CHAPTER IV

RESULTS AND CALCULATION

4.1 Concentration determination

Table 4-1 Atomic absorption spectrophotometric determination of concentration: Data for the calibration curve

Element	Concentration (ppm)	Absorbance
Ba	0	0
	150	0.017728
	300	0.035740
	450	0.053056
	600	0.070581
	750	0.090176
Ca	0	0
	5	0.002176
	10	0.004364
	15	0.006563
	20	0.008773
	25	0.109950

Table 4-1 (continued)

Element	Concentration (ppm)	Absorbance
Cs	0	0
	150	0.070581
	300	0.139661
	450	0.211124
	600	0.279840
	750	0.351639
K	0	0
	5	0.124938
	10	0.259637
	15	0.376750
	20	0.508638
	25	0.638272
Na	0	0
	0.5	0.065500
	1.0	0.130760
	1.5	0.207610
	2.0	0.267600
	2.5	0.337240

Table 4-1 (continued)

Element	Concentration (ppm)	Absorbance
Rb	0	0
	20	0.136677
	40	0.267606
	60	0.397940
	80	0.530177
	100	0.657577
Sr	0	0
	5	0.110698
	10	0.218244
	15	0.332544
	20	0.437707
	25	0.536020

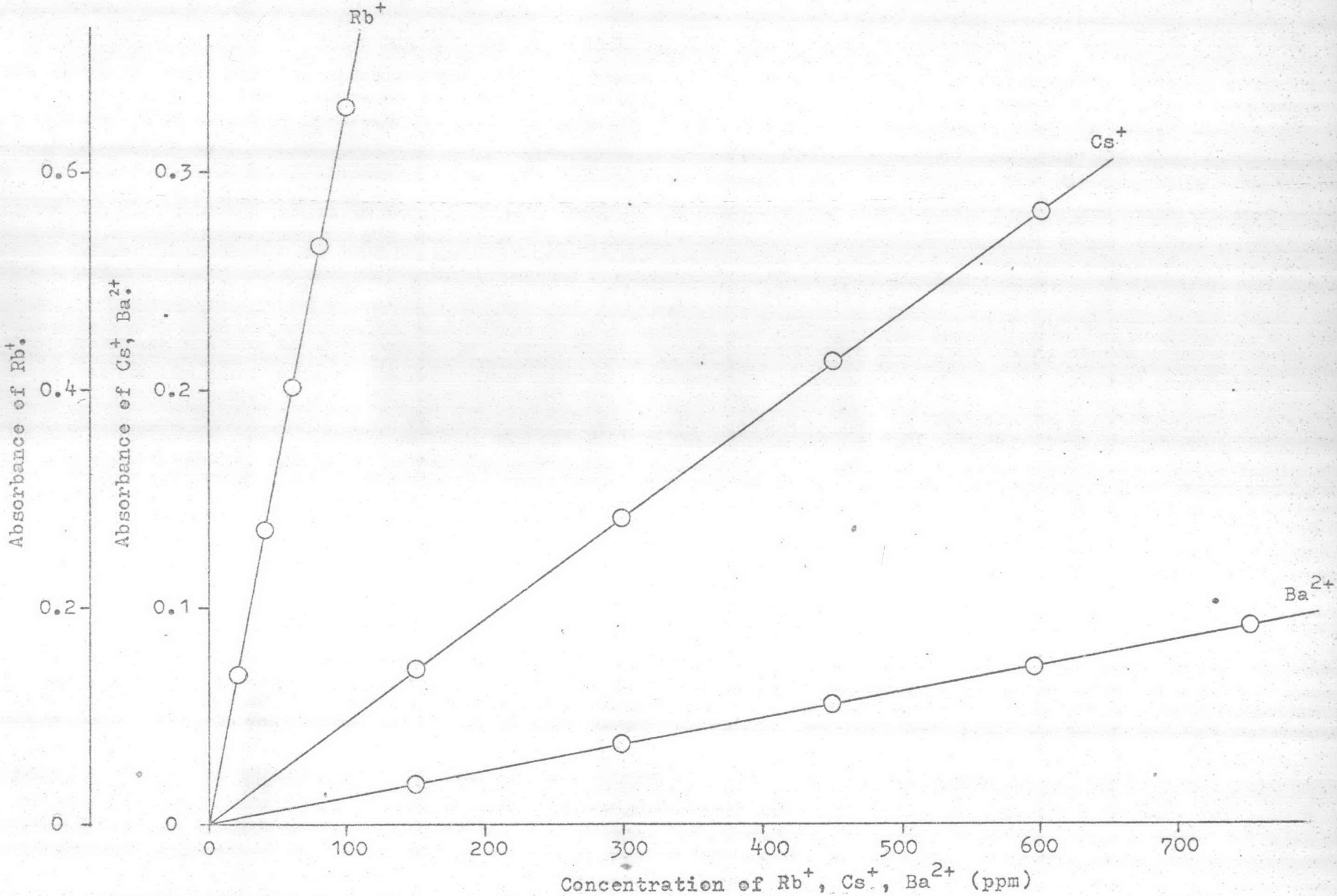

Fig. 4-1 Calibration curve of rubidium, caesium and barium ions.

