RESULTS AND CALCULATIONS

In this section experimental results and the calculation of chemical speciation of cadmium, lead and copper ions are presented. The analyses reported were carried out in triplicate and the numerical and graphical representation of results were treated statistically. The usual standardization of the methods were carried out prior to the commencing of the actual measurements. S and SS in the tables designate surface and subsurface level of water sample respectively.

3.1 Determination of Anions

3.1.1 Sulphate Ion

The amount of sulphate ion was determined by spectrophotometric method. The typical calibration curve is shown in Fig 3.1 and the concentrations of sulphate ions in samples are in Table 3.1.
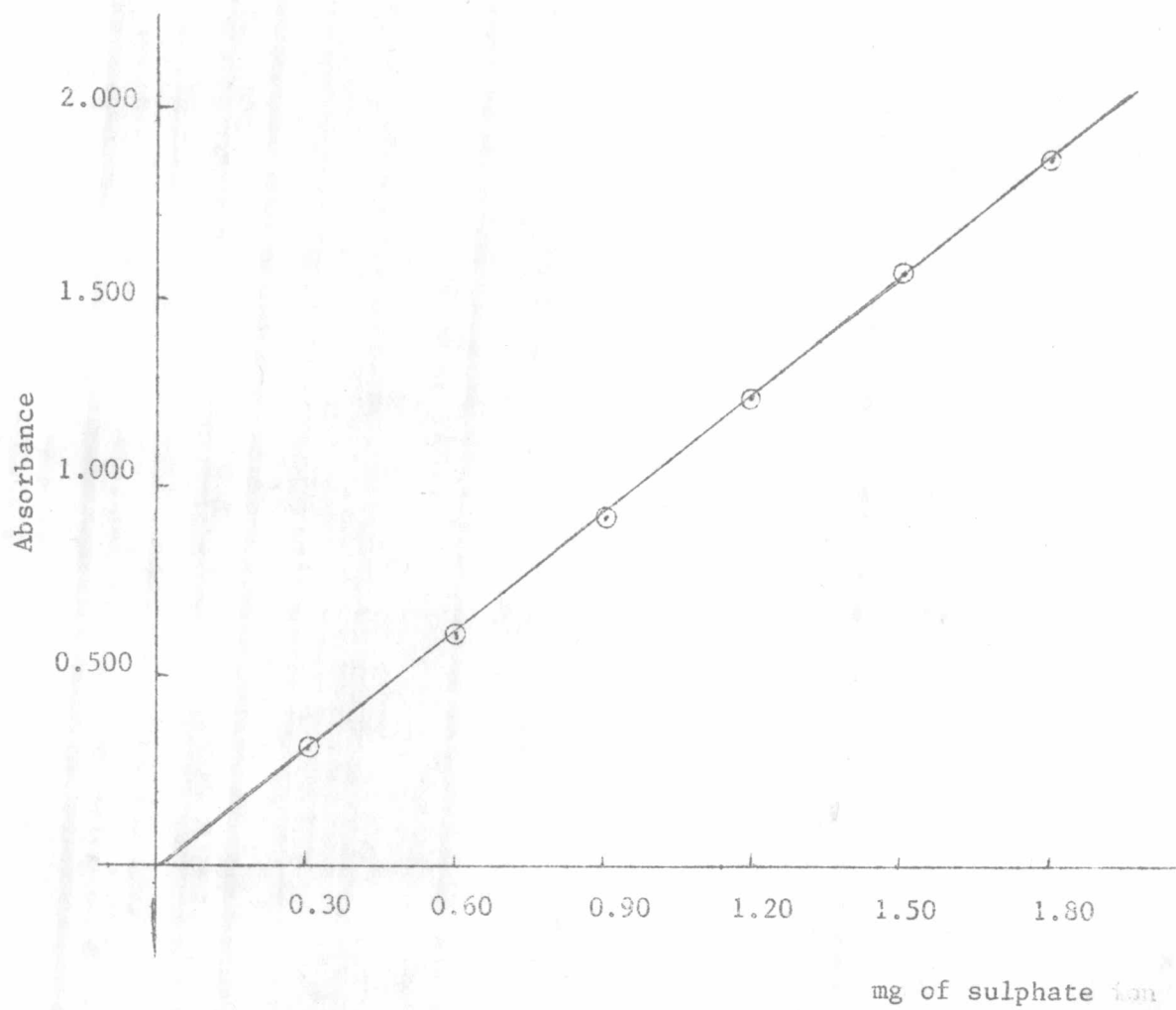
Figure 3.1 Calibration curve for the determination of sulphate ion by UV spectrophotometry.

Table 3.1   Concentrations of sulphate ions in samples.

Date	Sampling station	Absorbance	Concentration of SO_4^{2-} (mol. dm^{-3} x 10^3)
12/10/79	1 S	0.717	14.52 ± 0.17
	1 SS	0.760	15.44 ± 0.14
	2 S	0.596	12.02 ± 0.19
	2 SS	0.728	14.83 ± 0.37
	3 S	0.388	8.06 ± 0.10
	3 SS	0.457	9.37 ± 0.19
	4 S	0.150	3.27 ± 0.14
	4 SS	0.187	4.12 ± 0.19
18/12/79	1 S	0.803	16.35 ± 0.23
	1 SS	1.073	21.81 ± 0.21
	2 S	0.698	14.29 ± 0.21
	2 SS	0.984	20.31 ± 0.14
	3 S	0.552	11.31 ± 0.17
	3 SS	0.595	12.33 ± 0.19
	4 S	0.452	9.35 ± 0.12
	4 SS	0.532	10.94 ± 0.21

3.1.2 Chloride Ion

The amount of chloride ion was determined by potentiometric titration. Fig 3.2 is the titration curve, the equivalence point is at the point "a" which is the intersection of the lines "ab" and "ac" on the x-axis of the Gran's plot (see Appendix I). Concentrations of chloride ions in the samples calculated by using the principle of stoichiometry are shown in Table 3.2.

Table 3.2　Concentrations of chloride ions in samples

| Date	Sampling station	cm^3 of $AgNO_3$ used	Concentrations of Cl^- (mol. dm^3 x 10^2)
12/10/79	1 S	9.09 ± 0.05	27.24 ± 0.15
	1 SS	9.72 ± 0.02	27.78 ± 0.06
	2 S	7.22 ± 0.03	21.64 ± 0.09
	2 SS	9.04 ± 0.01	27.09 ± 0.03
	3 S	4.26 ± 0.07	12.77 ± 0.21
	3 SS	5.31 ± 0.03	15.91 ± 0.09
	4 S	1.57 ± 0.02	4.71 ± 0.06
	4 SS	1.60 ± 0.03	4.79 ± 0.09
18/12/79	1 S	10.49 ± 0.04	31.44 ± 0.12
	1 SS	14.73 ± 0.06	44.15 ± 0.18
	2 S	9.03 ± 0.03	27.06 ± 0.09
	2 SS	13.77 ± 0.02	41.27 ± 0.06
	3 S	6.56 ± 0.03	19.66 ± 0.09
	3 SS	7.18 ± 0.04	21.52 ± 0.12
	4 S	5.26 ± 0.01	15.76 ± 0.03
	4 SS	6.06 ± 0.02	18.16 ± 0.06

