

CHAPTER III

EXPERIMENTS

3.1 Materials

3.1.1 Preparation of standards

Stock solutions of Cd, Zn, Pb, Cu, Hg, Mn and Co in a concentration of 1 mg/cm^3 each, were prepared by dissolving the specpure grade oxide or mettalic powders (Cu and Mn) in dilute solution of A.R. grade nitric acid. The stock solution of Ag was prepared by dissolving specpure grade AgNO_3 in thrice-deionized water. Standard solutions with other concentrations were prepared by diluting appropriate amount of the stock solution with deionized water.

Standard water samples, 2 dm^3 each, were prepared and used as test material for the development of the concentration and separation procedure. This was made by pipetting appropriate amount of single standard solution into 2 dm^3 of deionized water, so that a final solutions containing $20 \text{ }\mu\text{g}$ of Zn and Cd, $50 \text{ }\mu\text{g}$ of Co and Ag, $100 \text{ }\mu\text{g}$ of Pb and Cu and $2,000 \text{ }\mu\text{g}$ of Hg was obtained. The concentrations of the elements were so arranged that they could be detected by the method of atomic absorption (A.A.) with good precision.

3.1.2 Sample collection and storage

Samples of surface water were collected from the middle of the Chao Phya River at the depth of about 1 metre from the surface at the following locations: Nonthaburi Bridge

(Pathum Thani), Ban Sai Ma (Nonthaburi), Bangkok bridge (Bangkok) and Samut Parkan (Fig 3-1). The sampling operations were performed on June 18, August 18, and August 24 of the year 1974. Two samples at one location were collected on each date, one at the low-tide and one at the high-tide period. A total of 24 samples were obtained.

The samples, 4-5 dm³ each, were separately stored in polyethylene bottles which were previously cleaned with concentrated nitric acid and distilled water. Each sample contained about 4-5 g suspended materials which settled down after standing. To prevent the loss of trace elements by adsorption on these particles and also on the container wall, 10 cm³ of concentrated nitric acid per dm³ of water was added into the samples (3). The clear solution was decanted and used for the analysis. Two cubicdecimetres per sample were used for one analysis.

3.1.3 Reagents

Unless otherwise stated, all reagents used were of analytical reagent grade.

A buffer solution of pH 6 was prepared by mixing 46.4 cm³ of a 0.2 M NaOH and 50 cm³ of a 0.2 M biphthalate solution

A 0.1 M oxalic acid-sodium oxalate solution at pH 4 was prepared by adding 0.1 M oxalic acid into a 0.1 M sodium oxalate solution until the pH of the mixture was 4 as measured by a pH-meter.



Fig. 3-1 Locations for sampling along the Chao Phya River

A solution of 4 % ammonium thiocyanate in 0.05 M H_2SO_4 was prepared by dissolving 4 g of ammonium thiocyanate in 100 cm^3 of 0.05 M H_2SO_4

Either Voltalef 300 LD-PL micro, a trade name for polytrifluorochloroethylene (Fabricator: Ugine Kuhlman; Sole distributor: Plastimer, 98 Boulevard. Victor Hugo, 92 Clichy, France), or cellulose acetate was used as supporting material. Powders with the grain size between -40 to + 60 mesh were used.

3.1.4 Preparation of coated-material

Ten grams of voltalef (or cellulose acetate) were mixed with 50 cm^3 0.1 % dithizone-carbon tetrachloride solution and the slurry was heated with constant agitation at the temperature of about 80°C on a hot plate until all carbon tetrachloride was evaporated. This could be easily observed since the colour of the material would change from blackish green to a light green, when no more solvent was present. The packing material will be stable for about 1 month, if stored at room temperature. The stability of the coated material will be less if the dithizone solution is more dilute and the storage temperature is higher.

3.1.5 Preparation of extraction columns

All columns were of the same size, 1 cm in diameter and 30 cm in height, closed at the bottom with a capillary stopcock and enlarged at the top with a ground glass joint.

Glass wools were plugged at both ends of the column to hold the packing materials (bottom) and to prevent stirring the packing material when solutions were poured into the column (top). The efficient filling height for tracer experiments, or experiments with small volume of sample, was 16 cm. In these cases the column was first packed with 2 g of untreated voltalef (or cellulose acetate) then with 2 g of treated voltalef (or cellulose acetate). The flow rate of the eluate was kept constant at 15 drops/minute. In the actual case, where 2 dm³ of water sample were required for one analysis, the column contained 3 g of treated voltalef only. The filling height was 12 cm and the flow rate of the eluate was 28 drops/minute. After the column was packed, 2 cm³ of carbontetrachloride were then added to the top of the column and drawn through the packing material by application of vacuum. A column to which carbontetrachloride had not been added gave practically no recovery and permitted rapid stripping of the dithizone from the support. Excessive wetting with carbontetrachloride permitted migration of the coated-dithizone out of the column along with the sample and eluting solutions. The column was successively washed with 50 cm³ of 1.0 M HCl and 100 cm³ of deionized water and was then ready for use.

3.1.6 Radioactive nuclides used as indicators

Radioactive nuclides were produced by neutron irradiation of the stable elements, either in form of solid salts (Co, Zn and Cd), or in form of solution (Mn, Cu, Ag, and Hg) in the Thai Research Reactor-I (TRR-I). The approximate thermal neutron flux in the reactor core was about 6×10^{12} n/cm².sec. The irradiation times ranged from a few minutes to several weeks, depending on the activation cross-section and the half-life of the radionuclide formed. The irradiated salts were then separately dissolved in dilute HNO₃ and the concentration was made to 50 µg/cm³. From these stock solution 0.2 cm³ fractions containing 10 µg of the required element, were taken for each tracer experiment. In the case where solutions were irradiated (Cu, Ag and Hg), the concentration of the solutions was 100 µg/cm³ and 0.1 cm³ fractions, also containing 10 µg of the required element, were taken for each experiment. Exception was made in the case of Mn where the concentration of the stock solution was 50 µg/cm³ and 0.1 cm³ fractions, containing 5 µg of Mn were used per experiment.

The radioactive nuclides used in the tracer experiments together with their γ -energies and half-life are reported in Table 3-1.

Table 3-1 Radiotracers used, measured γ energies and half-life

radioactive nuclide	γ Energy (Mev)	half-life
Mn ⁵⁶	0.845	2.58 h
Co ⁶⁰	1.33, 1.17	5.26 y
Cu ⁶⁴	0.511	12.9 h
Zn ⁶⁵	1.12	245 d
Ag ¹¹⁰	0.66	260 d
Cd ¹¹⁵	0.52	2.3 d
Hg ²⁰³	0.279	47 d

h = hours

d = days

y = years

3.2 Apparatus

3.2.1 γ - Spectrometer

The gross γ - activities of the radioactive nuclides were measured by a well-type NaI (Tl) crystal detector which was connected to a single channel analyzer (S.C.A) from Nuclear Chicago (Model 181 A). The spectrometer was first calibrated with standards from the Radiochemical Center Amersham, England. The energy calibration curves showing the relation of energy to channel number in the regions mostly used in the present investigation are given in Fig 3-2.

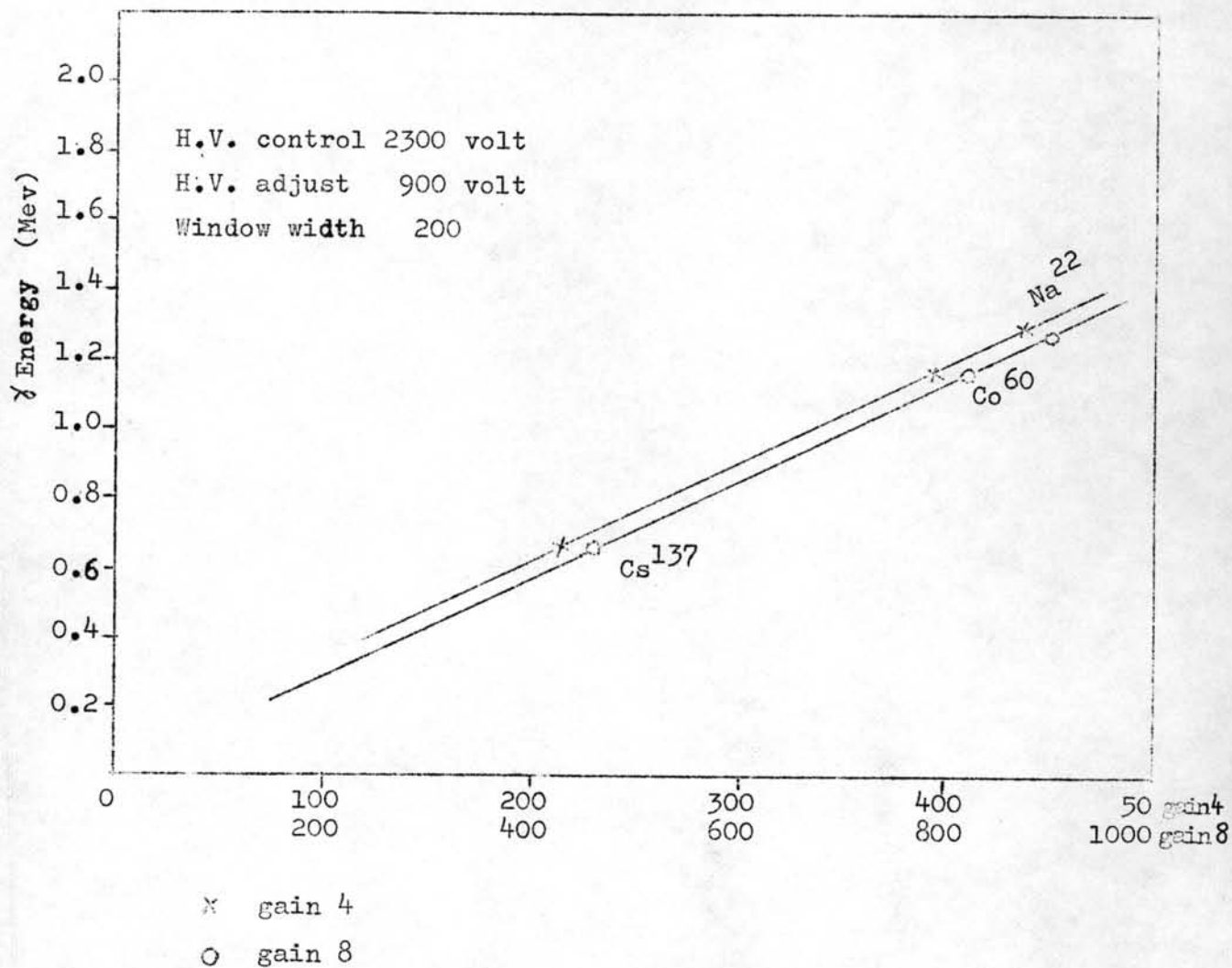


Fig 3-2 The relation of γ energy to channel number

3.2.2 Atomic absorption spectrometer

A Varian-Techtron model AA-5 atomic absorption spectrometer was used for the study. Hollow cathode lamps were used as radiation sources. The elements were determined according to the manufacture's recommended settings, which are summarized in Table 3-2. Since no permanent record of analytical results, such as chart recorder or a digital printer was available, the results were read by a digital readout which displays only temporary. This made it impossible to use the scale expansion part to determine very dilute solutions since the needle fluctuates extremely. A picture of the Varian-Techtron model AA-5 atomic absorption is reproduced in Fig 3-3.

