11	0.08	0.51
Mn^{2+}	1.0	45050	15096542	0.15	0.15	1.33
Zn^{2+}	0.5	65368	10523382	0.22	0.16	2.07
Ni^{2+}	1.0	5000	297046	0.75	0.84	37.95

3.5.6 Reproducibility of results

The precision of results was reported in terms of standard deviation and the data are shown in **Table 3.51**.

Table 3.51 The reproducibility of results obtained with IonPac CS 5 column, 50 mM oxalic acid pH 5.3 at flow rate 1.0 ml/min as eluent and 4×10^{-4} M PAR in 3.0 M NH_4OH /1.0M CH_3COOH at flow rate 0.5 ml/min as the post-column reagent at λ max 510 nm.

(a) Retention times of various metal ions investigated.

Run	RT (min)				
	Pb^{2+} 4.0 ng/ μl	Cu^{2+} 0.5 ng/ μl	Mn^{2+} 2 ng/ μl	Zn^{2+} 2 ng/ μl	Ni^{2+} 4 ng/ μl
1	2.22	2.87	4.08	10.27	13.52
2	2.23	2.88	4.10	10.27	13.52
3	2.22	2.87	4.08	10.23	13.50
4	2.23	2.88	4.10	10.27	13.55
5	2.22	2.88	4.10	10.27	13.53
mean	2.22	2.88	4.09	10.26	13.52
SD	0.007	0.007	0.011	0.006	0.006
% RSD	0.315	0.243	0.269	0.058	0.044

Table 3.51 (continued)

(b) Peak area of various metal ions investigated

Run	Peak area (1×10^5) (arbitrary units)				
	Pb ²⁺ 4.0 ng/ μ l	Cu ²⁺ 0.5 ng/ μ l	Mn ²⁺ 2 ng/ μ l	Zn ²⁺ 2 ng/ μ l	Ni ²⁺ 4 ng/ μ l
1	2.08	3.03	13.04	27.56	23.32
2	2.02	3.10	12.61	28.00	24.18
3	2.07	3.08	12.67	26.87	24.53
4	2.10	2.98	12.39	27.69	24.04
5	2.20	3.13	12.82	29.29	24.98
mean	2.09	3.06	12.71	27.88	24.21
SD	0.072	0.056	0.239	1.010	0.614
% RSD	3.430	1.830	1.880	3.623	2.536

3.6 Determination of Heavy Metal Ions in Drinking Water Samples by IC

The amounts of metal ions in drinking water samples, namely Pb²⁺, Cu²⁺, Mn²⁺, Zn²⁺ and Ni²⁺ were determined by the IC technique. The nonspecific metallochromic indicator 4-(2-pyridylazo) resorcinol (PAR) has been widely used for chromatographic detection of metals [27].

3.6.1 Standard calibration curves of Pb^{2+} , Mn^{2+} , Zn^{2+} and Ni^{2+}

Calibration curves of these metal ions in drinking water samples were constructed from the data in Tables 3.52-3.55 and calibration curve are shown in Figures 3.29-3.32.

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

Concentration (ng/ μl)	Peak area (arbitrary unit)
0.1	6654
0.2	13258
0.4	272076
0.6	320278
0.8	456230
1.0	505482

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

Concentration (ng/ μl)	Peak area (arbitrary unit)
0.012	12480
0.025	26272
0.050	51091
0.100	102464
0.200	204721
0.400	345285

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

Concentration (ng/ μ l)	Peak area (arbitrary unit)
0.006	27480
0.012	54277
0.025	107292
0.050	215078
0.100	429145
0.200	859062

Table 3.55 The data used for construction of the standard calibration curve of Ni^{2+} .

Concentration (ng/ μ l)	Peak area (arbitrary unit)
0.006	8472
0.012	16575
0.025	31028
0.500	63425
0.100	126442
0.200	251728