43
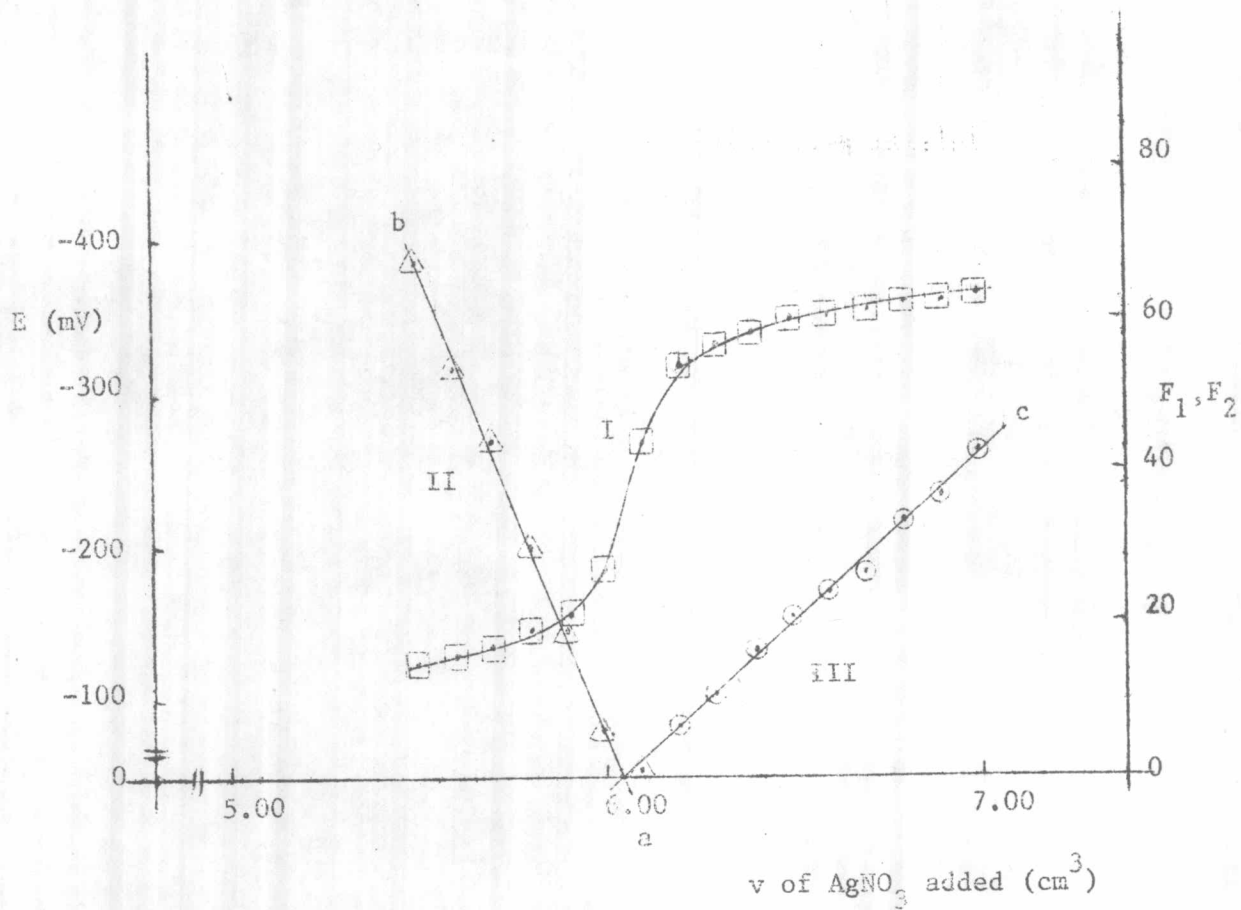
Figure 3.2 I: The titration curve of E **vs**. AgNO$_3$ added.

II and III: The Gran's plot (F$_1$ and F$_2$ vs. AgNO$_3$ added respectively).

3.1.3 Carbonate and Hydrogencarbonate Ions

The amount of carbonate and hydrogencarbonate ions was determined by potentiometric titration. The determination consisted of two parts, the first part, the titration of the water sample with standard hydrochloric acid yielded the sum of carbonate and hydrogencarbonate ions in the sample. Gran's plot was constructed and given two equivalence points at v_1 and v_2 cm^3 of standard hydrochloric acid (Fig 3.3). Obviously, (v_2-v_1) was equivalent to the sum of carbonate and hydrogencarbonate ions in that sample. The second part aimed at the determination of hydrogencarbonate ion concentration only. This was achieved by the titration of the water sample taken from the same batch and the same volume as the first part with standard carbonate-free sodium hydroxide solution. The difference of the results from the first and second part was the carbonate ion content in that volume of sample. Carbonate and hydrogencarbonate ions concentrations in samples are tabulated in Table 3.3.
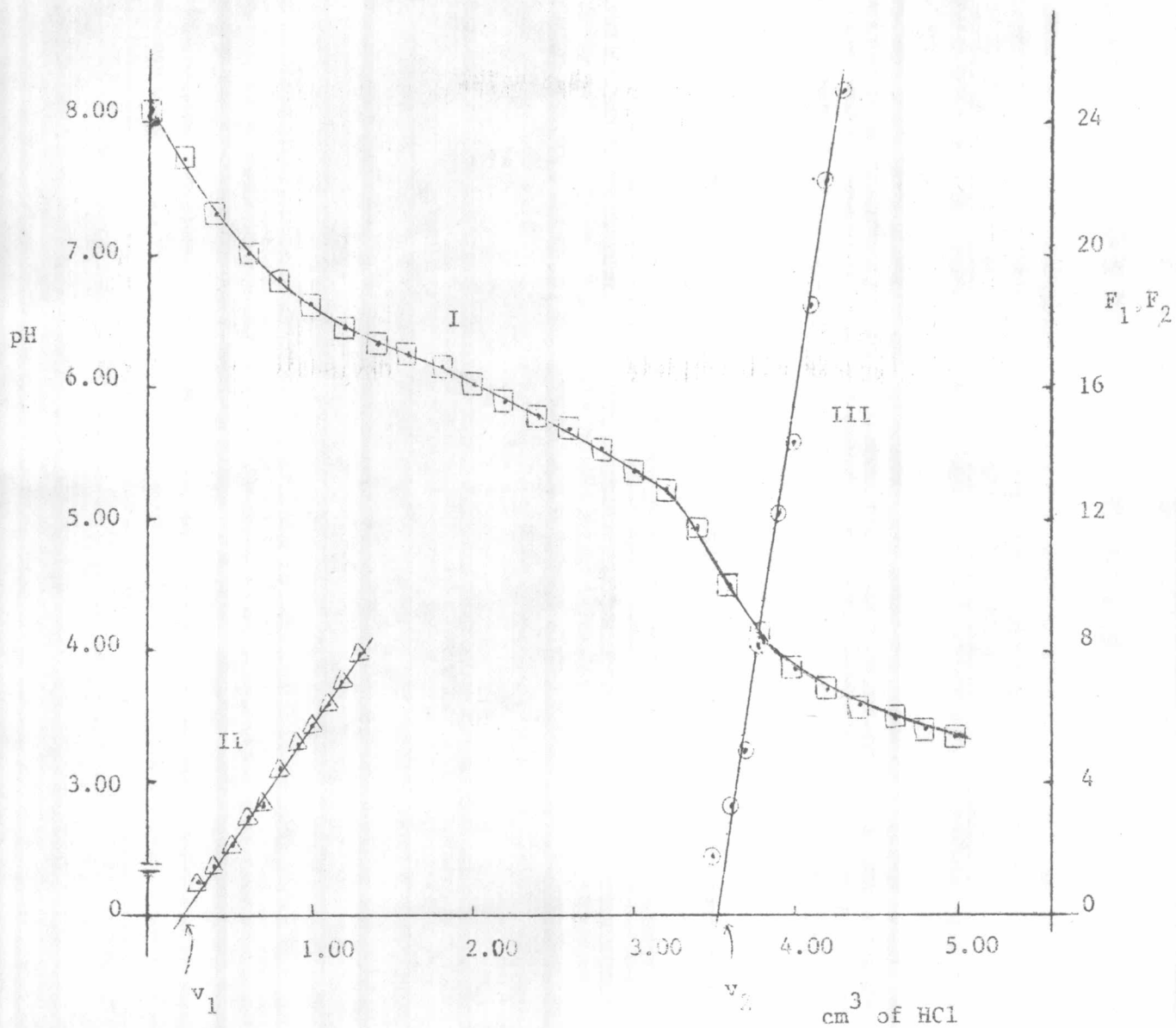
Figure 3.3 I: The titration curve of HCl vs. CO_3^{2-} and HCO_3^- in

water sample.

II and III: The Gran's plot (F_1 and F_2 vs. HCl

added respectively).

Table 3.3 Concentrations of hydrogencarbonate and carbonate ions in samples

Date	Sampling station	Part I: ($[CO_3^{2-}] + [HCO_3^-]$) $= \dfrac{(v_2 - v_1)[HCl]}{1000}$ (mol $\times 10^5$)	Part II: ($[HCO_3^-]$ only) mol of NaOH $\equiv$ HCO_3^- in 100cm^3 sample	$[HCO_3^-]$ (mol.dm$^{-3} \times 10^4$)	Part I–Part II $= [CO_3^{2-}]$ (mol.dm$^{-3} \times 10^5$)
12/10/79	1 S	23.02 ± 0.32	19.77 ± 0.35	19.77 ± 0.35	32.51 ± 0.33
	1 SS	21.67 ± 0.21	18.91 ± 0.23	18.91 ± 0.23	27.54 ± 0.22
	2 S	23.06 ± 0.02	22.47 ± 0.56	22.47 ± 0.56	6.13 ± 0.39
	2 SS	23.02 ± 0.02	22.97 ± 0.48	22.97 ± 0.48	5.07 ± 0.34
	3 S	21.99 ± 0.13	19.48 ± 0.32	19.48 ± 0.32	25.06 ± 0.22
	3 SS	21.67 ± 0.34	20.05 ± 0.28	20.05 ± 0.28	16.16 ± 0.31
	4 S	21.99 ± 0.14	21.76 ± 0.14	21.76 ± 0.14	2.31 ± 0.14
	4 SS	22.50 ± 0.13	21.76 ± 0.27	21.76 ± 0.27	7.45 ± 0.20
18/12/79	1 S	25.68 ± 0.25	21.70 ± 0.20	21.70 ± 0.20	39.77 ± 0.22
	1 SS	21.13 ± 0.21	22.10 ± 0.25	22.10 ± 0.25	30.38 ± 0.23
	2 S	25.57 ± 0.19	22.89 ± 0.36	22.89 ± 0.36	26.75 ± 0.27
	2 SS	25.51 ± 0.22	21.37 ± 0.13	21.37 ± 0.13	41.47 ± 0.17
	3 S	25.84 ± 0.37	22.03 ± 0.42	22.03 ± 0.42	38.08 ± 0.39
	3 SS	25.84 ± 0.41	23.89 ± 0.31	23.89 ± 0.31	19.50 ± 0.36
	4 S	25.89 ± 0.12	19.38 ± 0.14	19.38 ± 0.14	65.17 ± 0.13
	4 SS	25.68 ± 0.25	18.65 ± 0.22	18.65 ± 0.22	70.30 ± 0.23