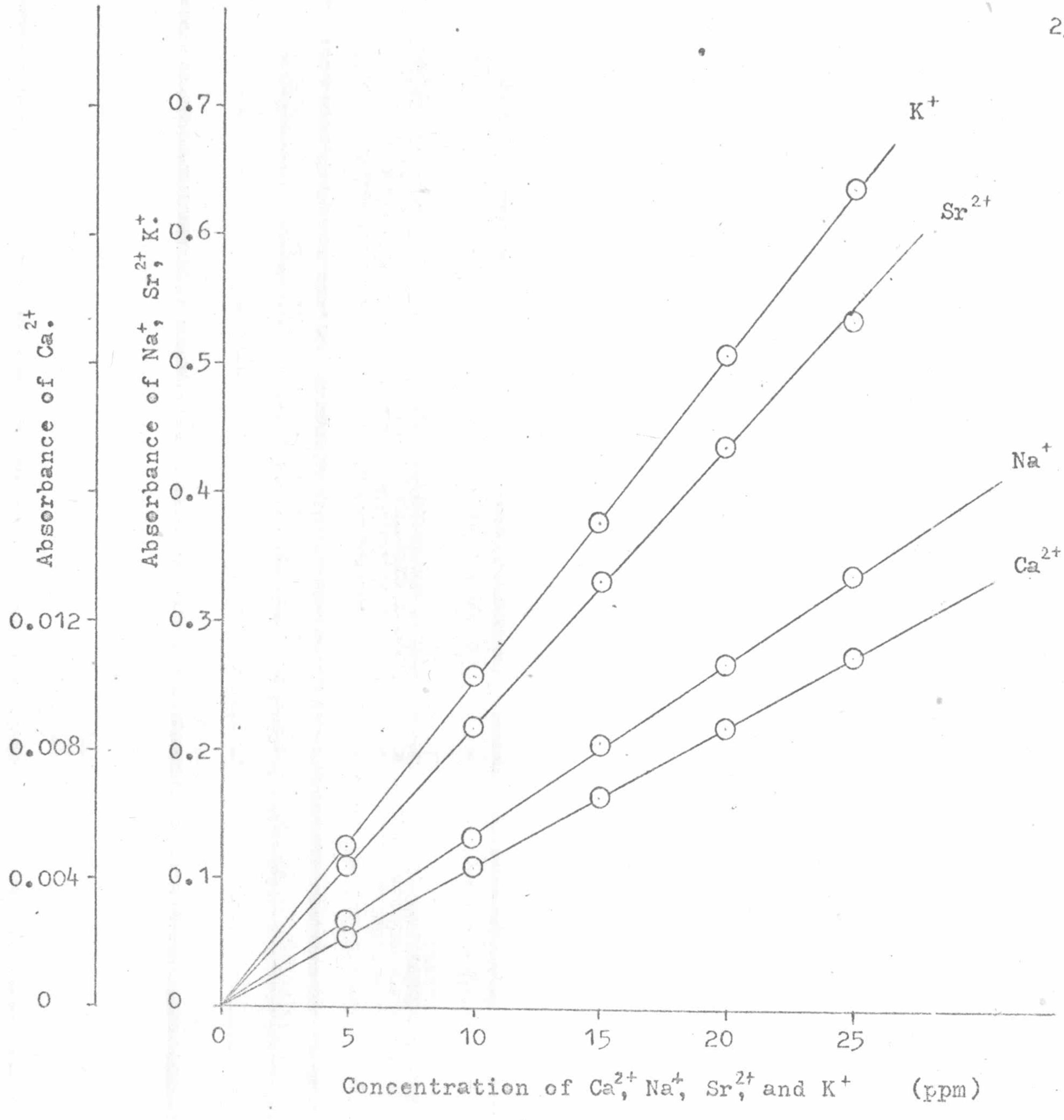

Fig.4-2 Calibration curve of calcium, sodium, strontium and potassium ions.

Table 4-2 Colorimetric determination of concentration: Data for the calibration curve.

λ_{max} = 374.045 nm.

Ion	Concentration (mole)	Absorbance
NH_4^+	2.5×10^{-6}	0.182
	5.0×10^{-6}	0.380
	7.5×10^{-6}	0.550
	10.0×10^{-6}	0.702
	12.5×10^{-6}	0.870