Table 3-2 Operation conditions for the analysis of Ag, Hg, Cu, Zn, Pb, Cd and Co by the Varian Techtron AA-5 atomic absorption spectrometer.

Metal	Light-source	Lamp current mA	wavelength nm	slit width μ m
Ag	Ag-lamp	3	328.1	100
Hg	Hg-lamp	3	253.7	100
Cu	Mn, Cu, Co, Cr, Fe, Ni lamp	4	324.8	100
Zn	Zn-lamp	5	213.9	100
Pb	Pb-lamp	5	217.0	100
Cd	Cd-lamp	3	228.8	200
Co	Mn, Cu, Co Cr, Fe, Ni lamp	5	240.7	100

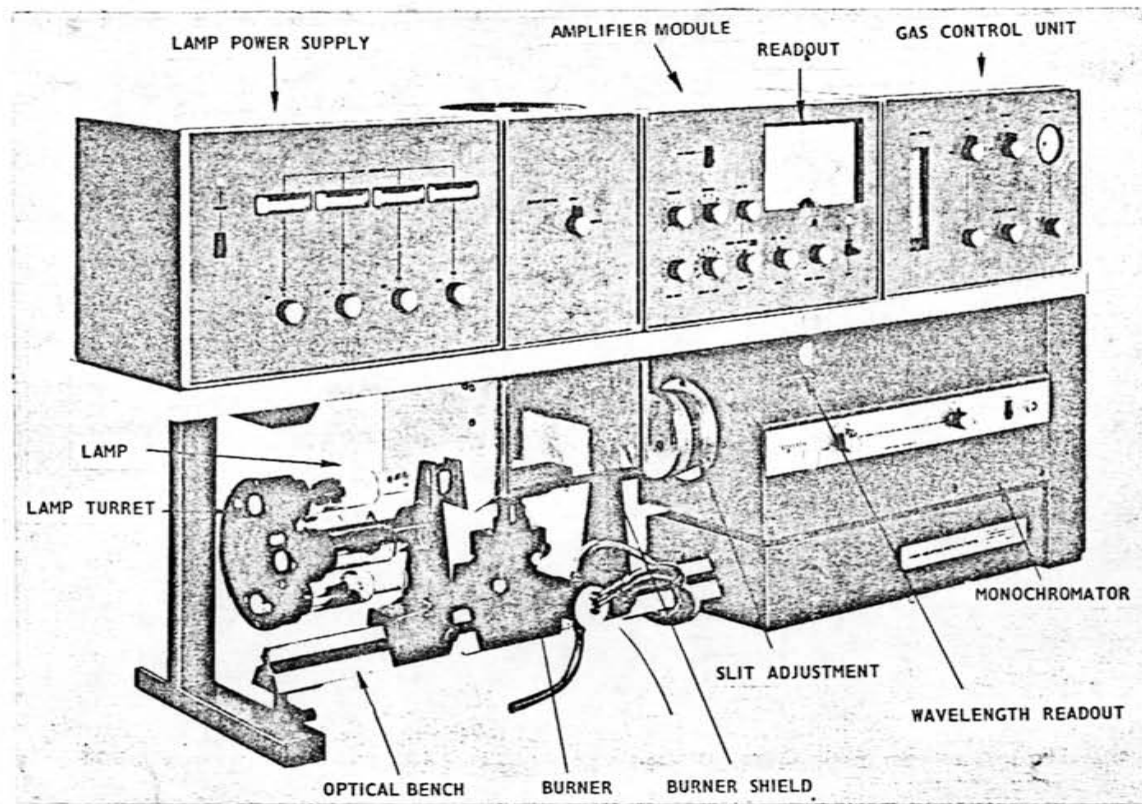


Fig. 3-3 Varian Techron model AA-5

3.2.3 pH - meter

A Copenhagen pH meter, model 28, was used for the pH measurements. Except in cases where the buffer solution was used, ammonium hydroxide and hydrochloric acid of appropriate strength were used to adjust the pH of the solutions.

3.2.4 Fraction collector

A fraction collector from Gallenkamp which could be set to turn automatically to the next tube position after collection of selected number of drops was used. Fractions of 2 cm³ were generally collected.

3.3 Tracer experiment

As the elements to be determined in most water samples will be present at trace levels and their concentrations will be generally lower than the detection limits of the atomic absorption spectrometer, concentration procedures are necessary. The method of extraction chromatography using dithizone as chelating agent was chosen in the present investigation. The best conditions for the concentration and subsequent separation of the interested elements from water samples were first studied using tracers.

3.3.1 Effect of pH on the adsorption of Ag, Hg, Cu, Cd, Co, Zn and Mn on dithizone coated-voltalef (or cellulose acetate)

The effect of the pH of a solution on the adsorption of an element on dithizone coated-voltalef was studied. One gram of the treated material was first wetted with 1 cm³ CCl₄ after which 10 cm³ of a solution containing the radioactive element to be investigated at various pH-values was added and the mixture was shaken vigorously for 10 minutes. After filtration, the activity of the solution was counted and compared to the activity of a standard stock solution containing an equivalent amount of the element under investigation. Care was taken to assure that the geometries of the standards and the samples were similar, so that the counting error would be minimum. The percent adsorption was calculated. The concentration of the elements added varied with the specific activity produced which were 10 µg for Ag, Hg, Cu, Cd and Co; 15 µg for Zn and 5 µg for Mn. Since the nuclides Pb²⁰⁵ and Pb²⁰⁹, the only two nuclides which could be produced by the (n, γ) reaction, emit no gamma-rays and no other radioactive nuclides of Pb were available, no tracer experiment on Pb was performed. From the results reported in Table 3-3 and Fig 3-4, one could observe that the elements Ag, Hg, Cu, Zn, Cd, Co and Mn could be separated into three groups based on the pH of the solution when passed through a column of dithizone coated-inert material.

Group I contains Ag, Hg and Cu which are adsorbed at pH 0-2

Group II contains Zn, Cd and Co which are adsorbed at pH 4-7

Group III contains Mn which is adsorbed at pH > 7

It was observed that if the pH of the solution is higher than 6, the coated dithizone would be easily stripped off from the column. The amount of dithizone washed from the column is greater for voltalef than for cellulose acetate. Hence it is recommended to use dithizone coated-cellulose acetate in cases where the pH of the solution is higher than 6

Table 3-3 Effect of pH on the adsorption of Ag, Hg, Cu, Zn, Cd, Co and Mn on dithizone coated-voltalef.

pH	Adsorption (%)						
	Ag	Hg	Cu	Zn	Cd	Co	Mn
0	99.77	95.23	100.00	-	-	-	-
1	98.34	100.00	100.00	0.42	0.00	0.00	0.00
2	96.88	94.89	99.91	0.00	0.97	0.00	0.00
3	-	-	-	60.29	38.31	1.64	0.00
4	96.21	97.75	99.91	80.95	78.59	5.25	0.60
5	-	-	-	100.00	81.91	98.41	0.00
6	99.19	67.88	98.09	96.13	94.08	95.28	0.70
7	-	-	-	79.43	95.81	93.81	0.00
8	33.41	66.84	99.14	44.52	-	-	96.70
9	-	-	-	-	-	-	95.50