3.1.4 Hydroxide Ion

The activities of hydroxide ions were calculated from the samples'
pH and Kw both of which depend on salinity of the samples under
investigation (Fig 2.3). The activities of hydroxide ions in samples are
shown in Table 3.4, the typical calculation has already been shown in
section 2.3.1.4.

Table 3.4 Activities of hydroxide ions in samples.

Date	Sampling station	Salinity (%)	Kw = pH+pOH	pH	$(a_{OH} = 10^{-pOH})$ x 10^6
12/10/79	1 S	17.15	13.14	7.38 ± 0.05	1.74 ± 0.21
	1 SS	18.28	13.13	7.63 ± 0.09	3.16 ± 0.61
	2 S	13.58	13.17	7.41 ± 0.07	1.74 ± 0.30
	2 SS	18.95	13.13	7.49 ± 0.02	2.29 ± 0.11
	3 S	8.06	13.22	7.45 ± 0.09	1.70 ± 0.40
	3 SS	10.01	13.20	7.32 ± 0.03	1.32 ± 0.11
	4 S	3.02	13.26	7.30 ± 0.05	1.10 ± 0.17
	4 SS	3.06	13.26	7.29 ± 0.10	1.07 ± 0.28
18/12/79	1 S	22.04	13.10	7.90 ± 0.03	6.31 ± 0.45
	1 SS	26.95	13.06	7.87 ± 0.07	6.46 ± 0.96
	2 S	18.70	13.13	7.80 ± 0.05	4.68 ± 0.51
	2 SS	26.11	13.07	7.84 ± 0.07	5.89 ± 0.85
	3 S	10.75	13.14	7.80 ± 0.08	4.57 ± 0.77
	3 SS	13.05	13.18	7.83 ± 0.03	4.47 ± 0.30
	4 S	9.92	13.20	7.64 ± 0.05	2.75 ± 0.30
	4 SS	11.09	13.19	7.53 ± 0.08	2.19 ± 0.37

3.2 Determination of Cations

3.2.1 Sodium and Potassium Ions

Sodium and potassium ions were determined by the flame photometric method. The typical calibration curves are shown in Figs 3.4 and 3.5. Table 3.5 shows the concentrations of sodium and potassium ions in the samples.

Table 3.5 Concentrations of sodium and potassium ions in samples

| Date	Sampling station	Sodium Ion		Potassium Ion	
		Relative Intensity	$[Na^+]$ $(mol.dm^{-3}x10^2)$	Relative Intensity	$[K^+]$ $(mol.dm^{-3}x10^4)$
12/10/79	1 S	65.73	24.17 ± 0.52	54.03	53.40 ± 0.82
	1 SS	69.37	26.09 ± 0.35	56.11	56.77 ± 0.31
	2 S	59.85	20.35 ± 0.48	46.23	40.30 ± 1.12
	2 SS	66.01	24.00 ± 0.17	52.12	50.33 ± 1.05
	3 S	47.08	12.52 ± 0.17	34.29	20.66 ± 0.14
	3 SS	52.85	16.00 ± 0.35	42.05	33.86 ± 0.92
	4 S	34.03	4.69 ± 0.35	23.50	3.78 ± 0.51
	4 SS	33.56	4.52 ± 0.49	27.22	9.92 ± 0.51
18/12/79	1 S	71.52	23.26 ± 0.17	58.13	60.05 ± 1.31
	1 SS	86.64	36.35 ± 0.20	69.27	78.46 ± 1.12
	2 S	62.27	21.74 ± 0.18	54.11	53.40 ± 0.51
	2 SS	77.33	30.78 ± 0.52	67.03	74.73 ± 0.41
	3 S	58.82	19.65 ± 0.20	45.57	39.59 ± 0.41
	3 SS	60.51	20.52 ± 0.35	49.21	46.03 ± 1.12
	4 S	52.77	16.00 ± 0.19	42.56	34.78 ± 0.21
	4 SS	54.85	17.22 ± 0.17	45.59	39.69 ± 0.61
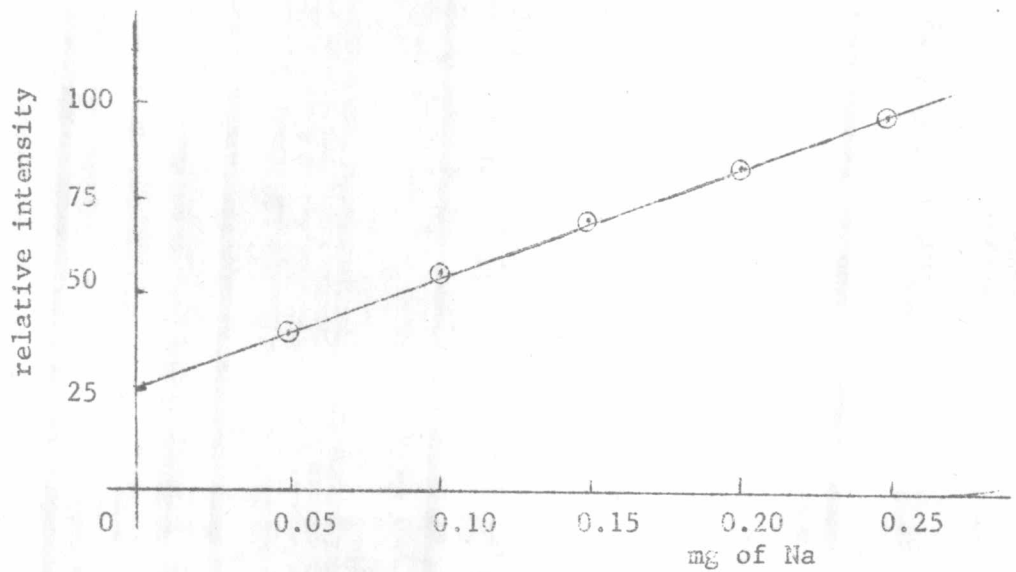
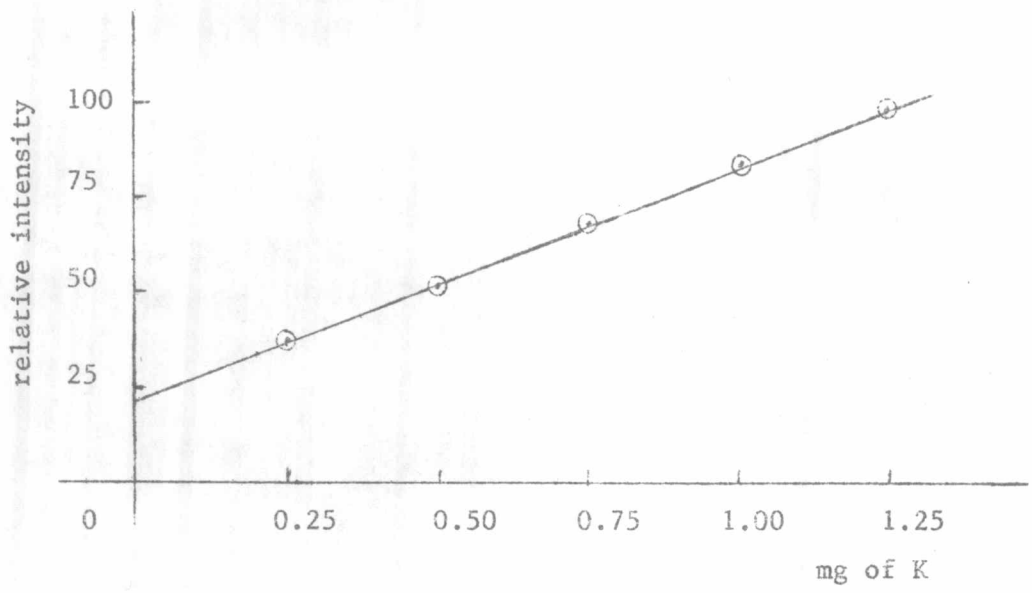Figure 3.4 Calibration curve for the determination of sodium ion by flame photometry.