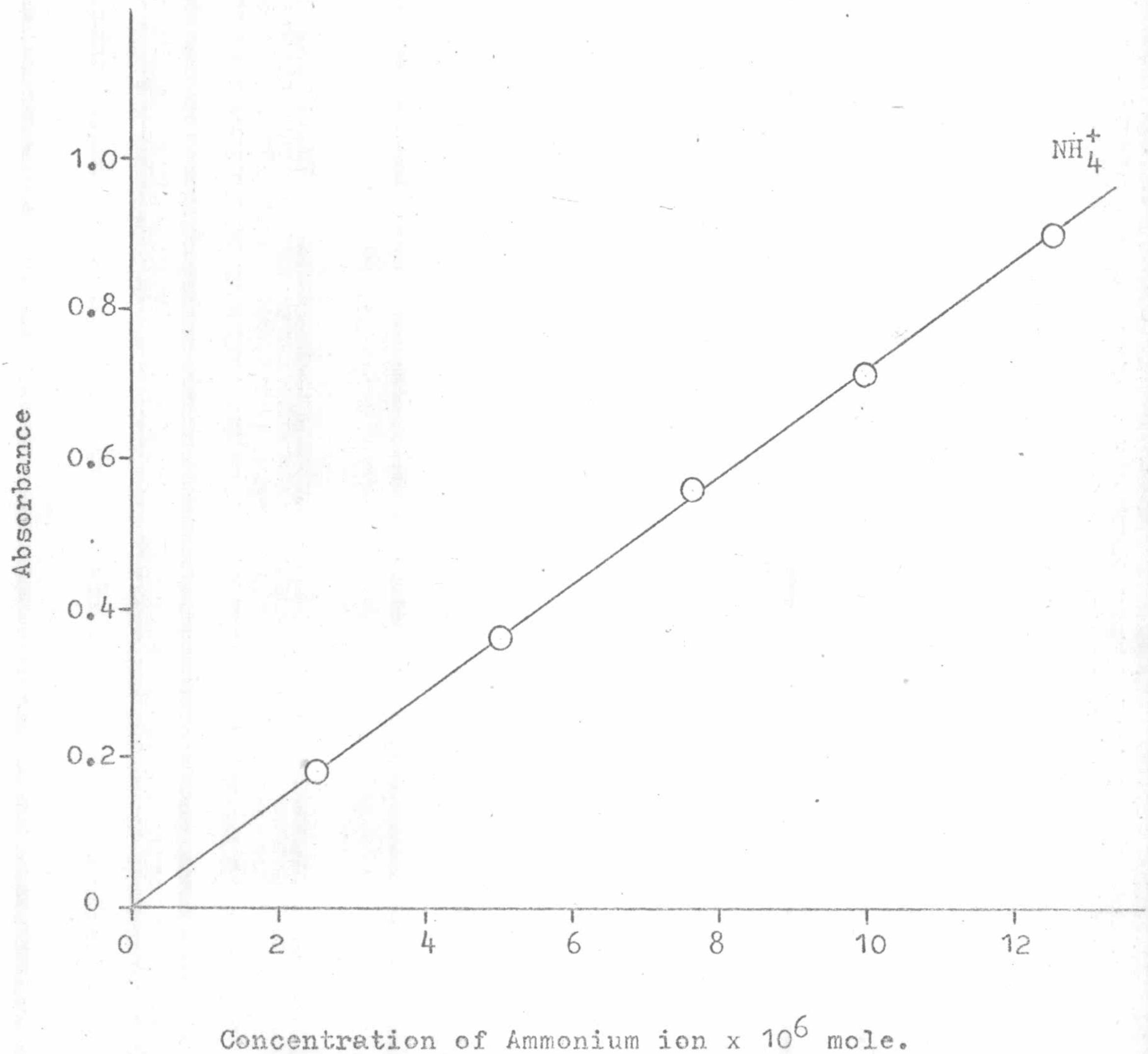

Fig. 4-3 Calibration curve of ammonium ion.

4.2 Exchanging process of certain cations with AMP

Table 4-3 Exchanging process of 0.25 gm. AMP with 30 ml. 0.015 M. $BaCl_2\,2H_2O$ solution.

Contacting time (mins)	Absorbance	Concentration of Ba^{2+}		Absorbance	Concentration of NH_4^+ (gm.ion/30 ml.filtrate)
		gm.ion/30 ml.filtrate	gm. ion in 0.25 gm.AMP		
30	0.092588	0.000424	0.000027	0.101	0.000056
60	0.091514	0.000419	0.000032	0.110	0.000062
90	0.090443	0.000414	0.000037	0.130	0.000077
120	0.089375	0.000409	0.000042	0.135	0.000081
150	0.086186	0.000395	0.000056	0.162	0.000101
180	0.084600	0.000386	0.000063	0.198	0.000127
210	0.082494	0.000378	0.000073	0.225	0.000147

Table 4-4 Exchanging process of 0.25 gm.AMP with 30 ml. 0.015 M $CaCl_2 2H_2O$ solution.

Contacting time (mins)	Absorbance	Concentration of Ca^{2+}		Absorbance	Concentration of NH_4^+ (gm.ion/30 ml.filtrate)
		gm.ion/30 ml.filtrate	gm. ion in 0.25 gm.AMP		
15	0.010283	0.000438	0.000013	0.088	0.000028
30	0.010238	0.000436	0.000015	0.095	0.000031
45	0.010194	0.000434	0.000017	0.098	0.000032
60	0.010149	0.000432	0.000019	0.101	0.000034