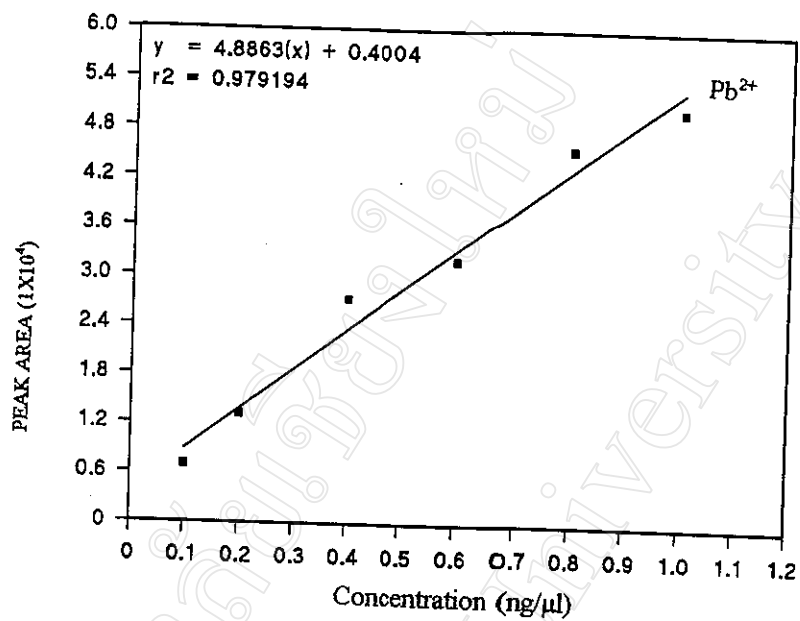


Figure 3.29 Calibration curve of Pb^{2+} .

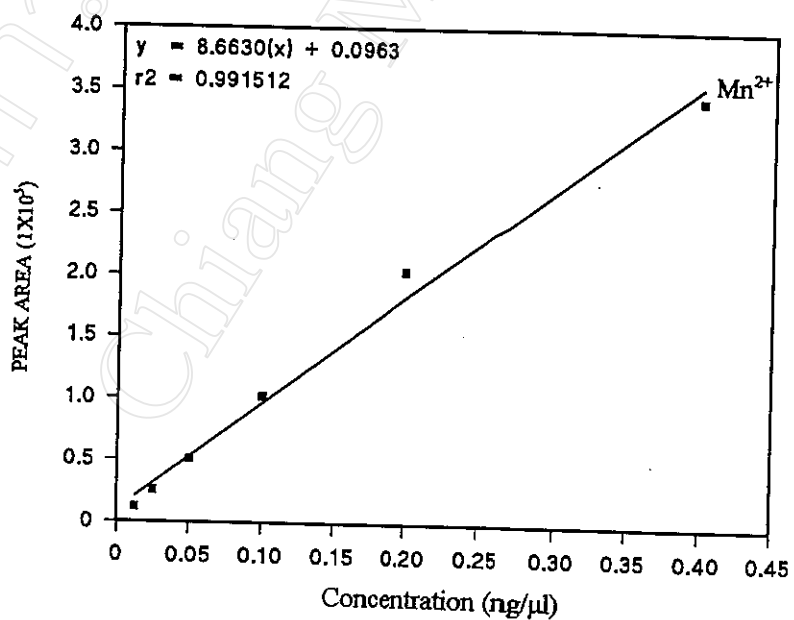


Figure 3.30 Calibration curve of Mn^{2+} .

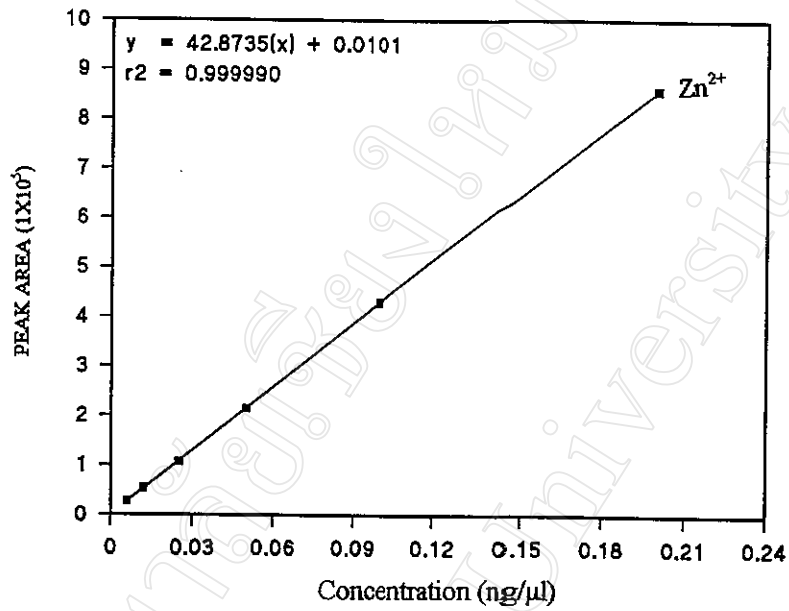


Figure 3.31 Calibration curve of Zn²⁺.