Figure 3.5 Calibration curve for the determination of potassium ion by flame photometry.

3.2.2 Calcium and Magnesium Ions.

The amount of calcium and magnesium ions was determined by the atomic absorption spectroscopic method. The typical calibration curves are shown in Figs. 3.6 and 3.7. Concentrations of calcium and magnesium ions are given in Table 3.6.

Table 3.6 Concentrations of calcium and magnesium ions in samples

| Date	Sampling station	Calcium ion		Magnesium ion	
		Absorbance	$[Ca^{2+}]$ $(mol.dm^{-3}x10^4)$	Absorbance	$[Mg^{2+}]$ $(mol.dm^{-3}x10^3)$
12/10/79	1 S	0.258	51.15 ± 0.99	0.370	26.82 ± 0.33
	1 SS	0.290	58.38 ± 0.62	0.380	27.64 ± 0.66
	2 S	0.210	40.17 ± 0.75	0.288	20.57 ± 0.23
	2 SS	0.275	54.89 ± 1.48	0.383	28.11 ± 0.33
	3 S	0.145	25.20 ± 1.25	0.160	11.19 ± 0.49
	3 SS	0.165	29.69 ± 0.75	0.232	3.39 ± 0.49
	4 S	0.110	17.46 ± 0.75	0.068	4.11 ± 0.47
	4 SS	0.120	19.71 ± 0.99	0.075	4.77 ± 0.23
18/12/79	1 S	0.290	58.58 ± 1.51	0.388	28.13 ± 0.66
	1 SS	0.365	75.60 ± 1.50	0.415	30.27 ± 0.82
	2 S	0.245	47.90 ± 0.75	0.335	24.18 ± 0.33
	2 SS	0.330	67.61 ± 0.99	0.498	36.52 ± 0.23
	3 S	0.195	36.68 ± 1.50	0.268	19.25 ± 0.11
	3 SS	0.197	36.93 ± 0.99	0.320	23.20 ± 0.19
	4 S	0.155	27.44 ± 1.25	0.205	14.15 ± 0.82
	4 SS	0.182	33.68 ± 0.99	0.258	18.43 ± 0.11
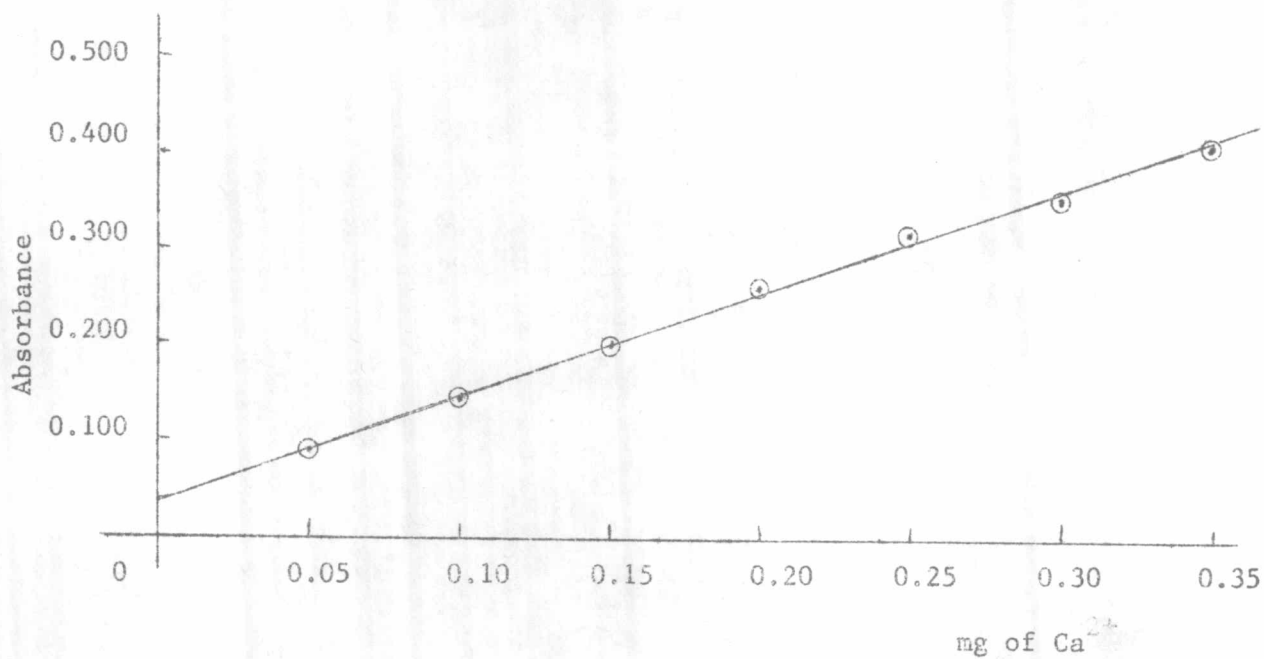
Figure   3.6 Calibration curve for the determination of calcium ion by atomic absorption spectroscopy.
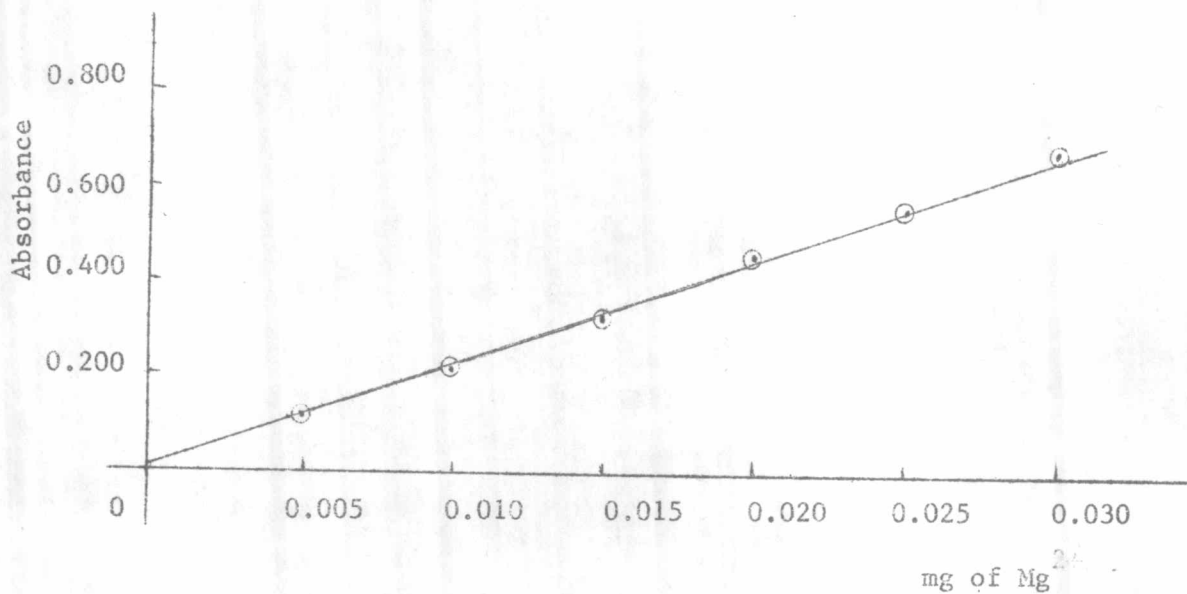
figure   3.7 Calibration curve for the determination of magnesium ion by atomic absorption spectroscopy.

3.2.3 Cadmium, Lead and Copper Ion

Cadmium, lead and copper ions concentrations were determined simultaneously by the anodic stripping voltammetric method (37, 57, 58). Under the present employed working conditions the reduction peaks appeared at -0.70 V, -0.55 V and -0.35 V vs. SCE for cadmium, lead and copper ions respectively (Fig 3.8). Since Fig 3.9 indicated that standard addition method could be applied for the determination of cadmium, lead and copper ions in the water sample both at natural pH and at 0.16 $mol.dm^{-3}$ HNO_3, the method was therefore adopted for such a purpose with the percentage error of the peak height readings being smaller than 4%. Results are shown in Tables 3.7-3.12.