- No experiment was conducted

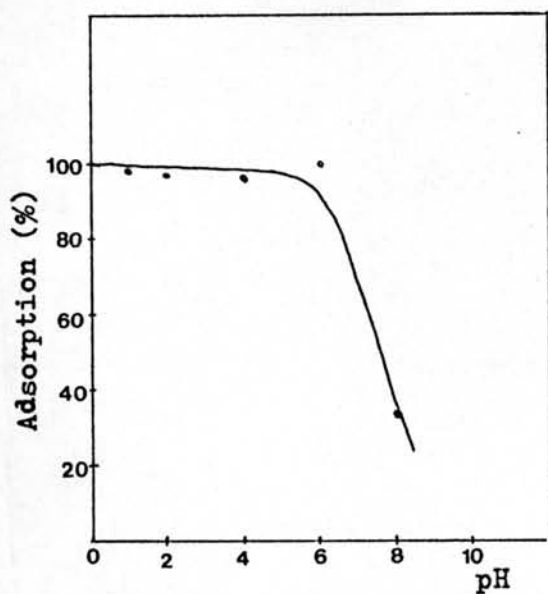


Fig 3-4.1 Effect of pH on adsorption of Ag on dithizone-voltalef

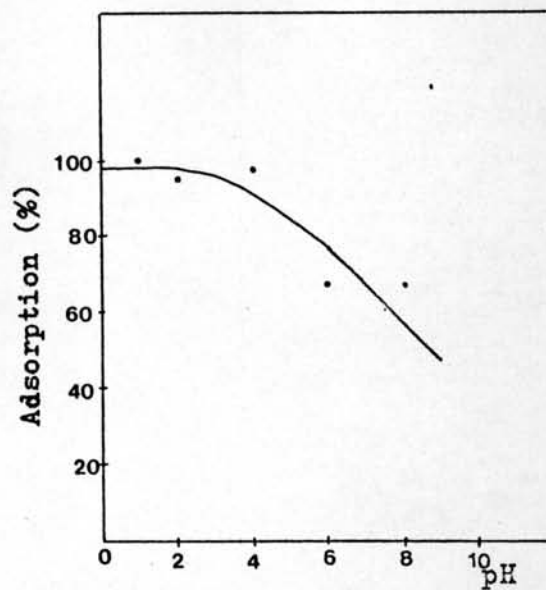


Fig 3-4.2 Effect of pH on adsorption of Hg on dithizone-voltalef

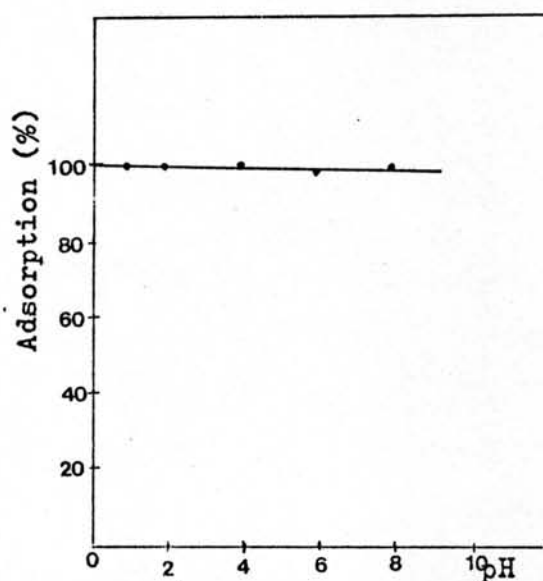


Fig 3-4.3 Effect of pH on adsorption of Cu on dithizone-voltalef



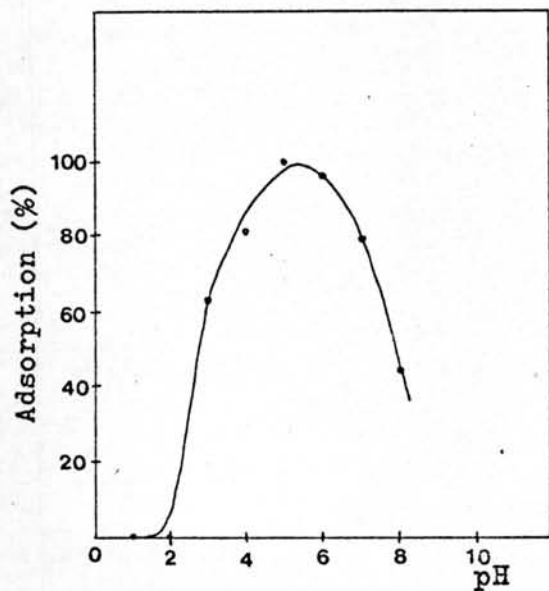


Fig 3-4.4 Effect of pH on adsorption of Zn on dithizone-voltalef

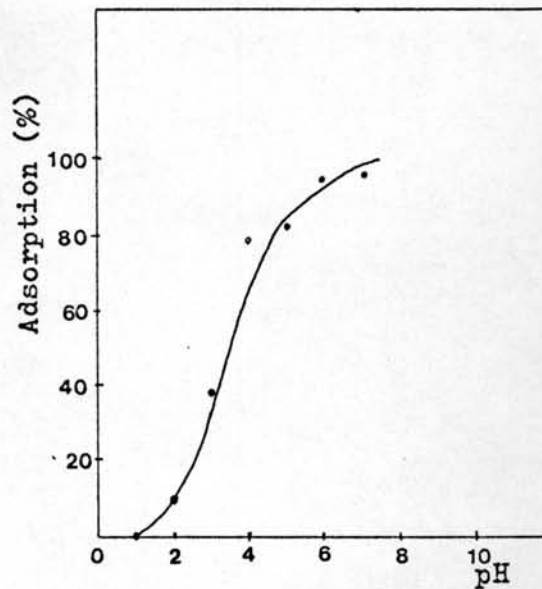


Fig 3-4.5 Effect of pH on adsorption of Cd on dithizone-voltalef

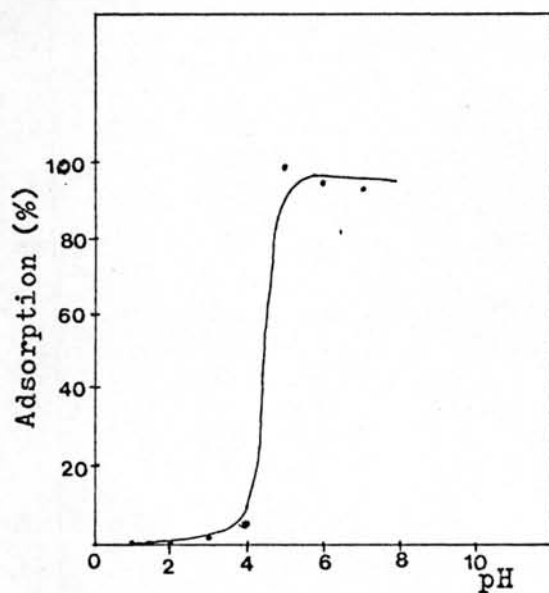


Fig 3-4.6 Effect of pH on adsorption of Co on dithizone-voltalef

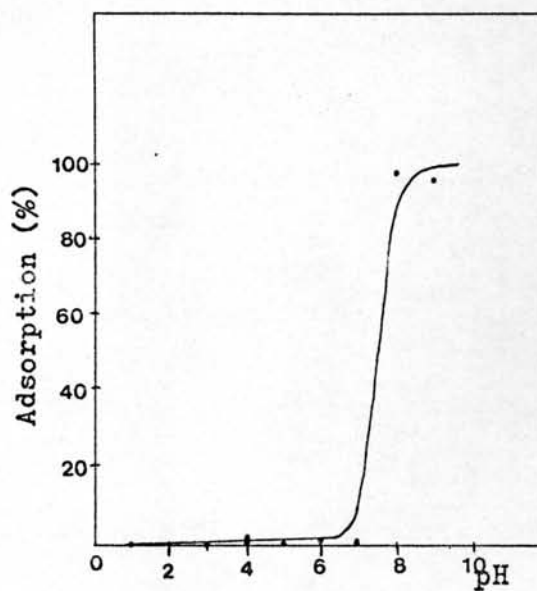


Fig 3-4.7 Effect of pH on adsorption of Mn on dithizone-voltalef

3.3.2 Effect of eluants on the elution of Ag, Hg, Cu, Cd, Co, Zn and Mn from dithizone coated-voltalef.

Efforts were made to separate each element individually from the column by various eluants. The radioactive elements were separately adsorbed on dithizone coated-voltalef (or cellulose acetate in the case of Mn) columns. Different eluting solutions were tried and the eluants were collected in 2 cm³ fractions. The activities of all fractions were measured and compared to the total activity of the solution prior to adsorption on the column. From the measured activities the percent elution in each fraction was calculated.

The separation of Ag, Hg and Cu after adsorption on dithizone-voltalef column was studied by S. Muangnoicharoen(4). After this author, silver was first eluted from the column by 4 % NH₄CNS in 0.05 M H₂SO₄. Copper and mercury were eluted together from the column by 6.0 M HCl. Mercury was then separated from copper by adsorption on a column of anion exchanger from a solution of 2.0 M HCl. It was first intended that this procedure would be adopted in the present study.

The separation of Zn, Cd and Co was investigated. Each of the three elements was adsorbed on dithizone-voltalef columns from a 20 cm³ aqueous solution which pH was adjusted to 6 by the addition of a buffer solution. Following eluting agents were tried: 0.1 M oxalic acid-sodium oxalate at pH 4, 0.1 M oxalic acid and 1.0 M HCl. The eluting curves are given in Figs 3-5 to 3-7 and the results are tabulated in Table 3-4.

Table 3-4 Elution of Zn, Cd and Co from dithizone coated-volalef column

fraction No	Elution with 0.1 M oxalic acid-oxalate solution at pH4 (%)			Elution with 0.1 M oxalic acid (%)			Elution with 1.0 M HCl (%)			Elution with EtOH (%)
	Zn	Cd	Co	Zn	Cd	Co	Zn	Cd	Co	Co
1	0.61	0.39	0.06	0.26	0.37	0.02	0.95	No	0	0
2	3.66	0	0.39	14.30	3.50	0.03	14.34	experi-	0.33	0.22
3	5.07	0.37	1.17	63.39	47.05	0.08	62.96	ments	1.85	32.75
4	22.30	0.12	0.44	8.60	27.03	0.31	9.76	were	1.98	50.36
5	32.62	0	0.02	3.54	9.73	0.26	3.28	per-	1.53	9.89
6	17.82	0	0	0.24	3.04	0.34	1.63	formed	1.09	0
7	8.24	0.14	0.01	0.77	0.77	0.29	0.17		1.29	0.08
8	4.03	0.09	0.07	0.95	0.57	0.46	0		0.22	0
9	2.40	0	0.02	0	0	0.64	0		0.09	0
10	0.59	0	0	0	0	0.05	0		0.22	0