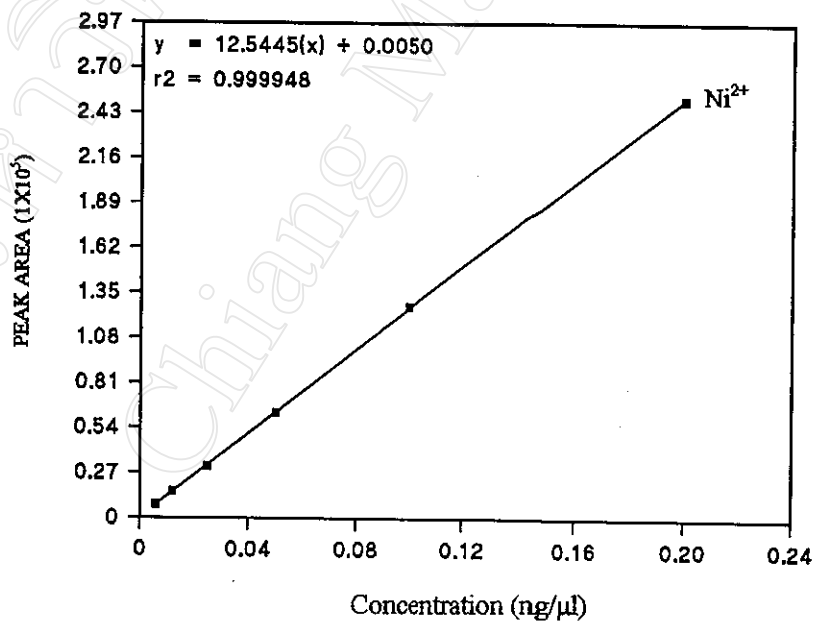


Figure 3.32 Calibration curve of Ni²⁺.

3.6.2 The amounts of Pb^{2+} , Mn^{2+} , Zn^{2+} and Ni^{2+}

The amounts of Pb^{2+} , Mn^{2+} , Zn^{2+} and Ni^{2+} in drinking water samples were obtained with IonPac CS 5. The results of analysis are shown in Tables 3.56-3.57. The chromatogram of some drinking water sample are shown in Figure 3.35.

Table 3.56 Peak areas of metal ions in bottled drinking water samples (b.w.) and well water samples (w.w.) obtained with IonPac CS 5 column.

Sample	Peak area (arbitrary unit)			
	Pb^{2+}	Mn^{2+}	Zn^{2+}	Ni^{2+}
b.w.1	3669	12836	19135	9630
b.w.2	NF.	NF.	24550	9079
b.w.3	NF.	NF.	24501	8027
b.w.4	NF.	NF.	69181	16585
b.w.5	NF.	NF.	23809	5486
b.w.6	NF.	NF.	29574	6005
b.w.7	NF.	NF.	24201	5019
b.w.8	NF.	NF.	40123	6886
b.w.9	NF.	NF.	42173	7889
b.w.10	NF.	1391	27870	6777
w.w.1	NF.	NF.	31841	6750
w.w.2	2130	NF.	24001	4991
w.w.3	4050	60492	75507	12990
w.w.4	NF.	NF.	15537	4432
w.w.5	NF.	NF.	70101	13510
w.w.6	NF.	NF.	26801	4001
w.w.7	2105	91113	25348	4682
w.w.8	NF.	NF.	72436	11987
w.w.9	NF.	250006	70965	10999
w.w.10	NF.	42242	27010	5984

Table 3.57 Concentrations of metal ions in bottled drinking water samples (b.w.) and well water samples (w.w.) obtained with IonPac CS 5 column.