Table 4-5 Exchanging process of 0.25 gm. AMP with 30 ml. 0.015 M CsCl solution.

Contacting time (mins)	Absorbance	Concentration of Cs^+		Absorbance	Concentration of NH_4^+ (gm.ion/30 ml.filtrate)
		gm.ion/30 ml.filtrate	gm. ion in 0.25 gm.AMP		
15	0.088842	0.000214	0.000236	0.290	0.000233
30	0.086186	0.000209	0.000243	0.300	0.000242
45	0.085128	0.000205	0.000245	0.303	0.000244
60	0.083546	0.000201	0.000249	0.305	0.000246
75	0.081969	0.000198	0.000253	0.312	0.000252
90	0.080921	0.000195	0.000256	0.315	0.000255

Table 4-6 Exchanging process of 0.25 gm. AMP with 30 ml. 0.015 M KCl solution.

Contacting time (mins)	Absorbance	Concentration of K^+		Absorbance	Concentration of NH_4^+ (gm.ion/30 ml. filtrate)
		gm.ion/30 ml.filtrate	gm. ion in 0.25 gm.AMP		
15	0.449771	0.000337	0.000113	0.150	0.000110
30	0.446116	0.000334	0.000116	0.152	0.000112
45	0.443697	0.000332	0.000117	0.155	0.000115
60	0.437707	0.000328	0.000122	0.160	0.000120
75	0.4341521	0.000325	0.000125	0.161	0.000120
90	0.4317982	0.000323	0.000126	0.162	0.000121

Table 4-7 Exchanging process of 0.25 gm. AMP with 30 ml. 0.015 M RbCl solution.