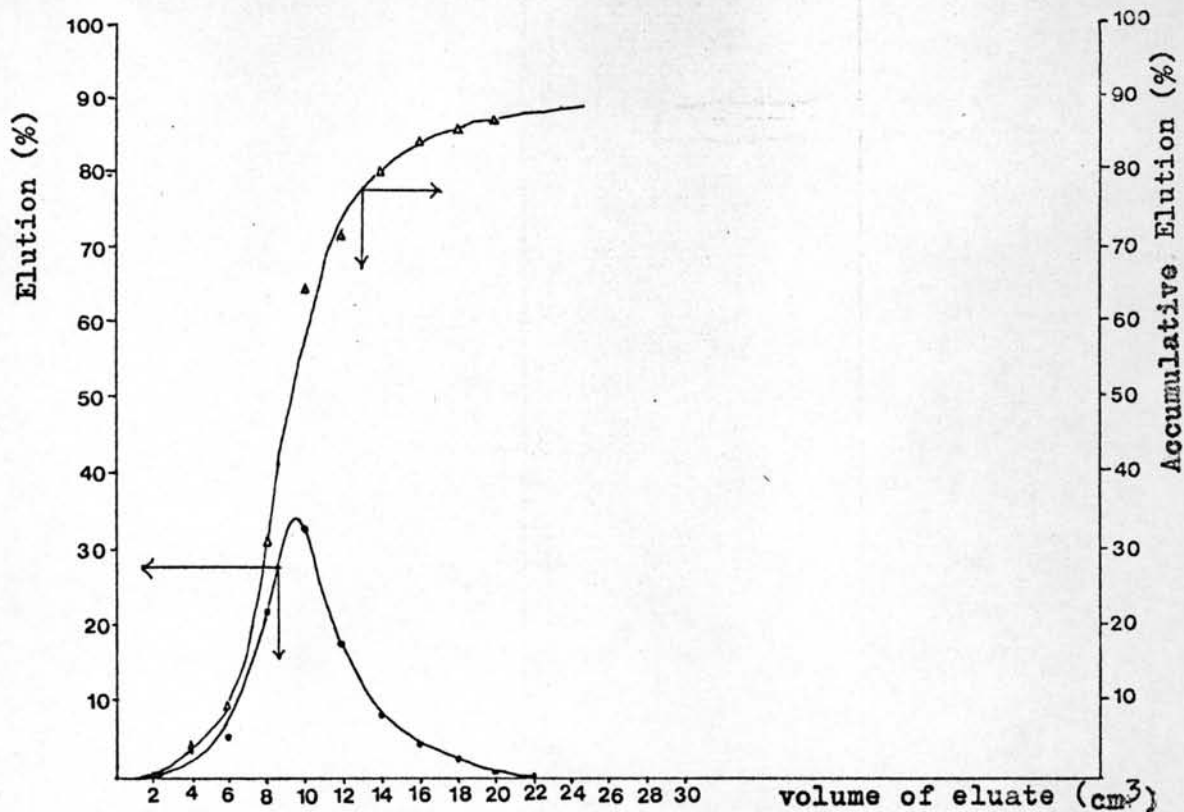


Fig 3-5 a Elution curve of zinc by 0.1 M oxalic acid - oxalate solution at pH 4

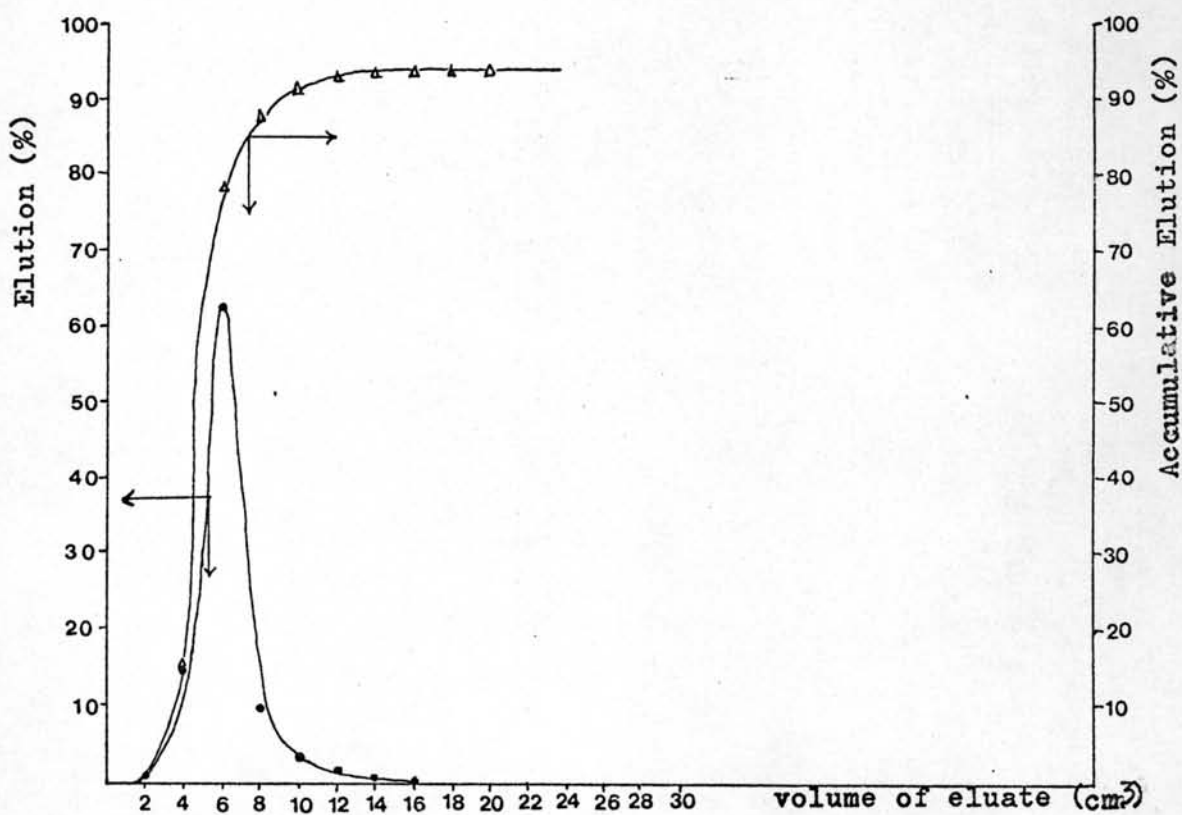


Fig 3-5 b Elution curve of zinc by 1.0 M HCl

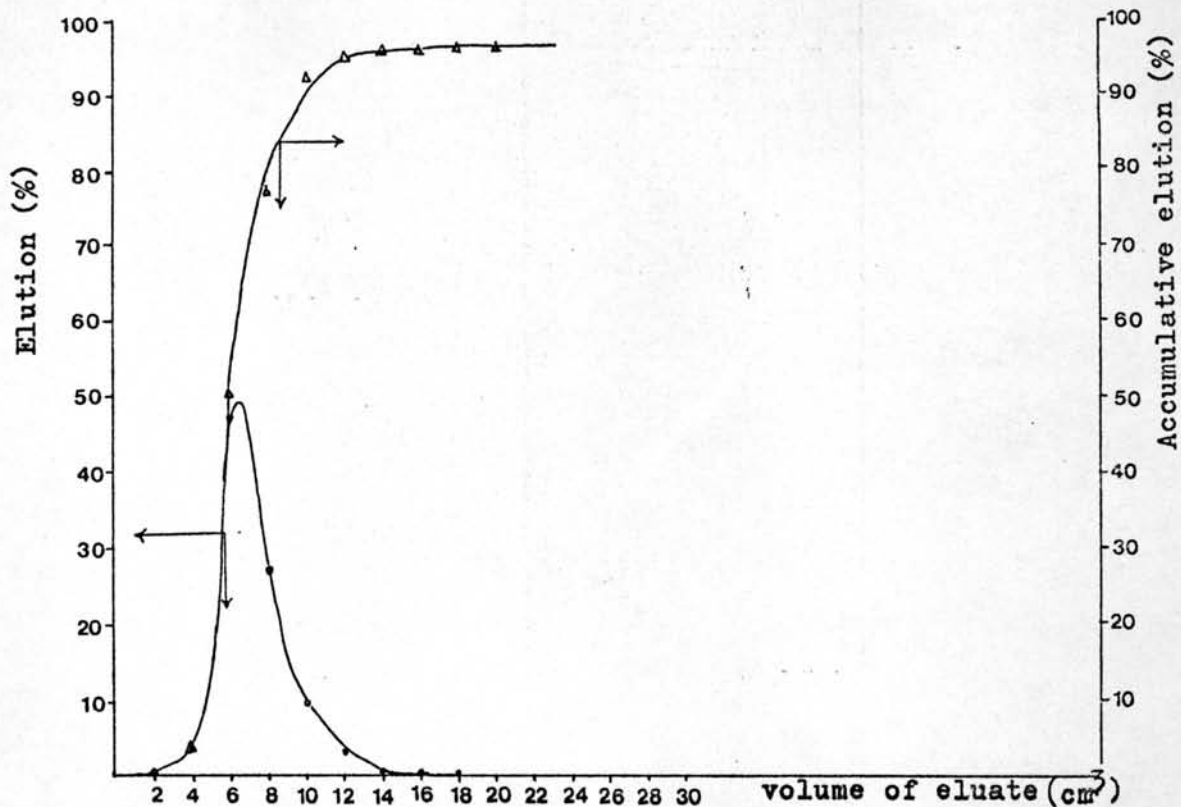


Fig 3-6 Elution curve of cadmium by 0.1M oxalic acid

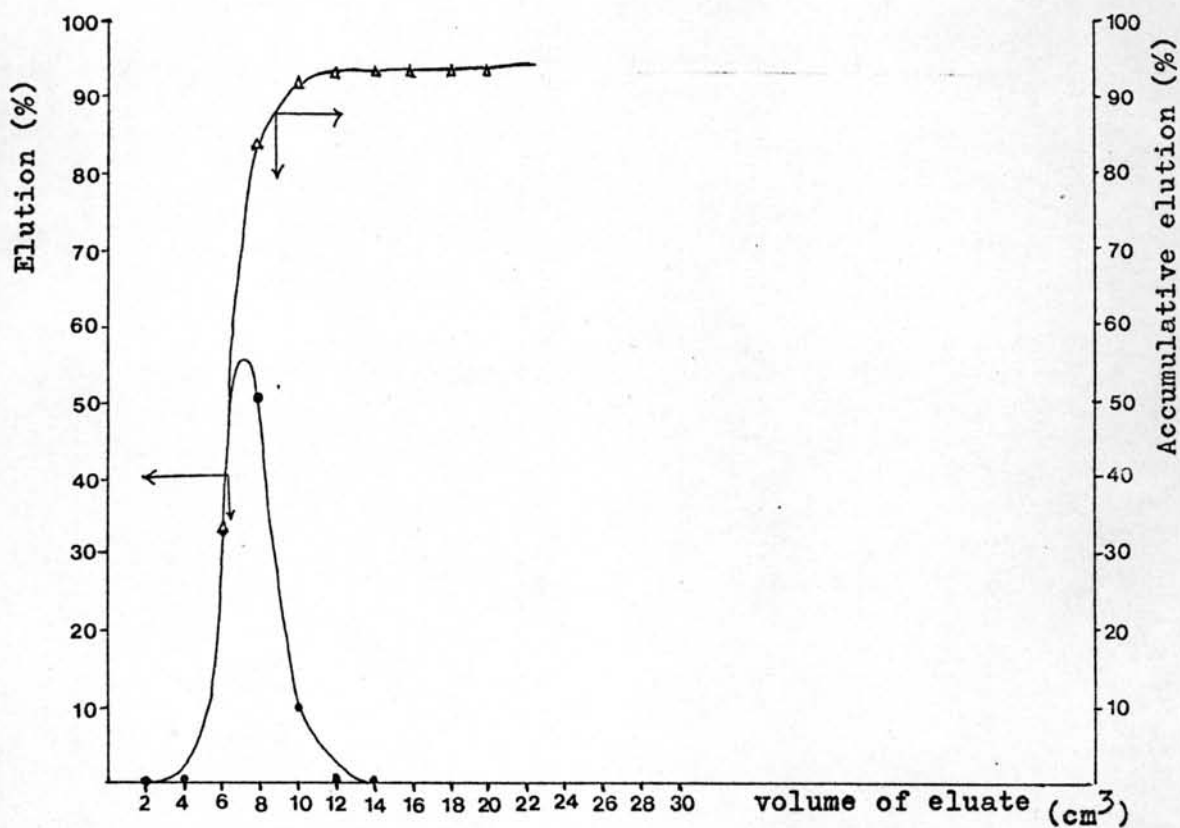


Fig 3-7 Elution curve of cobalt by EtOH

From these data it was concluded that Zn could be eluted from the column with any of the three solutions; Cd could be eluted by 0.1 M oxalic acid; none of the three solutions has any effect on the Co-dithizonate complex.

Hence it was decided that after Zn, Cd and Co are extracted from water samples by adsorption on a dithizone-voltaef column from a solution at pH6, Zn would be eluted with 30 cm³ 0.1 M oxalic acid-sodium oxalate solution at pH4. Fractions 2-6 which contained most of the zinc would be collected for analysis. Cd would be eluted with 30 cm³ 0.1 M oxalic acid and fractions 2-6 were collected for analysis. Since no appropriate eluting solution was found for cobalt, ethanol was used to dissolve dithizone, and also the Co-dithizonate, from the column.

Manganese in the divalent state could be adsorbed quantitatively on dithizone-cellulose acetate columns from a solution which pH is higher than 7. The complete elution of manganese from the column is, however, difficult, as Table 3-5 shows. Since the air oxidation of manganese (II) in alkali solution proceeds rapidly, the observed behavior on column suggests that dithizonate of higher oxidation states can not be removed from the column by the method described in the present study. The elution was not improved even if reducing agents, such as, hydroxylamine hydrochloride were added. The possibility of eluting manganese in inert atmosphere has not been studied. Manganese was hence not analysed.