Sample	Concentration (ng/ μ l)*			
	Pb ²⁺	Mn ²⁺	Zn ²⁺	Ni ²⁺
b.w. ₁	0.051	0.060	0.008	0.019
b.w. ₂	NF.	NF.	0.009	0.018
b.w. ₃	NF.	NF.	0.010	0.016
b.w. ₄	NF.	NF.	0.027	0.034
b.w. ₅	NF.	NF.	0.010	0.011
b.w. ₆	NF.	NF.	0.012	0.012
b.w. ₇	NF.	NF.	0.010	0.010
b.w. ₈	NF.	NF.	0.016	0.014
b.w. ₉	NF.	NF.	0.017	0.016
b.w. ₁₀	NF.	0.020	0.011	0.014
w.w. ₁	NF.	NF.	0.013	0.014
w.w. ₂	0.030	NF.	0.010	0.010
w.w. ₃	0.056	0.028	0.030	0.026
w.w. ₄	NF.	NF.	0.006	0.009
w.w. ₅	NF.	NF.	0.028	0.027
w.w. ₆	NF.	NF.	0.010	0.008
w.w. ₇	0.029	0.042	0.010	0.009
w.w. ₈	NF.	NF.	0.029	0.024
w.w. ₉	NF.	0.116	0.028	0.022
w.w. ₁₀	NF.	0.198	0.011	0.012

* averaged from 3 runs. However, actual concentration ranges in ng/ μ l) for Pb²⁺, Mn²⁺, Zn²⁺ and Ni²⁺ were NF.-0.056, NF.-1.968, 0.010-0.030 and 0.010-0.034, respectively.

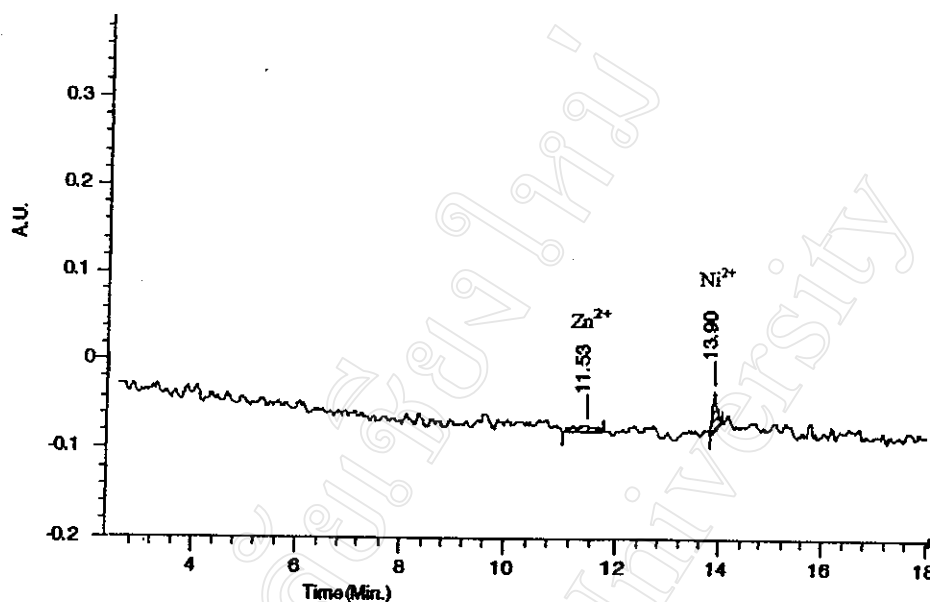


Figure 3.33 Typical chromatogram of w.w.₅ sample obtained with IonPac CS 5 column.

3.6.3 % Recovery of each metal ion in drinking water samples

The results and the chromatogram of % recovery of each metal ion in drinking water samples are shown in Tables 3.58-3.61.

Table 3.58 % Recovery of Pb²⁺ in b.w.₁ sample when spiked with standard Pb²⁺ at various concentration (ng/ μ l).

Spiked standard Pb ²⁺ (ng/ μ l)	Peak area (arbitrary unit)	Concentration (ng/ μ l)	% Recovery
b.w. ₁	3669	0.15	
b.w. ₁ + 1.0 (ng/ μ l)	75581	1.03	98.00
b.w. ₁ + 2.0 (ng/ μ l)	147493	2.01	98.00
b.w. ₁ + 3.0 (ng/ μ l)	218672	2.98	97.67
b.w. ₁ + 4.0 (ng/ μ l)	290584	3.96	97.75
		mean	97.86

Table 3.59 % Recovery of Mn^{2+} in b.w.₁ sample when spiked with standard Mn^{2+} at various concentrations (ng/ μ l).