Contacting time (mins)	Absorbance	Concentration of Rb^+		Absorbance	Concentration of NH_4^+ (gm.ion/30 ml.filtrate)
		gm.ion/30 ml.filtrate	gm. ion in 0.25 gm.AMP		
15	0.261219	0.000274	0.000177	0.104	0.000175
30	0.260427	0.000273	0.000178	0.105	0.000177
45	0.258060	0.000270	0.000181	0.106	0.000179
60	0.254925	0.000267	0.000184	0.108	0.000184
75	0.252976	0.000265	0.000186	0.109	0.000185
90	0.249491	0.000261	0.000190	0.110	0.000188
105	0.247185	0.000259	0.000192	0.111	0.000190
120	0.246416	0.000258	0.000193	0.112	0.000192

Table 4-8 Exchanging process of 0.25 gm. AMP with 30 ml. 0.015 M NaCl solution.

Contacting time (mins)	Absorbance	Concentration of Na^+		Absorbance	Concentration of NH_4^+ (gm.ion/30 ml.filtrate)
		gm.ion/30 ml.filtrate	gm. ion in 0.25 gm.AMP		
15	0.174703	0.000424	0.0000265	0.202	0.000026
30	0.174573	0.000424	0.0000268	0.205	0.000026
45	0.174379	0.000423	0.0000272	0.208	0.000027
60	0.174249	0.000423	0.0000275	0.212	0.000027

Table 4-9 Exchanging process of 0.25 gm. of AMP with 30 ml. 0.015 M $SrCl_2 6H_2O$ solution.

Contacting time (mins)	Absorbance	Concentration of Sr^{2+}		Absorbance	Concentration of NH_4^+ (gm.ion/30 ml.filtrate)
		gm.ion/30 ml.filtrate	gm. ion in 0.25 gm.AMP		
30	0.537602	0.000425	0.000026	0.140	0.000051
60	0.536107	0.000424	0.000027	0.145	0.000053
90	0.533132	0.000421	0.000029	0.160	0.000059
120	0.525783	0.000416	0.000035	0.182	0.000069
150	0.522878	0.000413	0.000038	0.200	0.000077
180	0.518557	0.000409	0.000041	0.210	0.000081
210	0.514278	0.000406	0.000044	0.225	0.000088
240	0.511449	0.000404	0.000047	0.240	0.000095
270	0.505845	0.000399	0.000051	0.256	0.000102
300	0.501689	0.000396	0.000055	0.270	0.000108
330	0.498940	0.000394	0.000057	0.285	0.000114
360	0.490797	0.000387	0.000063	0.310	0.000125

Table 4-10 Exchanging process of 0.25 gm.AMP with 30 ml. 0.0075 M Tl_2SO_4 solution.
(iodometric method)

Contacting time (mins)	ml. of 0.025 M. KIO_3	Concentration of Tl^+		Absorbance	Concentration of NH_4^+ (gm.ion/30 ml.filtrate)
		gm.ion/30 ml.filtrate	gm. ion in 0.25 gm.AMP		
30	4.81	0.000289	0.000161	0.205	0.000159
60	4.75	0.000285	0.000165	0.210	0.000163
90	4.70	0.000282	0.000168	0.214	0.000167
120	4.64	0.000278	0.000172	0.220	0.000172
150	4.60	0.000276	0.000174	0.225	0.000176
180	4.55	0.000273	0.000177	0.230	0.000180
210	4.50	0.000270	0.000180	0.232	0.000182

Table 4-11 Exchanging process of 0.25 gm. AMP with 30 ml. 0.0075 M. Tl_2SO_4 solution. (radiotracer method)

Initial countrate of 10 ml. 0.0075 M. $^{204}Tl_2SO_4$ = 129828 c.p.m.