I1553974X

Table 3-5 Elution of Mn by various eluants

Eluting solution	Elution (%)
1.0 M HCl	64.50 39.44
0.5 M H ₂ SO ₄	68.05
2.0 M HCl	87.00 71.45 46.27 45.15
100 cm ³ 1.0 M HCl + 5 cm ³ 0.005 M Na ₂ S ₂ O ₃	38.90
0.0025 M Na ₂ S ₂ O ₃ at pH5 (0.0621 g of Na ₂ S ₂ O ₃ was dissolved in 100 cm ³ of an aqueous solution which pH was previously adjusted to 5 by adding HCl)	55.90
0.0025 M Na ₂ S ₂ O ₃ at pH3 (0.0621 g of Na ₂ S ₂ O ₃ was dissolved in 100 cm ³ of an aqueous solution which pH was previously adjusted to 3 by adding HCl)	47.20
1 % Na ₂ S ₂ O ₃	20.00
4 % hydroxylamine hydrochloride in 1.0 M HCl	55.25

3.3.3 Adsorption and elution of lead

As stated in section 3.3.1., no appropriate isotope of lead could be produced by the (n, γ) reaction, the behavior of lead was therefore checked by the method of atomic absorption. 50 μg of lead in 20 cm^3 of a pH6 buffer solution was allowed to pass through a dithizone-voltaef column. The effluent was analysed for the amount of lead which was not adsorbed on the column. It was found that the concentration of lead in the effluent was lower than the detection limit of the instrument which indicates that the percent adsorption was or nearly was, complete. The column was then washed with 30 cm^3 of 0.1 M oxalic acid-sodium oxalate at pH4 which was previously found to be a suitable eluant for zinc. From Table 3-6, in which the percent recovery of lead in each fraction was shown, it is obvious that up to 60 % of lead could be eluted with about 10 cm^3 of 0.1 M oxalic acid-sodium oxalate at pH4. The eluting curve is shown in Fig 3.8.

3.3.4 Concentration and separation scheme for the analysis of trace amounts of Ag, Hg, Cu, Pb, Zn, Cd and Co in water samples as developed by tracer experiments.

The concentration and separation scheme for the analysis of trace amount of Ag, Hg, Cu, Pb, Zn, Cd and Co in water samples as developed by tracer experiments is shown in Fig 3-9.

Table 3-6 Elution of Pb with 0.1 M oxalic acid-sodium oxalate solution at pH⁴.

Fraction No.	Absorbance	Elution (%)	accumulative elution (%)
1	0.0049	0.52	0.52
2	0.1938	22.07	22.59
3	0.2149	25.17	47.76
4	0.0809	9.46	57.22
5	0.0132	1.82	58.04
6	0.0132	1.82	59.86
7	0	0	-
8	0	0	-
9	0	0	-
10	0	0	-
Standard	0.8539		

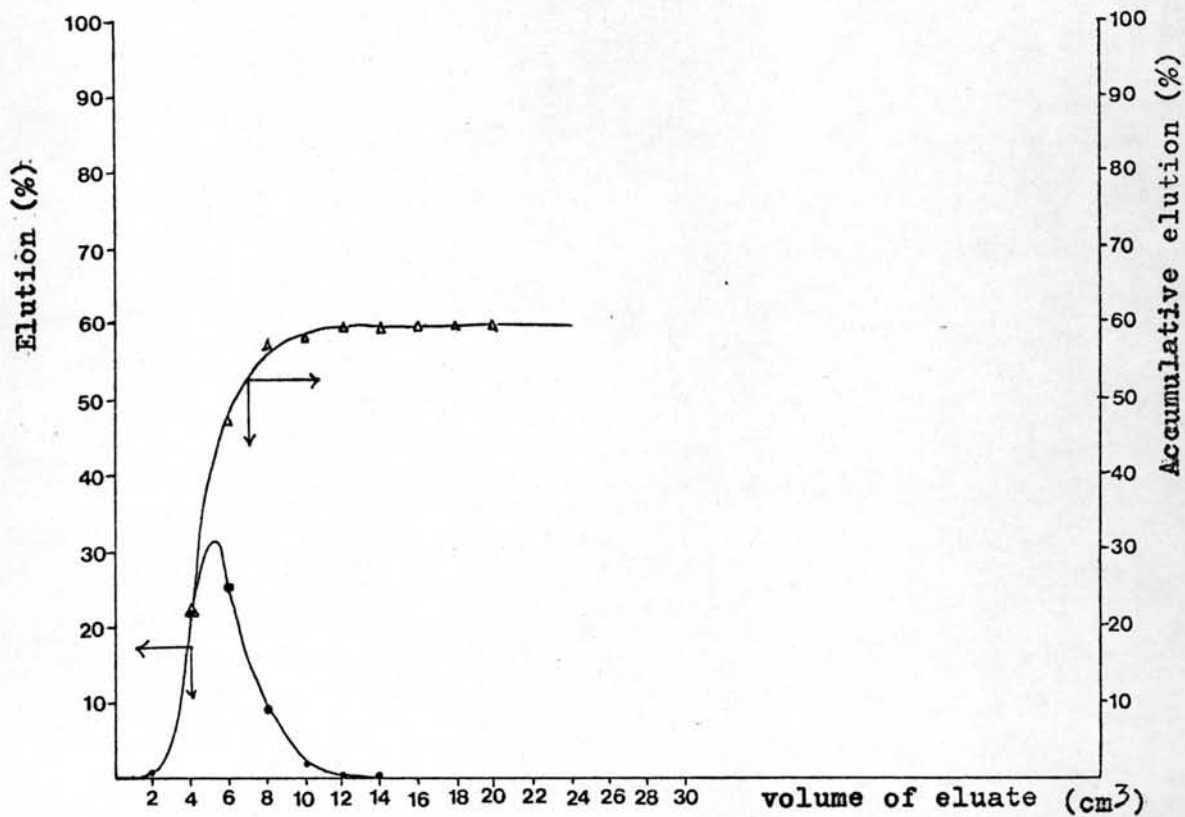


Fig 3-8 Elution curve of lead by 0.1 M oxalic acid-oxalate solution at pH4

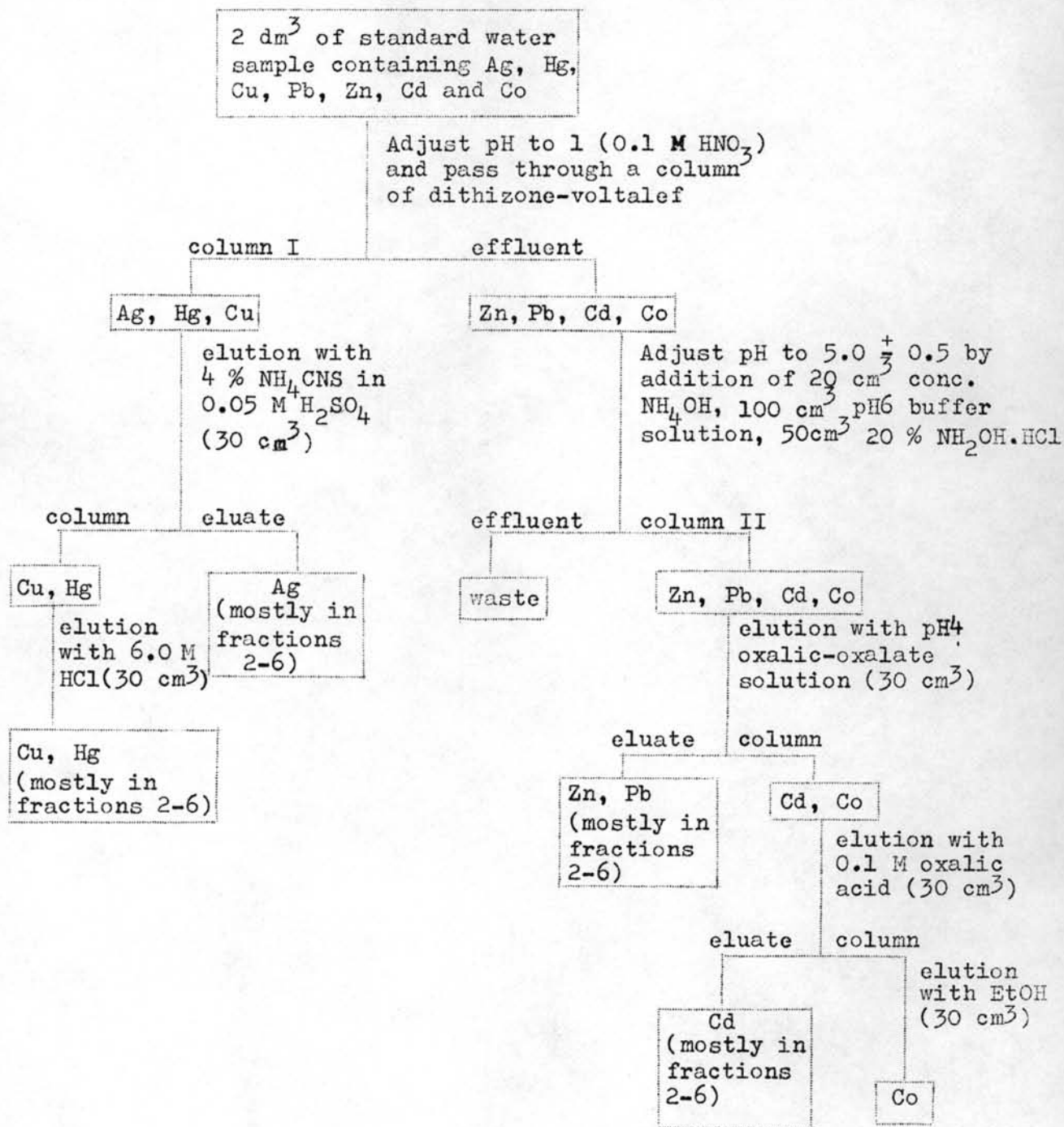


Fig 3-9 Concentration and separation scheme for the analysis of trace amounts of Ag, Hg, Cu, Pb, Zn, Cd and Co in water samples as developed by tracer experiments

3.4 Applicability of the developed concentration and separation scheme.

Since the concentrations of the dissolved trace metals in surface water are usually too low for determination with the required precision, large volume samples must be used. The applicability of the concentration and separation technique studied in Section 3.3 for such large volume samples must therefore be checked. For this purpose, standard water samples containing 20 μg of Zn and Cd, 50 μg of Ag and Co, 100 μg Cu and Pb, 2,000 μg of Hg (all inactive) in 2 dm³ of deionized water were prepared and the concentration and separation scheme in Fig 3-9 was followed. Hydroxylamine hydrochloride solution was added to the effluent after adsorption of Ag, Hg, and Cu on column I to prevent oxidation of dithizone (2). It was found that the colour of the dithizone layer of both columns, column I for trapping Ag, Hg, Cu and column II for Zn, Cd, Pb and Co, turned to red before all of the solution was passed through. This indicates that the amount of dithizone for complexing was not sufficient. One more detrimental effect was that the time consumption was very long, namely, 40 hours per column. In order to eliminate these disadvantages, the concentration of the dithizone was doubled to 0.1 g per 10 g of voltalef and only 3 g of such treated voltalef were used for one column. By the reduction of voltalef the flow rate was raised from 15 drops per minute to 28 drops per minute. Thus, the time

consumption was reduced to 20 hours per column. The percent recovery of the seven metals from six experiments as measured by the atomic absorption spectrometer are shown in Table 3-7. The standard solutions which were used for comparison are listed in column II. Since cobalt was eluted with ethanol, which also dissolved all the dithizone and dithizonate from the column, these had to be destroyed before the solution could be subjected to measurement. This was done by evaporating the ethanol solution to dryness. The residue was then heated to dryness with 4 cm³ of a mixture containing HNO₃: H₂SO₄: HClO₄: H₂O in a ratio of 1.5 : 1 : 1 : 0.5 (2, 5) after which the residue was taken into a small volume of deionized water and filtered. The volume of the filtrate was made into 10 cm³ with water and was then ready for the determination of Co. From the results which are shown in Table 3-7, it is evident that the separation method which was found to be suitable when the volume of the sample is small, is not applicable to large volume samples. From trial experiments it was found that the percent of elution shows a tendency to increase, but extremely slow, if the volume of eluant was increased. When large volume of eluant is used, the concentration of the element in the eluate will be low and concentration method such as evaporation must be again necessary which makes the analysis become tedious. So it was determined that eluants which could elute the elements required within a small volume will be preferable.