Spiked standard Mn^{2+} (ng/ μ l)	Peak area (arbitrary unit)	Concentration (ng/ μ l)	% Recovery
b.w. ₁	12836	0.06	
b.w. ₁ + 0.5 (ng/ μ l)	117663	0.55	98.00
b.w. ₁ + 1.0 (ng/ μ l)	224630	1.05	99.00
b.w. ₁ + 1.5 (ng/ μ l)	327318	1.53	98.00
b.w. ₁ + 2.0 (ng/ μ l)	434284	2.03	98.50
		mean	98.38

Table 3.60 % Recovery of Zn^{2+} in b.w.₁ sample when spiked with standard Zn^{2+} at various concentrations (ng/ μ l).

Spiked standard Zn^{2+} (ng/ μ l)	Peak area (arbitrary unit)	Concentration (ng/ μ l)	% Recovery
b.w. ₁	19135	0.008	
b.w. ₁ + 0.5 (ng/ μ l)	1253110	0.506	99.60
b.w. ₁ + 1.0 (ng/ μ l)	2491355	1.005	99.70
b.w. ₁ + 1.5 (ng/ μ l)	3729605	1.505	99.80
b.w. ₁ + 2.0 (ng/ μ l)	4960777	2.000	99.60
		mean	99.68

Table 3.61 % Recovery of Ni^{2+} in b.w.1 sample when spiked with standard Ni^{2+} at various concentrations ($\text{ng}/\mu\text{l}$).

Spiked standard Ni^{2+} ($\text{ng}/\mu\text{l}$)	Peak area (arbitrary unit)	Concentration ($\text{ng}/\mu\text{l}$)	% Recovery
b.w. ₁	9630	0.02	
b.w. ₁ + 1.0 ($\text{ng}/\mu\text{l}$)	471870	0.98	96.00
b.w. ₁ + 2.0 ($\text{ng}/\mu\text{l}$)	967815	2.01	99.50
b.w. ₁ + 3.0 ($\text{ng}/\mu\text{l}$)	1439685	2.99	99.00
b.w. ₁ + 4.0 ($\text{ng}/\mu\text{l}$)	1930815	4.01	99.75
		mean	98.56

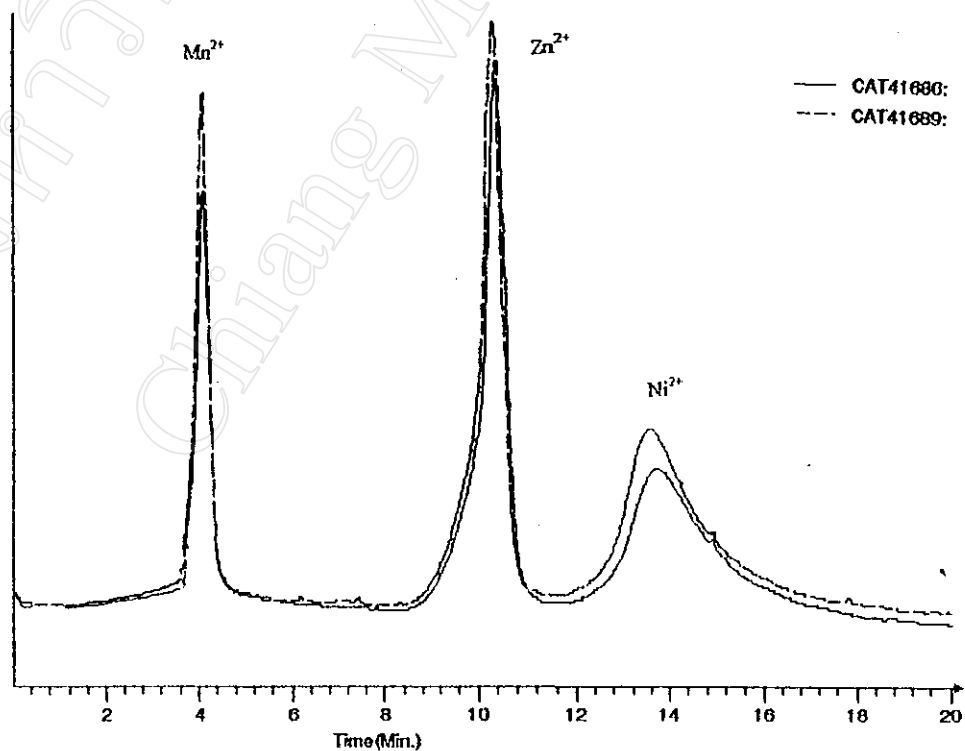


Figure 3.34 Chromatograms of w.w.₉ sample (CAT. 41686) and w.w.₉ sample with spiked Mn^{2+} , Zn^{2+} and Ni^{2+} (CAT. 41689) in comparison.