Contacting time (mins)	Corrected counts per minute for 10 ml. of filtrate	Concentration of Tl^+	
		gm.ion/30 ml.filtrate	gm. ion in 0.25 gm.AMP
30	84208	0.000292	0.000158
60	83074	0.000287	0.000162
90	82397	0.000285	0.000164
120	81271	0.000281	0.000168
150	80504	0.000279	0.000170
180	79445	0.000275	0.000174
210	78526	0.000272	0.000177

Typical calculation for thallous ion concentration

(a) By iodometric titration method

Thallous salts were oxidised by potassium iodate under the Andrews[6] conditions in accordance with the equations given stepwisely below:

$$4IO_3^- + 24H^+ + 10Tl^+ \longrightarrow 10Tl^{3+} + 2I_2 + 12H_2O \qquad (4\text{-}1)$$

$$IO_3^- + 2I_2 + 6H^+ + 5Cl^- \longrightarrow 5ICl + 3H_2O \qquad (4\text{-}2)$$

$$5IO_3^- + 30H^+ + 10Tl^+ + 5Cl^- \longrightarrow 5ICl + 10Tl^{3+} + 15\ H_2O \qquad (4\text{-}3)$$

Equation (4-3) can be reduced to

$$IO_3^- + 6H^+ + 2Tl^+ + Cl^- \longrightarrow ICl + 2Tl^{3+} + 3H_2O \qquad (4\text{-}4)$$

$$1 \text{ mole of } KIO_3 \equiv 2 \text{ gm. ions of } Tl^+ \qquad (4\text{-}5)$$

Calculations for thallous ion concenttration were proceeded by the application of equation (4-2) and the known stoichiometry.

A typical experiment data are shown below.

Standard solution: 0.025 M. KIO_3, total volume used: 4.5 ml.

Exchanging solution: 0.0075 M. Tl_2SO_4, total volume used: 25 ml.

The content of thallous ion in 25 ml. filtrate $= \dfrac{2 \times 0.025 \times 4.5}{1000}$

$= 0.000225$ gm. ion

Hence, for 30 ml. filtrate the thallous ion concentration is $0.000225 \times \dfrac{30}{25}$

$= 0.00027$ gm.ion

It follows that thallous ion concentration which exchange with 0.25 gm.AMP

= (initial concentration of thallous ion in 30 ml. soln.) - 0.00027 gm.ion

= 0.00045 - 0.00027 gm. ion

= 0.00018 gm. ion

(b) By radiotracer technique

The initial countrate of 10 ml. 0.0075 M. $^{204}Tl_2SO_4$ = 129,828 cpm. After 30 minutes contacting with the AMP, the countrate of the same 10 ml. $^{204}Tl_2SO_4$ = 84,208 cpm.

Hence the initial countrate, 129,828 cpm./10 ml. $\equiv$ initial concentration of Tl^+ i.e., $\equiv$ 0.00015 gm. ion of Tl^+

Therefore the final countrate, 84,208 cpm/10 ml. $\equiv$ final concentration of Tl^+ $\equiv \frac{84208 \times 0.00015}{129828}$ gm. ion

But the total volume of the exchanged solution was 30 ml.

Thus amounts of Tl^+ in 30 ml. of the final solution

$$= \frac{84208 \times 0.00015 \times 30}{129828 \times 10} \text{ gm. ion}$$

$$= 0.000292 \text{ gm. ion}$$

But the amounts of Tl^+ in 30 ml. of the initial solution

$$= \frac{0.0075 \times 30 \times 2}{1000} \text{ gm. ion}$$

$$= 0.00045 \text{ gm. ion}$$

Therefore, amounts of Tl^+ that exchanged with AMP = 0.00045 - 0.000292

$$= 0.000158 \text{ gm. ion}$$

4.3 Selectivity

Table 4-12 Maximum exchange and selectivity coefficient of univalent and divalent cations on AMP.