Table 3-7 Recovery of the elements as measured by the atomic absorption spectrometer after 2 dm³ of standard water samples were processed as the concentration and separation scheme in Fig 3-9

Element	Standard solution for the comparative measurement	Recovery (%)					
		Exp1	Exp2	Exp3	Exp4	Exp5	Exp6
Ag	50 µg Ag in 10 cm ³ 4 % NH ₄ CNS in 0.05 M H ₂ SO ₄	76.1	61.8	65.4	71.4	70.0	62.0
Hg	2,000 µg Hg and 100 µg Cu in 10 cm ³ 6.0 M HCl	41.6	60.5	50.9	54.2	50.5	55.0
Cu		60.3	62.1	56.8	69.8	69.5	51.5
Zn	20 µg Zn and 100 µg Pb in 0.1 M oxalic acid-sodium oxalate solution at pH 4	51.0	14.1	34.5	> 100	74.0	104.0
Pb		10.0	12.1	10.3	12.1	20.0	16.5
Cd	20 µg Cd in 10 cm ³ 0.1 M oxalic acid	16.0	12.5	24.1	21.3	14.2	15.5
Co	50 µg Co in 10 cm ³ deionized water	63.1	74.8	71.2	65.6	78.0	76.5

The concentration method, after changing the column parameters as already described in this section, was later confirmed to be suitable to large volume sample in Section 3.5.

3.5 Concentration of trace elements from large volume samples and subsequent measurement by the method of atomic absorption.

Since the method of atomic absorption does not suffer the spectral interferences of other metals, system specific to a metal are not required. Thus, the elements Ag, Hg and Cu were eluted together from column I, the elements Zn, Pb, Cd and Co from column II with a mixture of carbontetra-
chloride: acetone in a ratio 1 : 1 until the colour of the two columns turned to white. A volume of 30-40 cm³ was usually required for each column. The eluate was separately evaporated to dryness and the organic materials were destroyed by a mixture of HNO₃: H₂SO₄: HClO₄: H₂O in a ratio of 1.5 : 1 : 1 : 0.5 as already described above. The residues were taken into a few cubiccentimetres of water and the solution was subjected to filtration. The filtrates were made into 10 cm³ with water and the solutions were ready for measurement by the atomic absorption method for the elements Ag, Hg and Cu (solution from column I) and the elements Zn, Pb, Cd and Co (solution from column II). Two standard solutions were used for the comparative measurements. One contained 50 µg Ag, 100 µg Cu and 2,000 µg Hg. The other contained 50 µg Co, 20 µg Zn and Cd, 100 µg Pb. In the course of elution of the elements Zn, Pb, Cd and Co, it was found that the amount of zinc that was recovered from the column and measured by the method of atomic absorption always fluctuated and exceeded the added amount. Since the gas flow and acetylene flow were set to

be constant for every measurement, the variation of the absorption could not be caused by the absorption of the flame gases, although this was proved to absorb largely at the wavelength of zinc line (6). In order to prove that interference was due to some dissolved dithizone in the eluate the following experiment was conducted. Two cubicdecimetres of deionized water was adjusted to a pH of about 5 ± 0.5 by the addition of 100 cm^3 of the buffer solution. This was then allowed to pass through a column prepared in the same manner as in the previous experiments. The column was then washed with 1.0 M HCl and the fractions 2-6 (10 cm^3) were kept for measurement. After washing the column with water the dithizone was eluted with a mixture of acetone and carbontetrachloride. The dithizone in the eluate was destroyed as previously described. Table 3-8a shows the results of the absorbance measurement for the three fractions at various wavelength. **It is obvious that at the wavelength of zinc line, non atomic species, which in this case must be originated from the traces of dithizone presented, were interfering.** Similar experiments using different kinds of eluants show similar effects, as one could observe from Table 3-8 b. After C.R. Parker (7), when the sample has a high concentration of dissolved solids, it is necessary to correct for non-atomic absorption by using a hydrogen continuum lamp. This has not been tried in the present investigation. The quantitative analysis of zinc was hence cancelled.

Table 3-8 a Effect of interference from non atomic species to the determination of Zn by the method of atomic absorption.

measurement at wavelength of	effluent		elution from 1.0 M HCl (in 10 cm ³)		eluate from CCl ₄ : acetone (10 cm ³) ⁴	
	Abs	conc. ppr	Abs	conc. ppm	Abs	conc. ppm
Zn	0.3188	1.24	0.3565	1.40	0.1739	0.6
Pb	0	0	0	0	0	0
Cd	0	0	0	0	0	0
Co	0	0	0	0	0	0
Ag	0	0	0	0	0	0
Hg	0	0	0	0	0	0
Cu	0	0	0	0	0	0

Table 3-8 b Effect of Interference from non atomic species to the determination of Zn by the method of atomic absorption.

eluant (10 cm ³)	Absorbance at 213.9 nm	calculated as concentration of Zn (ppm)
1.0 M HCl	0.3468	1.49
0.1 M HCl	0.0605	0.24
pH 2	0.0339	0.15
pH 3	0.0223	0.10
pH 4	0.0044	0.03
pH 5	0.0044	0.03
pH 6	0.0088	0.04
pH 7	0.0044	0.03
pH 8	0.0044	0.03
pH 9	0.0088	0.04
pH 4 oxalic acid-oxalate solution	0.0706	0.28

Fig 3-10 gives the final concentration and separation scheme for the quantitative analysis of Ag, Hg, Cu, Pb, Cd and Co from water samples prior to measurement by the method of atomic absorption.

3.6 Chemical yield

The chemical yield of the elements obtained from the concentration and separation scheme was checked by analysing the standard samples. The absorbance in the appropriate fractions were compared with the absorbance of the the standards. The results are tabulated in Table 3-9.

3.7 Calibration curves

Series of pure aqueous standard solutions with concentrations extending between the two limiting points of the concentration scale were prepared. The upper limit was defined by the maximum concentration of the sample solutions which were to be measured, whereas the lower limit was defined by the accuracy and precision of the measurement. After the instrument was aligned and optimum flame condition was set, the readout (absorbance) was calibrated by reference to these standard solutions which concentrations were exactly known. Since it was possible that the working curves might change slightly from day to day due to small variations in lamp and flame conditions, the instrument was recalibrated for each batch of samples. Some typical results showing the relation between the absorbance and the concentration of the elements under investigation are given as examples in Table 3-10. These relations are reproduced as curves in

Table 3-9 Results of replicate determinations of Ag, Hg, Cu, Pb, Cd and Co in standard water samples

No of experiment	Ag recovery (50 µg)		Hg recovery (2,000 µg)		Cu recovery (100 µg)		Pb recovery (100 µg)		Cd recovery (20 µg)		Co recovery (50 µg)	
	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%
1	40.18	80.36	1713.80	85.69	95.71	95.71	94.81	94.81	17.36	86.80	47.84	95.68
2	38.40	76.09	1433.40	71.67	100.00	100.00	91.00	91.00	20.56	102.80	42.40	84.80
3	37.49	74.98	1713.80	85.69	82.60	82.60	95.90	95.90	16.98	84.90	45.69	91.37
4	38.15	76.30	1855.40	92.77	105.59	105.59	89.46	89.46	20.06	100.31	51.10	102.20
5	36.58	73.16	1849.60	92.48	93.38	93.38	105.68	105.68	17.19	85.95	48.05	96.10
6	46.28	92.56	1632.20	81.61	97.29	97.29	108.12	108.12	16.56	82.80	41.42	82.83
7	45.95	91.90	1879.60	93.48	84.68	84.68	100.00	100.00	18.03	90.16	46.47	92.94
8	44.69	89.38	1682.20	84.11	87.02	87.02	96.77	96.77	16.22	81.09	41.35	82.70
9	40.21	80.41	1885.60	94.28	103.03	103.03	88.02	88.02	18.92	94.62	49.00	98.00
10	47.34	94.68	1737.00	86.85	89.08	89.08	92.34	92.34	17.64	87.19	43.17	86.34
11	43.14	87.27	1664.00	83.20	91.05	91.05	100.00	100.00	18.20	91.02	51.65	103.31
12	42.89	85.78	1650.60	82.53	88.04	88.04	95.00	95.00	20.00	100.00	42.09	84.19
13	35.09	70.18	1560.60	78.03	100.00	100.00	103.22	103.22	18.28	91.40	50.00	100.00
	41.23	82.54	1712.14	85.41	93.47	93.47	96.95	96.95	18.15	90.70	46.17	92.34
	±4.07	±8.09	±131.98	±6.59	±6.99	±6.99	±6.19	±6.19	±1.38	±6.94	±3.86	±7.50

Figs 3-11 to 3-16. All working curves, with lead in exception, were linear. In the case of lead, a linear relation was found between the concentration 1-5 ppm (Fig 3-13 a). With higher concentrations, a slight curvature away from the concentration axis was observed (Fig 3-13 b).

3.8 Determination of detection limits

Standard solutions containing $0.2 \mu\text{g}/\text{cm}^3$ of Ag, $25 \mu\text{g}/\text{cm}^3$ of Hg, $0.5 \mu\text{g}/\text{cm}^3$ of Cu, $1.0 \mu\text{g}/\text{cm}^3$ of Pb, $0.1 \mu\text{g}/\text{cm}^3$ of Cd and $0.5 \mu\text{g}/\text{cm}^3$ of Co were prepared.

The operation conditions of the atomic absorption spectrometer for the analysis of these elements were set according to Table 3-2, and maximum scale expansion was selected. Before each measurement, water was aspirated at least two minutes to thoroughly clean the spray chamber. Each sample was aspirated ten times, with aspiration of water as blank solution before and after each aspiration. The ten readings were then calculated by subtracting the mean of the adjacent blanks from the appropriate readings, and the mean, \bar{X} , and standard deviation, S , of the signals were then calculated. The detection limit was then calculated according to the formula described in section 2.2.3.2. The results of the measurements and a calculation example are given in Appendix I, whereas the results of the detection limits are given in Table 3-11.