Figure 3.8 Differential pulse stripping voltammogram for cadmium, lead and copper ion.
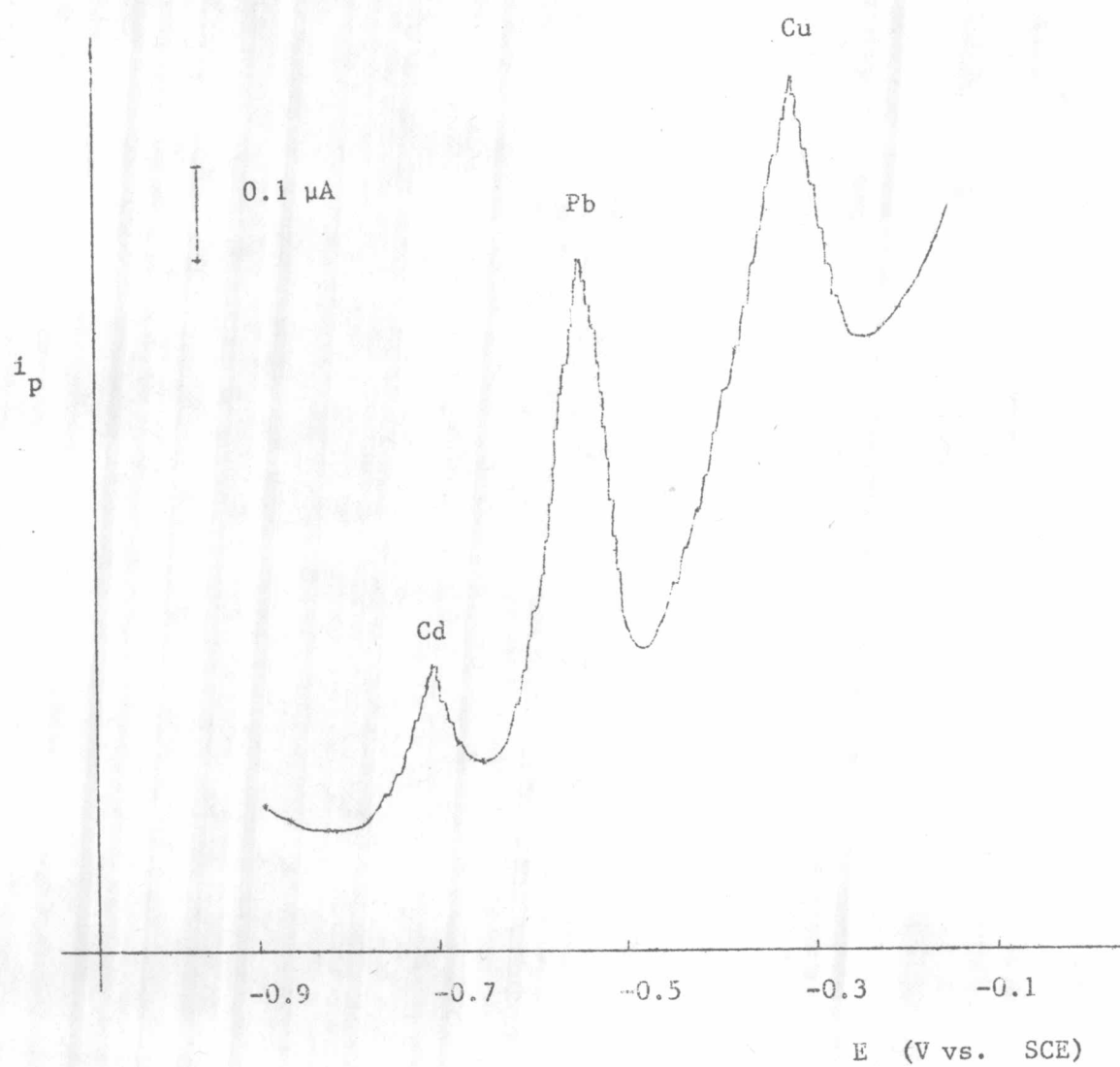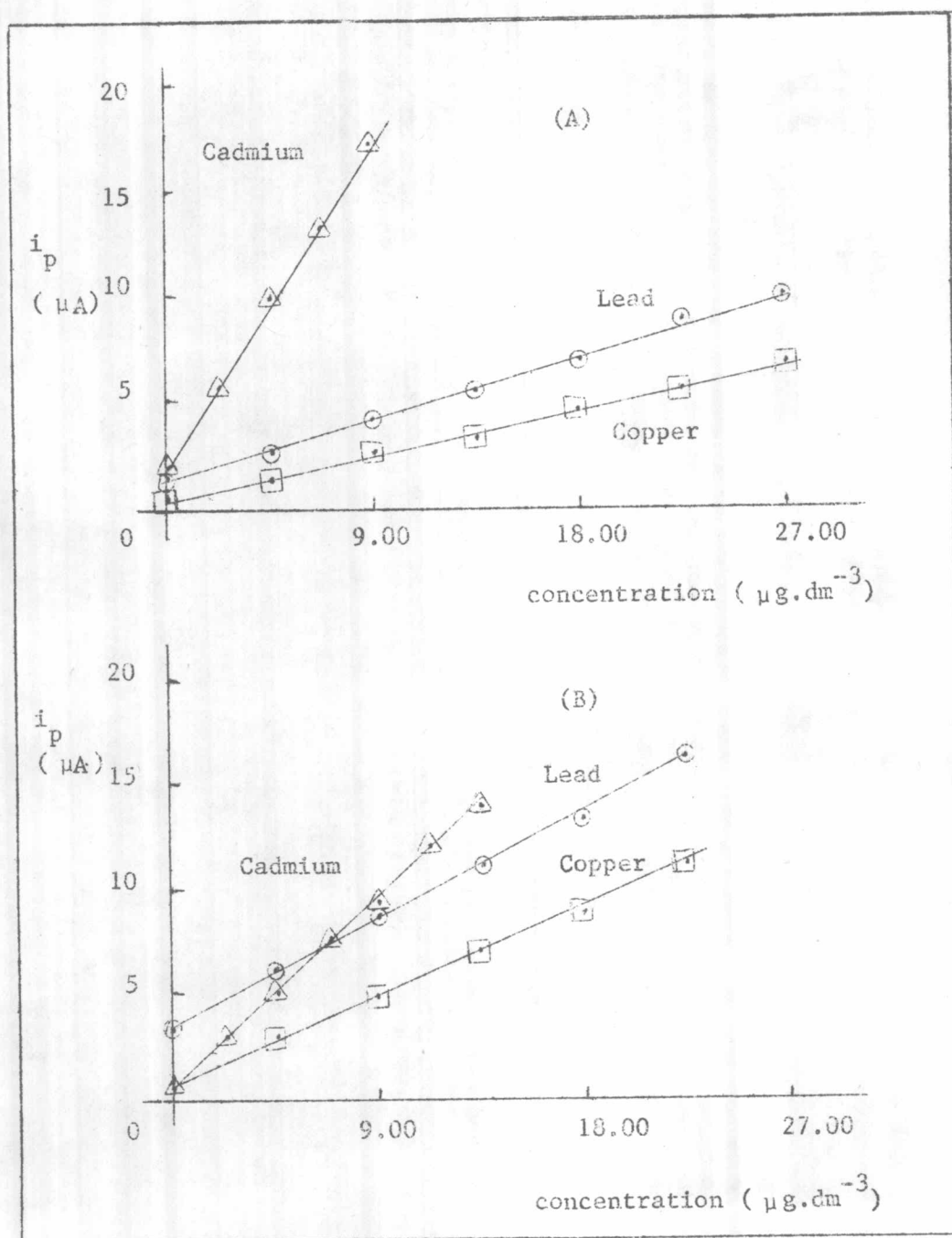
Figure 3.9 Linear dependence of peak currents on concentrations of

DPASV analysis of cadmium ion (△), lead ion (☉), and copper

ion (▢) in water sample

A). at natural pH   B). at 0.16 mol.dm^{-3} HNO$_3$

Table 3.7 Data for DPASV analyses of cadmium ion in samples at 0.16 mol.dm^{-3} HNO$_3$

Date	Sampling station	i_p sample (μA)	i_p sample + standard (μA)	μg Cd dm^{-3} added	μg Cd.dm^{-3} sample
12/10/79	1 S	0.26	0.42	0.57	0.91 ± 0.09
	1 SS	0.53	0.76	0.29	0.67 ± 0.03
	2 S	0.24	0.39	0.28	0.46 ± 0.01
	2 SS	0.20	0.65	0.85	0.35 ± 0.02
	3 S	0.20	0.32	0.29	0.48 ± 0.03
	3 SS	0.18	0.36	0.58	0.32 ± 0.02
	4 S	1.24	1.88	0.58	1.07 ± 0.05
	4 SS	0.68	1.10	0.29	0.46 ± 0.04
18/12/79	1 S	0.76	1.44	0.59	0.62 ± 0.05
	1 SS	0.60	1.17	0.59	0.60 ± 0.09
	2 S	0.79	1.25	0.58	0.93 ± 0.08
	2 SS	1.40	2.75	0.86	1.24 ± 0.02
	3 S	0.80	1.18	0.28	0.58 ± 0.05
	3 SS	0.41	0.83	0.59	0.55 ± 0.01
	4 S	0.41	0.82	1.16	1.09 ± 0.12
	4 SS	0.33	0.48	0.58	1.25 ± 0.09