Cation	Ionic radii(Å)	Maximum exchange per mole AMP		$K^{M}_{NH_4}$
		mole of metal ion	mole of ammonium ion	
Na^+	0.95	0.207	0.206	0.0048
K^+	1.33	0.950	0.908	0.1698
Tl^+	1.44	1.352	1.371	0.5608
Rb^+	1.48	1.453	1.446	0.6970
Cs^+	1.69	1.924	1.919	2.3250
Ca^{2+}	0.99	0.142	0.253	0.0004
Sr^{2+}	1.13	0.477	0.943	0.0344
Ba^{2+}	1.35	0.550	1.104	0.0656

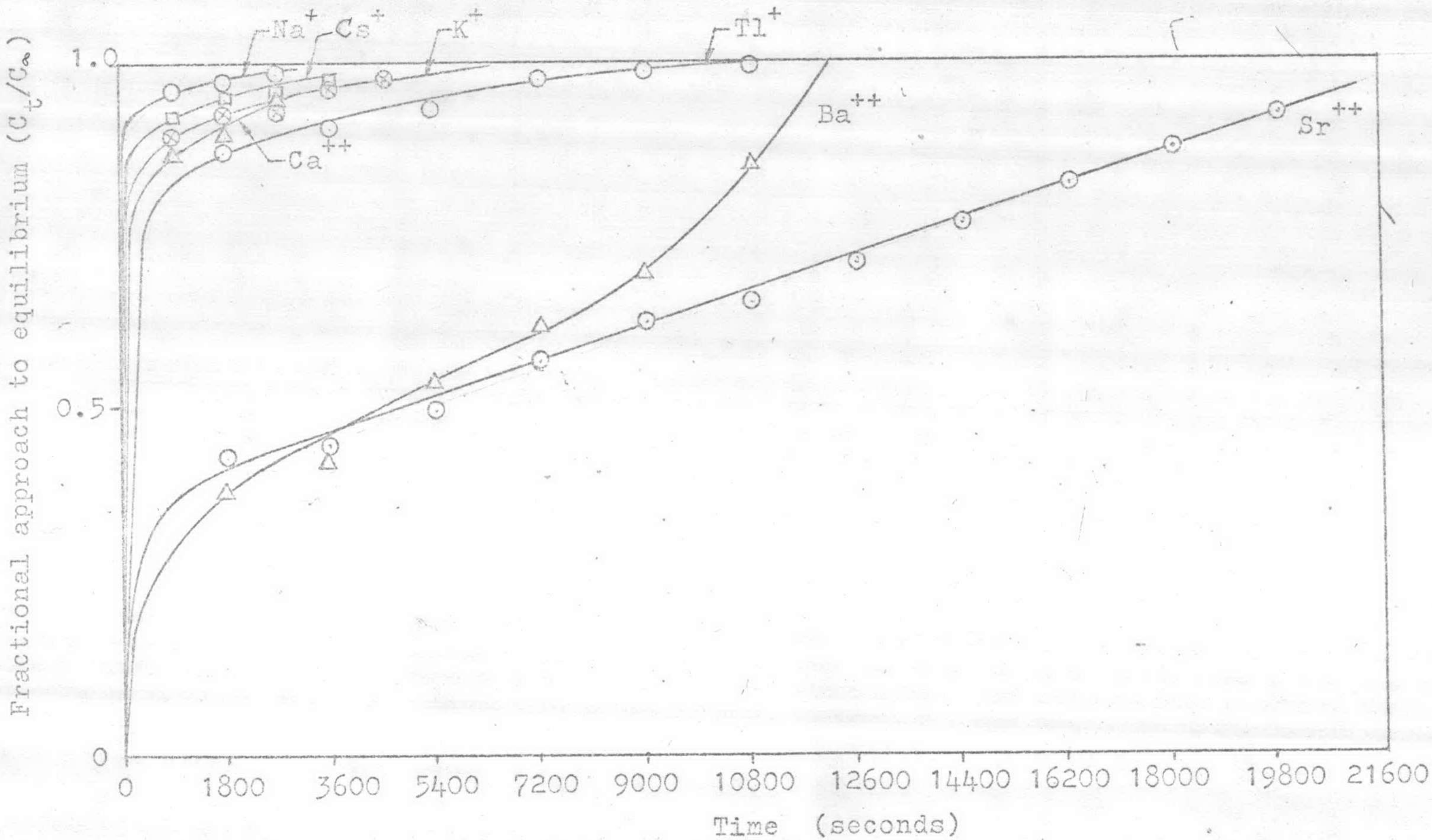

Fig. 4-4 Fractional approach to equilibrium of the cation in the electrolyte solution with the AMP.