3.6.4 Analysis for Pb^{2+} , Mn^{2+} , Zn^{2+} and Ni^{2+} by the AAS technique

The amounts of Pb^{2+} , Mn^{2+} , Zn^{2+} and Ni^{2+} in bottled drinking water samples and well water samples were determined using the AAS technique. The results of analysis were compared with the results of IC technique in Tables 3.62-3.65.

Table 3.62 Comparison of the results of Pb^{2+} in bottled drinking water samples and well water samples by IC technique and by AAS technique.

Sample	IC technique (ng/ μ l)	AAS technique (ng/ μ l)	D_i	$(D_i - \bar{D})$	$(D_i - \bar{D})^2$
b.w. ₁	0.051	0.048	0.003	0.001	1.0×10^{-6}
w.w. ₂	0.030	0.029	0.001	0.003	9.0×10^{-6}
w.w. ₃	0.056	0.050	0.006	0.002	4.0×10^{-6}
w.w. ₇	0.029	0.021	0.008	0.004	1.6×10^{-5}
			Σ 0.018		Σ 3.0×10^{-5}
\bar{D}					0.004
S_d					0.003
$t_{calc.}$					2.667

Table 3.63 Comparison of the results of Mn^{2+} in bottled drinking water samples and well water samples by IC technique and by AAS technique.

Sample	IC technique (ng/ μ l)	AAS technique (ng/ μ l)	D_i	$(D_i - \bar{D})$	$(D_i - \bar{D})^2$
b.w. ₁	0.006	0.005	0.001	0.004	1.6×10^{-5}
b.w. ₁₀	0.002	0.000	0.002	0.003	9.0×10^{-6}
w.w. ₃	0.028	0.029	-0.001	-0.006	3.6×10^{-5}
w.w. ₇	0.042	0.036	0.006	0.001	1.0×10^{-6}
w.w. ₉	0.116	0.103	0.013	0.008	6.4×10^{-5}
w.w. ₁₀	0.198	0.190	0.008	0.003	9.0×10^{-6}
			Σ 0.029		Σ 1.4×10^{-4}
\bar{D}					0.005
S_d					0.005
$t_{calc.}$					2.450

Table 3.64 Comparison of the results of Zn^{2+} in bottled drinking water samples and well water samples by IC technique and by AAS technique.

Sample	IC technique (ng/ μ l)	AAS technique (ng/ μ l)	D_i	$(D_i - \bar{D})$	$(D_i - \bar{D})^2$
b.w. ₁	0.008	0.009	-0.001	-0.002	4.0×10^{-6}
b.w. ₃	0.010	0.012	-0.002	-0.003	9.0×10^{-6}
b.w. ₁₀	0.011	0.012	-0.001	-0.002	4.0×10^{-6}
w.w. ₃	0.030	0.026	0.004	0.003	9.0×10^{-6}
w.w. ₆	0.010	0.008	0.002	0.001	1.0×10^{-6}
w.w. ₉	0.028	0.023	0.005	0.004	1.6×10^{-5}
			Σ 0.007		Σ 4.3×10^{-5}
\bar{D}					0.001
S_d					0.003
$t_{calc.}$					0.817

Table 3.65 Comparison of the results of Ni^{2+} in bottled drinking water samples and well water samples by IC technique and by AAS technique.

Sample	IC technique (ng/ μl)	AAS technique (ng/ μl)	D_i	$(D_i - \bar{D})$	$(D_i - \bar{D})^2$
b.w. ₁	0.019	0.010	0.009	0.006	3.6×10^{-5}
b.w. ₃	0.016	0.012	0.004	0.001	1.0×10^{-6}
b.w. ₁₀	0.014	0.012	0.002	0.001	1.0×10^{-6}
w.w. ₄	0.009	0.010	-0.001	0.004	1.6×10^{-5}
w.w. ₅	0.027	0.022	0.005	0.002	4.0×10^{-6}
w.w. ₆	0.008	0.008	0.000	0.003	9.0×10^{-6}
			Σ 0.019		Σ 6.7×10^{-5}
\bar{D}					0.003
S_d					0.004
$t_{\text{calc.}}$					1.840