Table 3.8 Data for DPASV analyses of cadmium ions in samples at natural pH

Date	Sampling station	i_p sample (μA)	i_p sample + standard (μA)	$\mu g\ Cd.dm^{-3}$ added	$\mu g\ Cd.dm^{-3}$ sample	% of Cd at natural pH
12/10/79	1 S	0.25	1.22	0.29	0.73 ± 0.03	80.22
	1 SS	0.31	1.01	0.15	0.65 ± 0.02	97.01
	2 S	0.29	1.30	0.59	0.17 ± 0.03	36.96
	2 SS	1.03	3.55	0.29	0.12 ± 0.04	34.29
	3 S	0.33	0.93	0.29	0.16 ± 0.02	33.33
	3 SS	0.19	0.68	0.29	0.11 ± 0.02	34.37
	4 S	0.80	1.31	0.29	0.46 ± 0.03	42.99
	4 SS	1.22	2.03	0.29	0.43 ± 0.05	93.48
18/12/79	1 S	0.44	1.02	0.58	0.44 ± 0.03	74.58
	1 SS	1.31	2.43	0.29	0.34 ± 0.07	56.67
	2 S	1.68	2.77	0.58	0.86 ± 0.04	92.47
	2 SS	1.40	2.75	1.17	1.16 ± 0.09	93.55
	3 S	0.32	1.30	0.59	0.19 ± 0.01	32.76
	3 SS	2.68	3.43	0.59	0.49 ± 0.03	89.09
	4 S	1.57	3.25	0.58	0.54 ± 0.02	49.54
	4 SS	0.27	0.58	0.59	0.48 ± 0.05	38.40

Table 3.9 Data for DPASV analyses of lead ions in samples at 0.16 mol.dm^{-3} sample

Date	Sampling station	i_p sample (μA)	i_p sample + standard (μA)	μg Pb.dm^{-3} added	μg Pb.dm^{-3} sample
12/10/79	1 S	1.91	2.31	1.48	6.85 ± 0.07
	1 S	3.84	4.63	1.48	6.90 ± 0.12
	2 S	2.71	4.22	2.94	5.03 ± 0.19
	2 SS	3.08	3.95	1.43	4.75 ± 0.09
	3 S	4.09	6.28	2.94	7.01 ± 0.13
	3 SS	2.03	2.73	2.93	8.05 ± 0.25
	4 S	2.09	3.37	5.84	8.43 ± 0.09
	4 SS	5.52	10.34	5.78	6.16 ± 0.14
18/12/79	1 S	2.49	4.93	5.83	5.59 ± 0.17
	1 SS	6.43	10.63	4.38	6.34 ± 0.24
	2 S	2.35	4.20	5.85	6.98 ± 0.15
	2 SS	3.17	4.56	2.94	6.37 ± 0.13
	3 S	6.40	8.99	2.94	6.91 ± 0.20
	3 SS	1.44	1.86	1.46	4.77 ± 0.19
	4 S	5.45	9.22	2.91	4.02 ± 0.23
	4 SS	2.12	2.85	2.91	7.96 ± 0.17

Table 3.10 Data for DPASV analyses of lead ions in sample at natural pH

Date	Sampling station	i_p sample (μA)	i_p sample + standard (μA)	μg $Pb.dm^{-3}$ added	μg $Pb.dm^{-3}$ sample	% of Pb at natural pH
12/10/79	1 S	3.72	5.23	0.73	1.75 ± 0.13	20.00
	1 SS	2.26	3.43	0.74	1.41 ± 0.07	16.07
	2 S	1.95	3.28	2.17	2.12 ± 0.20	47.43
	2 SS	2.97	4.12	0.74	1.86 ± 0.14	23.70
	3 S	0.79	1.55	2.96	2.97 ± 0.09	42.65
	3 SS	0.88	1.65	1.47	1.66 ± 0.13	26.82
	4 S	2.63	4.27	1.47	2.29 ± 0.13	34.60
	4 SS	1.32	1.83	0.74	1.87 ± 0.22	58.67
18/10/79	1 S	4.25	6.53	0.74	1.35 ± 0.05	40.14
	1 SS	6.45	11.52	1.47	1.80 ± 0.21	62.08
	2 S	5.06	9.05	1.47	1.81 ± 0.13	26.82
	2 SS	1.02	1.80	0.74	0.95 ± 0.07	13.02
	3 S	6.40	8.99	0.74	1.77 ± 0.10	47.60
	3 SS	5.25	6.85	0.74	2.36 ± 0.12	70.63
	4 S	5.90	7.90	0.73	2.10 ± 0.20	43.30
	4 SS	7.55	10.02	0.73	2.17 ± 0.15	24.12

Table 3.11 Data for DPASV analyses of copper ions in samples at 0.16 mol.dm^{-3} HNO$_3$

Date	Sampling station	i_p sample (μA)	i_p sample + standard (μA)	μg Cu.dm^{-3} added	μg Cu.dm^{-3} sample
12/10/79	1 S	1.92	3.02	1.48	2.47 ± 0.20
	1 SS	2.95	5.52	2.97	3.23 ± 0.18
	2 S	1.60	2.73	1.47	2.00 ± 0.07
	2 SS	0.80	1.38	4.31	5.46 ± 0.21
	3 S	1.12	1.39	1.47	5.83 ± 0.20
	3 SS	3.51	4.98	2.93	3.35 ± 0.13
	4 S	1.03	2.42	2.91	2.06 ± 0.05
	4 SS	0.64	2.22	7.22	2.73 ± 0.07
18/12/79	1 S	0.52	1.01	2.91	2.94 ± 0.13
	1 SS	3.90	5.82	1.46	2.84 ± 0.13
	2 S	0.81	1.18	1.46	3.06 ± 0.11
	2 SS	4.60	6.12	1.47	4.26 ± 0.08
	3 S	2.95	4.07	1.47	3.72 ± 0.05
	3 SS	0.66	1.22	2.92	3.28 ± 0.06
	4 S	2.50	4.22	4.36	5.95 ± 0.21
	4 SS	5.92	8.75	2.97	5.76 ± 0.32

Table 3.12 Data for DPASV analyses of copper ions in samples at natural pH

Date	Sampling station	i_p sample (μA)	i_p sample + standard (μA)	$\mu g\ Cu.dm^{-3}$ added	$\mu g\ Cu.dm^{-3}$ sample	% of Cu at natural pH
12/10/79	1 S	1.25	2.21	1.47	1.86 ± 0.08	35.30
	1 SS	1.65	3.65	1.47	1.19 ± 0.02	36.84
	2 S	0.93	2.05	1.49	1.21 ± 0.05	60.50
	2 SS	1.40	2.36	1.48	2.11 ± 0.10	38.64
	3 S	0.89	1.98	1.47	1.19 ± 0.05	20.42
	3 SS	1.38	1.59	1.47	0.93 ± 0.05	27.76
	4 S	2.41	4.80	1.47	1.45 ± 0.11	70.39
	4 SS	0.78	1.66	1.48	1.28 ± 0.02	46.89
18/12/79	1 S	2.82	5.15	1.48	1.75 ± 0.03	59.52
	1 SS	1.02	3.55	1.49	0.57 ± 0.02	20.07
	2 S	2.42	4.48	1.48	1.70 ± 0.11	55.55
	2 SS	2.98	5.02	1.48	2.11 ± 0.07	49.53
	3 S	0.82	1.37	1.48	2.15 ± 0.09	57.79
	3 SS	0.43	0.93	1.48	1.25 ± 0.03	38.11
	4 S	4.20	12.25	2.94	1.49 ± 0.08	25.04
	4 SS	3.82	9.42	2.94	1.95 ± 0.04	33.85

3.3 Calculations of the Distribution of Metal Species in Samples

In order to calculate the distribution of chemical species, a mass balance equation as used by Zirino and Yamamoto (27) was written for each metal. For any given metal, M the equations are, as shown in section 1.3, that

$$[M]\text{total} = [M] + \sum_{n=1}^{4} \sum_{i=1}^{j} [ML_{(i)_n}] \dots \dots \dots \dots (3.3.1)$$

and

$$[ML_{(i)_n}] = \beta_{(i)_n} [M][L_{(i)}]^n \frac{\gamma_M \gamma_{L_{(i)}}^n}{\gamma_{ML_{(i)_n}}} \dots \dots \dots \dots (3.3.2)$$

therefore,

$$[M]\text{total} = [M] + \sum_{n=1}^{4} \sum_{i=1}^{j} \beta_{(i)_n} [M][L_{(i)}]^n \frac{\gamma_M \gamma_{L_{(i)}}^n}{\gamma_{ML_{(i)_n}}} \dots (3.3.3)$$