<u>Calculation for selectivity coefficient</u> ($K^{M}_{NH_4}$)

Typical calculations for monovalent and divalent cations are given below:

(a) Monovalent cation

The exchange reaction represented by:

$$\overline{R^-A^+} + B^+ \rightleftharpoons \overline{R^-B^+} + A^+$$

$$(b-y) \quad (a-x) \quad x \quad y$$

$$K^{B}_{A} = \frac{[\overline{B^+}][A^+]}{[\overline{A^+}][B^+]} = \frac{(x)(y)}{(a-x)(b-y)}$$

Calculation for $K^{Rb}_{NH_4}$ is cited as an example below:

Here a = initial concentration of cation in solution, in this case equal to 0.00045 gm. ion/30ml solution.

b = initial concentration of ammonium ion in AMP, in this case equal to 0.00039 gm. ion/0.25 gm. AMP.

$[\overline{B^+}]$ = x = concentration at equilibrium of cation within the exchanger, in this case equal to 0.000193 gm. ion/0.25 gm. AMP

$[A^+]$ = y = concentration at equilibrium of ammonium ion in the filtrate, in this case equal to 0.000192 gm. ion/30 ml. filtrate

$[B^+]$ = (a-x) = concentration at equilibrium of cation in the filtrate, in this case equal to 0.000257 gm. ion/30 ml. filtrate.

$[\overline{A^+}]$ = (b-y) = concentration at equilibrium of ammonium ion within the exchanger, in this case equal to 0.000207 gm. ion/0.25 gm. AMP.

$$\text{Therefore } K^{Rb}_{NH_4} = \frac{(x)(y)}{(a-x)(b-y)} = \frac{(0.000193)(0.000192)}{(0.000257)(0.000207)}$$

$$= 0.6970$$

(b) Divalent cation

The exchange reaction is generally represented by:

$$\overline{2A^{+}R^{-}} + B^{2+} \rightleftharpoons \overline{R^{-}B^{2+}} + 2A^{+}$$
$$2(b-y) \qquad (a-x) \qquad\qquad x \qquad\qquad 2y$$

$$K_{A}^{B} = \frac{[\overline{B^{2+}}][A^{+}]^{2}}{[\overline{A^{+}}]^{2}[B^{2+}]} = \frac{(x)(y)^{2}}{(a-x)(b-y)^{2}}$$

Here x = 0.000019 gm. ion of calcium ion/0.25 gm. AMP

y = 0.000034 gm. ion of ammonium ion/30 ml. filtrate

a = 0.000452 gm. ion of calcium ion/30 ml. solution

b = 0.000399 gm. ion of ammonium ion/0.25 gm. AMP

$(a-x)$ = 0.000433 gm. ion of calcium ion/30 ml. filtrate

$(b-y)$ = 0.000365 gm. ion of ammonium ion/0.25 gm. AMP

$$K_{NH_4}^{Ca} = \frac{(0.000019)(0.000034)^{2}}{(0.000433)(0.000365)^{2}}$$

$$= 0.0004$$

4.4 Reversibility.

Table 4-13 Reversibility study of the metal ions with the AMP.

Ions	Forward reaction	Reverse reaction	
	Concentration of ammonium ion(gm.ion/30ml. filtrate)	Absorbance	Concentration of ammonium ion in 0.25 gm. AMP
Na^{+}	0.000027	0.510	0.000026
K^{+}	0.000120	0.398	0.000124
Tl^{+}	0.000182	0.328	0.000186
Rb^{+}	0.000192	0.322	0.000191
Cs^{+}	0.000255	0.245	0.000259
Ca^{2+}	0.000033	0.503	0.000032
Sr^{2+}	0.000125	0.402	0.000121
Ba^{2+}	0.000146	0.370	0.000149