The percentage of the uncomplexed metal ion and the percentage of the complex $ML_{(i)_n}$ were expressed by equations (3.3.4) and 3.3.5) respectively.

$$\% [M] = 100 / 1 + \sum_{n=1}^{} \sum_{i=1}^{} \beta_{(i)_n} [L_{(i)}]^n \frac{\gamma_M \gamma_{L_{(i)}}^n}{\gamma_{ML_{(i)_n}}} \dots (3.3.4)$$

$$\% [ML_{(i)_n}] = \frac{100 \beta_{(i)_n} [L_{(i)}]^n \frac{\gamma_M \gamma_{L_{(i)}}^n}{\gamma_{ML_{(i)_n}}}}{1 + \sum_{n=1}^{4} \sum_{i=1}^{j} \beta_{(i)_n} [L_{(i)}]^n \frac{\gamma_M \gamma_{L_{(i)}}^n}{\gamma_{ML_{(i)_n}}}} \dots (3.3.5)$$

The utilization of equations (3.3.4) and (3.3.5) is possible if γ_M, γ_L, γ_{ML} and β_i are known. The values of the later were taken from Sillen and Martell (32,34) and are shown in Table 3.13. As for γ's, they were calculated by the conventional method and results are shown in Table 3.14. It is worth mentioning that the ionic strength, $I = \frac{1}{2} \Sigma C_i Z_i^2$, which is part of the computation of γ's were calculated by assuming that in the water sample only free ions of the abundant constituents were present.

A typical calculation for the percentage of metal species is shown in Appendix III for cadmium. Results from such calculations for cadmium, lead and copper species are tabulated in Tables 3.15 and 3.16.

Table 3.13 Stability constants of metals ion-ligand complexes

M	L	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$
Cd^{2+}	Cl^-	1.46	1.83	1.96	--
	SO_4^{2-}	1	--	--	--
	CO_3^{2-}	3.2	--	--	--
	HCO_3^-	1.2	--	--	--
	OH^-	4.3	10.6	10.0	10.0
	OH^-, Cl^-	6.1	--	--	--
Pb^{2+}	Cl^-	0.88	1.49	1.09	0.94
	SO_4^{2-}	1	--	--	--
	CO_3^{2-}	3.0	--	--	--
	HCO_3^-	2.2	--	--	--
	OH^-	6.0	10.9	13.9	16.3
	OH^-, Cl^-	6.2	--	--	--
Cu^{2+}	Cl^-	1.2	0.9	0.8	0.9
	SO_4^{2-}	1	--	--	--
	CO_3^{2-}	5.6	--	--	--
	HCO_3^-	1.5	--	--	--
	OH^-	6.4	14.0	15.0	16.4
	OH^-, Cl^-	7.9	--	--	--

Table 3.14 Activity coefficients of anions and metal species

Date	Sampling station	Ionic strength	γ's anions				γ's metal species**		
			$\gamma_{Cl^-}^*$	$\gamma_{HCO_3^-}^*$	$\gamma_{CO_3^{2-}}^*$	$\gamma_{SO_4^{2-}}^*$	γ_0	γ_1	γ_2
12/10/79	1 S	0.354	0.654	0.714	0.262	0.213	0.956	0.706	0.217
	1 SS	0.371	0.654	0.710	0.255	0.199	0.954	0.704	0.213
	2 S	0.286	0.656	0.727	0.281	0.257	0.964	0.716	0.236
	2 SS	0.356	0.654	0.712	0.259	0.213	0.956	0.706	0.217
	3 S	0.129	0.754	0.777	0.365	0.361	0.984	0.763	0.322
	3 SS	0.132	0.754	0.777	0.365	0.361	0.983	0.761	0.319
	4 S	0.067	0.799	0.814	0.437	0.434	0.992	0.803	0.406
	4 SS	0.070	0.797	0.812	0.434	0.432	0.991	0.801	0.400
18/12/79	1 S	0.382	0.654	0.708	0.252	0.199	0.953	0.702	0.211
	1 SS	0.527	0.648	0.690	0.226	0.164	0.935	0.690	0.186
	2 S	0.334	0.655	0.719	0.268	0.227	0.959	0.709	0.222
	2 SS	0.493	0.651	0.694	0.232	0.163	0.939	0.692	0.191
	3 S	0.286	0.656	0.727	0.281	0.257	0.964	0.716	0.236
	3 SS	0.292	0.656	0.727	0.281	0.257	0.964	0.715	0.234
	4 S	0.143	0.722	0.772	0.357	0.374	0.982	0.756	0.310
	4 SS	0.246	0.685	0.735	0.293	0.251	0.969	0.724	0.251

* $\gamma_{Cl^-}, \gamma_{SO_4^{2-}}, \gamma_{HCO_3^-}$ and $\gamma_{CO_3^{2-}}$ calculated from $\gamma_\pm^\nu = \gamma_1^{\nu_1} \gamma_2^{\nu_2}$ using the published values of $\gamma_{\pm KCl}, \gamma_{\pm K_2SO_4}$ [25] and $\gamma_{KHCO_3}, \gamma_{K_2CO_3}$ [20]

** γ's metal species calculated from the Robinson and Stoke modified Debye-Huckel expression [30]

$$\log \gamma_Z = \frac{-0.5115\ Z^2\sqrt{I}}{1 + 1.316\sqrt{I}} + 0.055\ I$$

where Z is the ionic charge, in this case is equal to 0, 1, 2 corresponding to γ's of various species, neutral species (γ_0), monovalent species (γ_1) and divalent species (γ_2).

I is the ionic strength.

Table 3.15 Percentage speciation of cadmium, lead and copper ions in samples on 12/10/79

Sampling station	S ‰	pH	Metal (M)	%Free ion	Complex (ML_n)	Ligands (L)					
						Cl^-	SO_4^{2-}	CO_3^{2-}	HCO_3^-	OH^-	OH^-,Cl^-
1 S	17.15	7.38	Cd^{2+}	23.43	ML_1	37.01	1.64	0.99	0.16	0.25	20.73
					ML_2	11.41				0.64	
					ML_3	3.72					
			Pb^{2+}	45.74	ML_1	19.01	0.32	1.22	3.15	24.43	1.77
					ML_2	0.49				2.49	
					ML_3	0.98					
					ML_4	0.40					
			Cu^{2+}	1.17	ML_1	1.02	0.01	12.49	0.02	1.58	6.56
					ML_2	0.07				77.06	
					ML_3	0.01					
					ML_4	0.01					
1 SS	18.28	7.63	Cd^{2+}	28.83	ML_1	45.71	0.20	0.72	0.18	0.55	4.66
					ML_2	14.37				2.56	
					ML_3	4.77					
			Pb^{2+}	32.24	ML_1	13.44	0.22	0.50	2.08	30.84	6.55
					ML_2	7.43				5.72	
					ML_3	0.72				0.02	
					ML_4	0.31					
			Cu^{2+}	0.41	ML_1	0.35	–	2.54	0.01	0.98	4.15
					ML_2	0.02				90.84	4.15
					ML_3	0.01					
					ML_4	0.69					

Table 3.15 (continued)

Sampling station	S ‰	pH	Metal (M)	%Free ion	Complex (ML_n)	Ligands (L)					
						Cl^-	SO_4^{2-}	CO_3^{2-}	HCO_3^-	OH^-	OH^-,Cl^-
2S	13.58	7.41	Cd^{2+}	34.38	ML_1	46.39	0.26	0.23	0.29	0.39	2.61
					ML_2	11.47				1.01	
					ML_3	2.96					
			Pb^{2+}	42.41	ML_1	15.05	0.32	0.18	3.62	24.76	4.06
					ML_2	6.46				2.49	
					ML_3	0.49					
					ML_4	0.15					
			Cu^{2+}	1.19	ML_1	0.89	0.01	2.01	0.02	1.72	5.73
					ML_2	0.05				88.37	
					ML_3	0.01					
					ML_4	—					
2 SS	18.95	7.49	Cd^{2+}	29.46	ML_1	46.27	0.01	0.01	0.23	0.41	3.42
					ML_2	14.19				1.40	
					ML_3	4.59					
			Pb^{2+}	37.20	ML_1	15.37	0.01	0.01	2.96	26.20	5.43
					ML_2	8.19				3.52	
					ML_3	0.78					
					ML_4	0.32					
			Cu^{2+}	0.77	ML_1	0.66	-	0.09	0.01	1.36	5.62
					ML_2	0.04				91.43	
					ML_3	0.01					
					ML_4	0.01					

Table 3.15 (continued)

Sampling station	S ‰	pH	Metal (M)	%Free ion	Complex (ML_n)	Ligands (L)					
						Cl^-	SO_4^{2-}	CO_3^{2-}	HCO_3^-	OH^-	OH^-, Cl^-
3 S	8.06	7.45	Cd^{2+}	38.54	ML_1	45.15	0.37	1.83	0.30	0.55	2.59
					ML_2	7.90				1.45	
					ML_3	1.32					
			Pb^{2+}	41.66	ML_1	12.84	0.40	1.25	3.21	29.85	3.53
					ML_2	3.90				3.12	
					ML_3	0.19					
					ML_4	0.03					
			Cu^{2+}	0.87	ML_1	0.56	0.01	10.43	0.01	1.57	3.93
					ML_2	0.02				83.04	
					ML_3	0.02					
					ML_4						
3 SS	10.01	7.32	Cd^{2+}	33.53	ML_1	48.64	0.37	1.02	0.35	0.37	2.17
					ML_2	10.59				0.75	
					ML_3	2.21					
			Pb^{2+}	42.57	ML_1	16.24	0.47	0.81	4.41	23.52	3.46
					ML_2	6.15				1.91	
					ML_3	0.38					
					ML_4	0.08					
			Cu^{2+}	1.40	ML_1	1.12	0.01	10.68	0.03	1.94	5.71
					ML_2	0.05				79.03	
					ML_3	0.01					
					ML_4	-					

Table 3.15 (continued)

Sampling station	S %	pH	Metal (M)	%Free ION	Complex (ML_n)	Cl^-	SO_4^{2-}	CO_3^{2-}	HCO_3^-	OH^-	OH^-, Cl^-
4 S	3.02	7.30	Cd^{2+}	59.95	ML_1	32.86	0.35	0.39	0.85	0.66	1.27
					ML_2	2.34				1.17	
					ML_3	0.15					
			Pb^{2+}	51.85	ML_1	7.48	0.03	0.21	7.34	28.73	1.36
					ML_2	0.93				2.02	
					ML_3	0.02					
					ML_4	—					
			Cu^{2+}	1.82	ML_1	0.55	0.01	3.00	0.05	2.54	2.44
					ML_2	0.01				89.58	
					ML_3	—					
					ML_4	—					
4 SS	3.06	7.29	Cd^{2+}	59.34	ML_1	32.66	0.43	1.27	0.83	0.63	1.23
					ML_2	2.36				1.09	
					ML_3	0.15					
			Pb^{2+}	52.21	ML_1	7.56	0.04	0.70	7.30	27.92	1.37
					ML_2	0.95				1.92	
					ML_3	0.02					
					ML_4						
			Cu^{2+}	1.80	ML_1	0.54	0.01	9.66	0.05	2.41	2.36
					ML_2	0.01				83.16	
					ML_3	—					
					ML_4	—					

Table 3.16 Percentage speciation of cadmium, lead and copper in samples on 18/12/79.

Sampling station	S %	pH	Metal (M)	%Free ion	Complex (ML_n)	Ligands (L)					
						Cl^-	SO_4^{2-}	CO_3^{2-}	HCO_3^-	OH^-	OH^-,Cl^-
1 S	22.04	7.90	Cd^{2+}	22.45	ML_1	40.02	0.16	0.79	0.16	0.85	8.12
					ML_2	14.21				7.88	
					ML_3	5.35					
			Pb^{2+}	20.13	ML_1	9.44	0.14	0.45	1.47	38.19	9.17
					ML_2	5.82				14.10	
					ML_3	0.65				0.12	
					ML_4	0.31					
			Cu^{2+}	0.11	ML_1	0.11		0.96		0.52	2.48
					ML_2	0.01				95.80	
					ML_3	—				0.01	
					ML_4	—					
1 SS	26.95	7.87	Cd^{2+}	17.35	ML_1	28.59	0.12	0.37	0.11	0.60	8.02
					ML_2	19.10				5.73	
					ML_3	9.99					
			Pb^{2+}	18.88	ML_1	11.04	0.13	0.26	1.23	32.85	10.99
					ML_2	9.50				12.43	
					ML_3	1.46				0.11	
					ML_4	1.10					
			Cu^{2+}	0.11	ML_1	0.14	0.01	0.62	—	0.50	3.35
					ML_2	0.01				95.23	
					ML_3	—				0.01	
					ML_4	—					

Table 3.16 (continued)

Sampling station	S ‰	pH	Metal (M)	%Free ion	Complex (ML$_n$)	Cl^-	SO_4^{2-}	CO_3^{2-}	HCO_3^-	OH-	OH^-,Cl^-
2 S	18.70	7.80	Cd^{2+}	26.62	ML$_1$	46.61	0.27	0.70	0.22	0.78	6.43
					ML$_2$	13.09				5.37	
					ML$_3$	3.91					
			Pb^{2+}	27.34	ML$_1$	11.51	0.28	0.45	2.23	40.04	8.32
					ML$_2$	6.14				11.00	
					ML$_3$	0.54				0.22	
					ML$_4$	0.23					
			Cu^{2+}	0.19	ML$_1$	0.16	–	1.24	3.05	0.69	2.85
					ML$_2$	0.01				94.83	
					ML$_3$	–				0.02	
					ML$_4$	–					
2 SS	26.11	7.84	Cd^{2+}	18.60	ML$_1$	29.77	0.12	0.58	0.04	0.60	7.55
					ML$_2$	18.46				5.22	
					ML$_3$	9.08					
			Pb^{2+}	22.51	ML$_1$	12.66	0.15	0.44	0.47	36.58	11.28
					ML$_2$	0.49				12.61	
					ML$_3$	1.48				0.10	
					ML$_4$	1.02					
			Cu^{2+}	0.13	ML$_1$	0.16	–	1.04	–	0.55	3.43
					ML$_2$	0.01				94.65	
					ML$_3$	0.01				0.01	
					ML$_4$	0.01					

Table 3.16 (continued)

Sampling station	S ‰	pH	Metal (M)	%Free ion	Complex (ML_n)	Ligands (L)					
						Cl^-	SO_4^{2-}	CO_3^{2-}	HCO_3^-	OH–	OH^-, Cl^-
3 S	10.75	7.80	Cd^{2+}	32.91	ML_1	40.35	0.23	1.37	0.27	0.99	5.98
					ML_2	9.06				6.70	
					ML_3	2.12					
			Pb^{2+}	26.89	ML_1	8.67	0.19	0.70	2.25	40.51	6.15
					ML_2	3.38				10.92	
					ML_3	0.23				0.02	
					ML_4	0.06					
			Cu^{2+}	0.18	ML_1	0.12	–	0.01	–	1.93	2.13
					ML_2	–				94.91	
					ML_3	–				0.01	
					ML_4	–					
3 SS	13.05	7.83	Cd^{2+}	31.29	ML_1	11.69	0.24	0.66	0.66	0.28	6.03
					ML_2	10.23				0.91	
					ML_3	2.63				6.03	
			Pb^{2+}	26.91	ML_1	9.43	0.21	0.36	2.42	39.34	6.53
					ML_2	4.02				10.35	
					ML_3	0.30				0.02	
					ML_4	0.09					
			Cu^{2+}	0.20	ML_1	0.14	–	1.04	–	0.72	2.40
					ML_2	0.01				95.47	
					ML_3	–				0.01	
					ML_4	–					

Table 3.16 (continued)

Sampling station	S ‰	pH	Metal (M)	%Free ion	Complex (ML_n)	Cl^-	SO_4^{2-}	CO_3^{2-}	HCO_3^-	OH^-	OH^-,Cl^-
4 S	9.92	7.64	Cd^{2+}	32.71	ML_1	44.03	0.36	3.81	0.30	0.74	4.07
					ML_2	9.04				3.12	
					ML_3	1.80					
			Pb^{2+}	31.77	ML_1	11.25	0.35	2.33	3.09	35.87	4.98
					ML_2	4.01				6.04	
					ML_3	0.24				0.02	
					ML_4	0.05					
			Cu^{2+}	0.36	ML_1	0.26	–	10.40	0.01	1.01	2.79
					ML_2	0.01				85.15	
					ML_3	–					
					ML_4	–					
4 SS	11.09	7.53	Cd^{2+}	35.36	ML_1	43.98	0.06	2.99	0.27	0.53	3.14
					ML_2	9.58				1.74	
					ML_3	2.15					
			Pb^{2+}	38.97	ML_1	12.75	0.28	2.09	2.93	29.56	4.35
					ML_2	4.83				3.84	
					ML_3	0.32					
					ML_4	0.08					
			Cu^{2+}	0.65	ML_1	0.44	–	13.75	0.01	1.23	3.62
					ML_2	0.02				80.26	
					ML_3	–					
					ML_4	–					