Table 3-10 Relation between absorbance and concentration of solution

element	concentration (ppm)	absorbance
Ag	0	0
	0.40	0.0386
	0.80	0.0809
	1.20	0.1163
	1.60	0.1549
	2.00	0.2076
Hg	0	0
	20.0	0.0200
	40.0	0.0410
	60.0	0.0605
	80.0	0.0783
	100.0	0.0969
Cu	0	0
	0.50	0.0410
	1.00	0.0809
	1.50	0.1221
	2.00	0.1643
	2.50	0.2007
	3.00	0.2557
Pb	0	0
	1.00	0.0246
	2.00	0.0506
	3.00	0.0757
	4.00	0.1024
	5.00	0.1308
	6.00	0.1838
	8.00	0.2596
	10.00	0.3468
Cd	0	0
	0.20	0.0458
	0.40	0.0809
	0.60	0.1337
	0.80	0.1805
	1.00	0.2219
Co	0	0
	0.50	0.0200
	1.00	0.0410
	1.50	0.0555
	2.00	0.0809
	2.50	0.1051

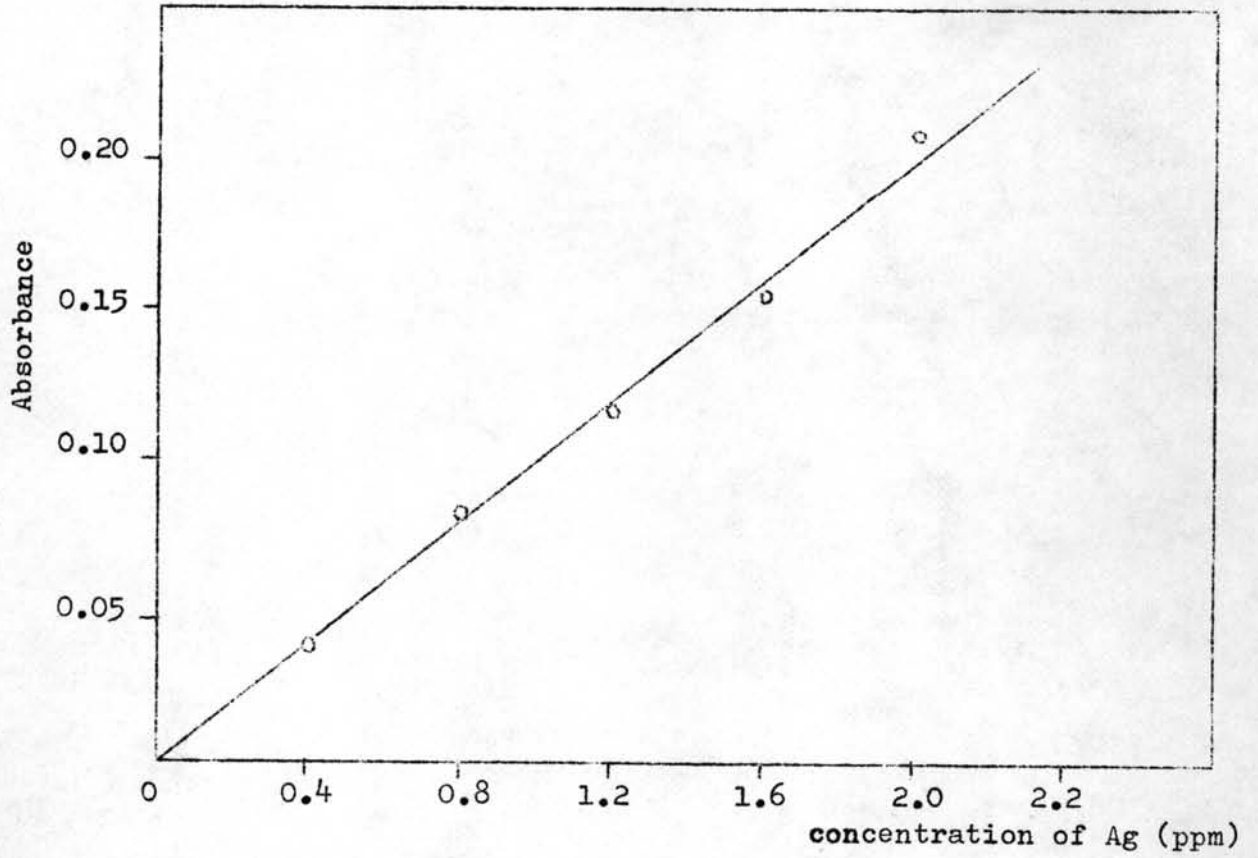


Fig 3-11 Calibration curve for silver

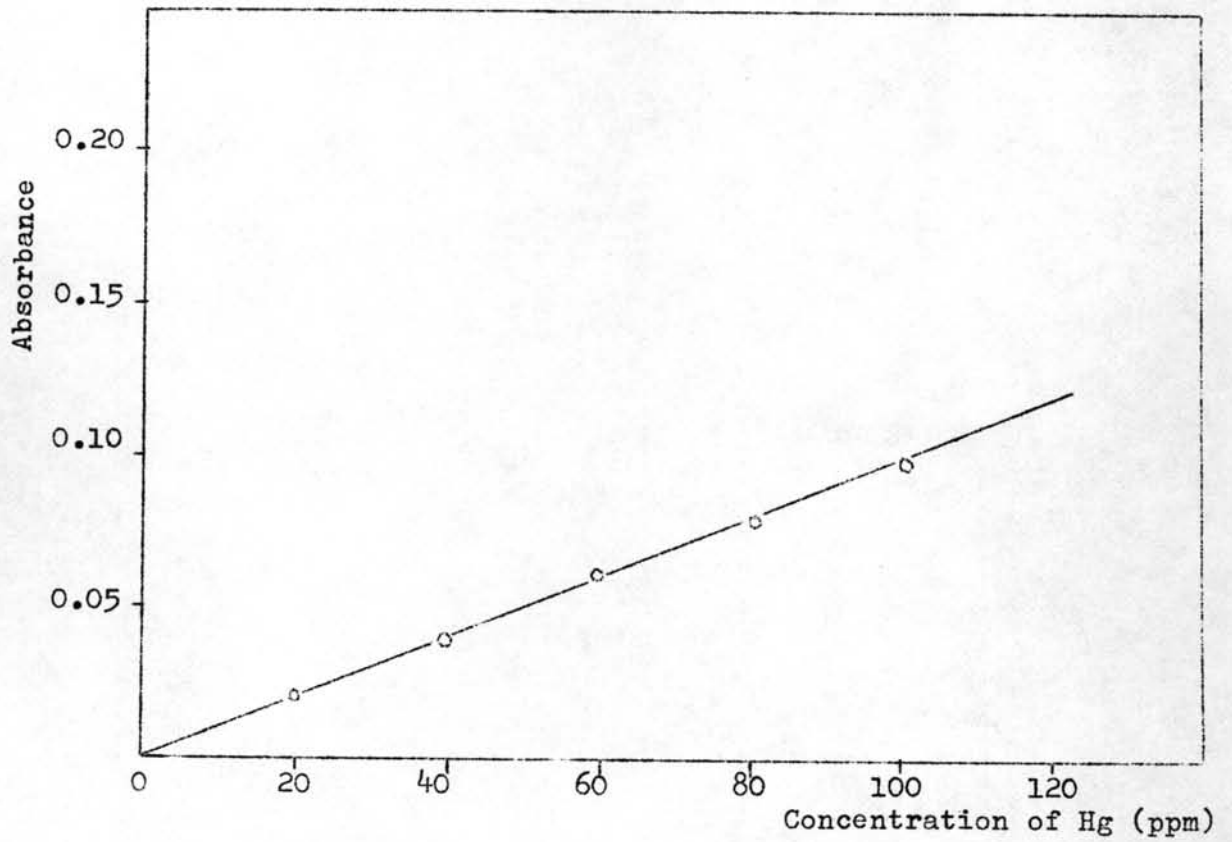


Fig 3-12 Calibration curve for mercury

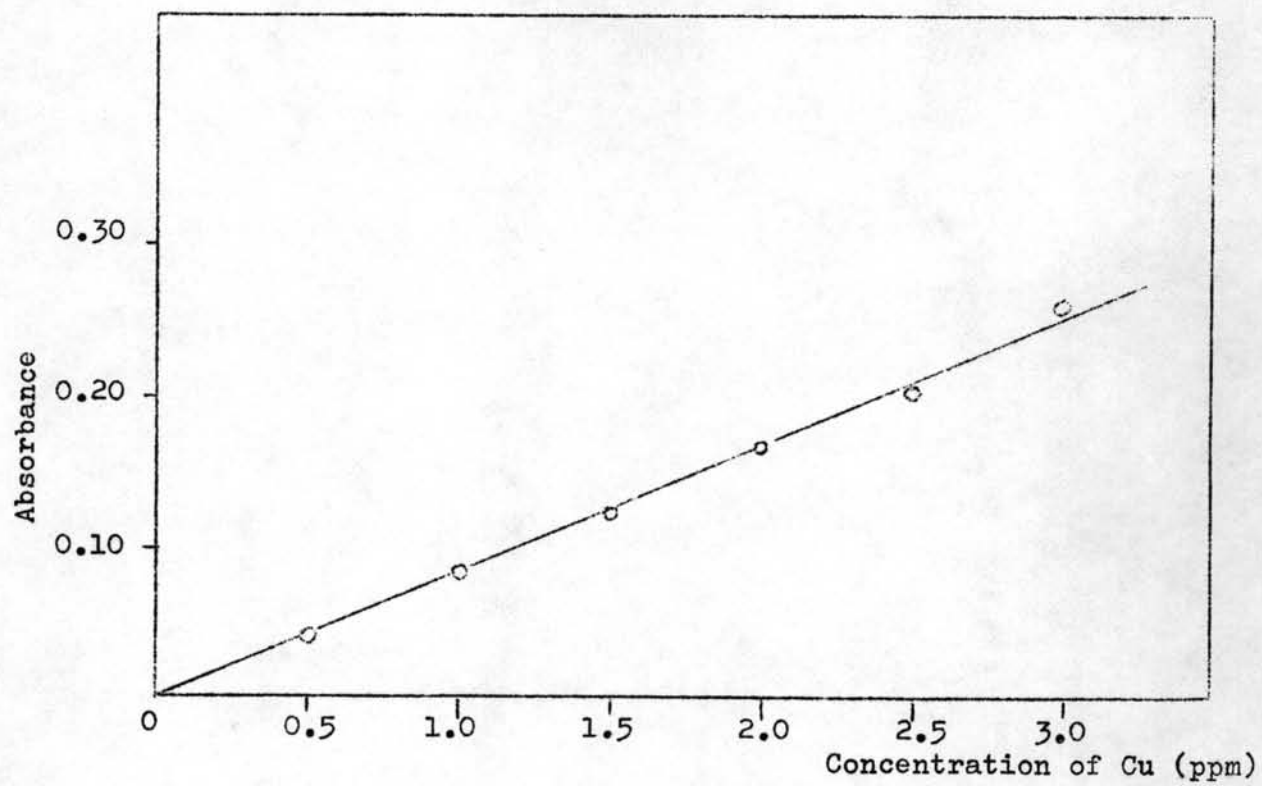


Fig 3-13 Calibration curve for copper

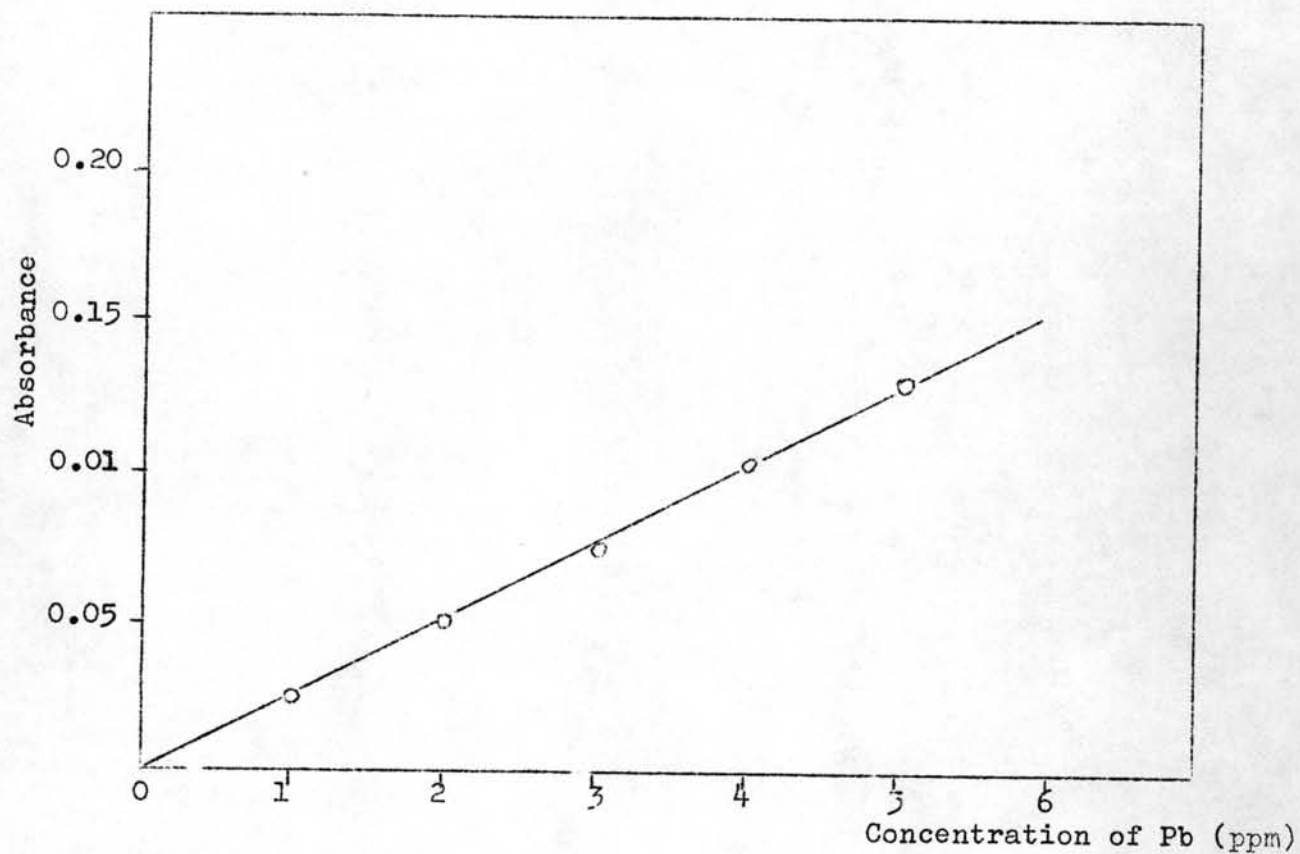


Fig 3-14 a Calibration curve for lead
concentration:- 0-5.0 ppm

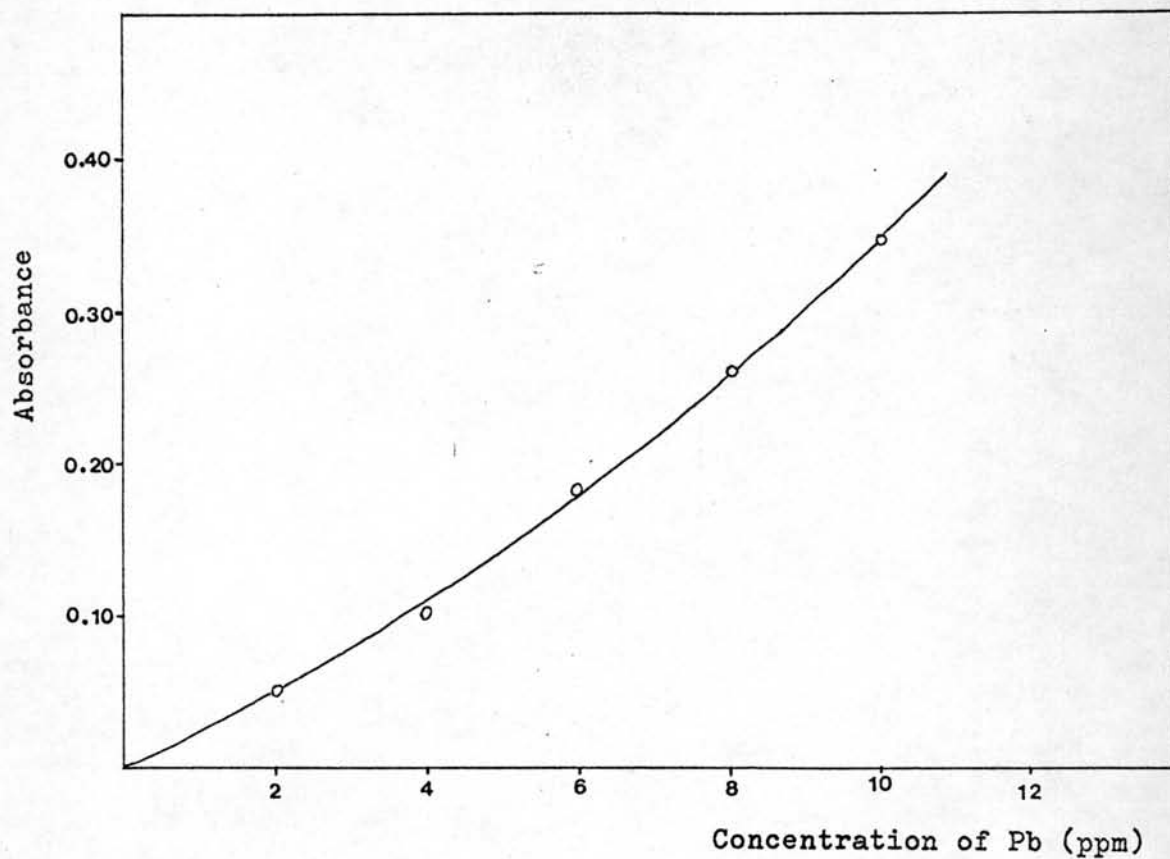


Fig 3-14 b Calibration curve for lead
concentration :- 0-10.0 ppm

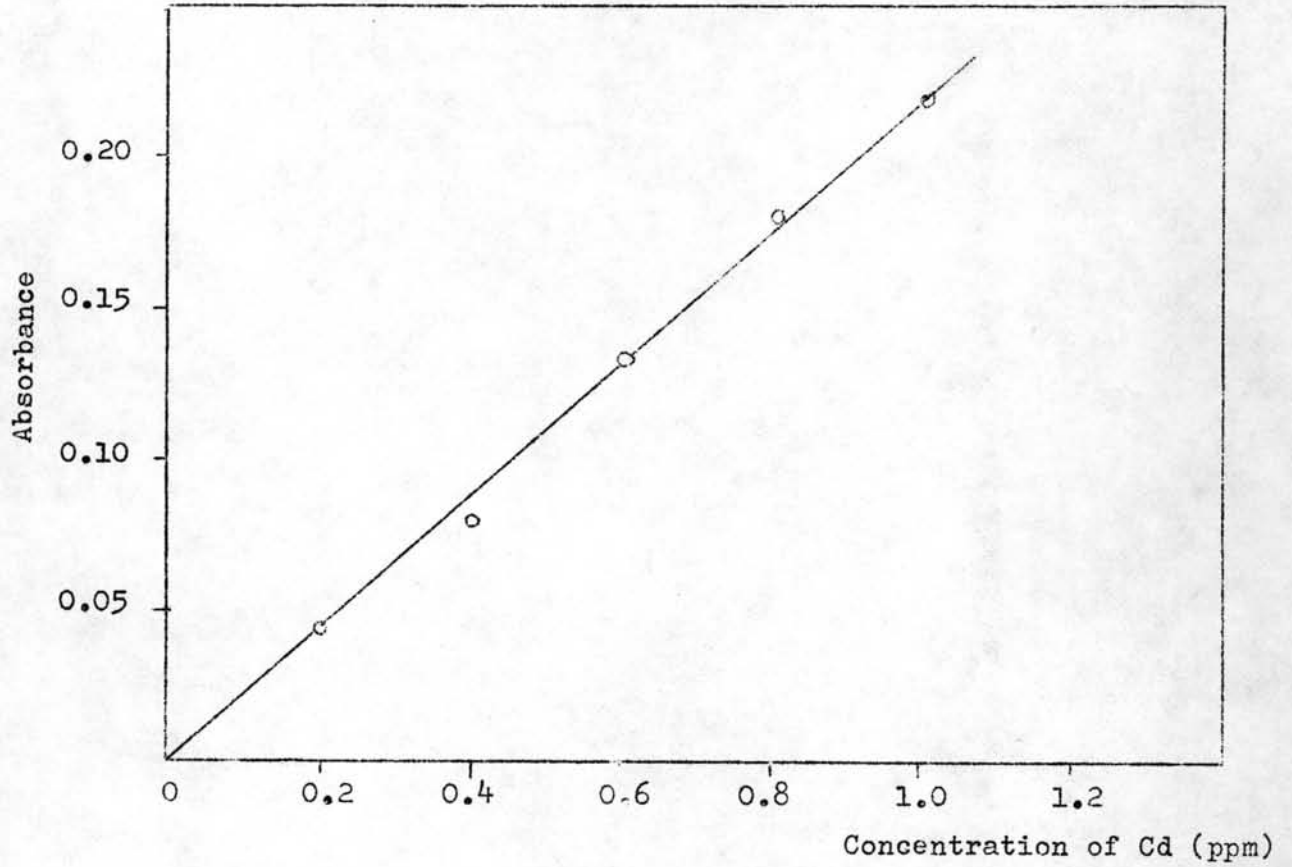


Fig 3-15 Calibration curve for cadmium

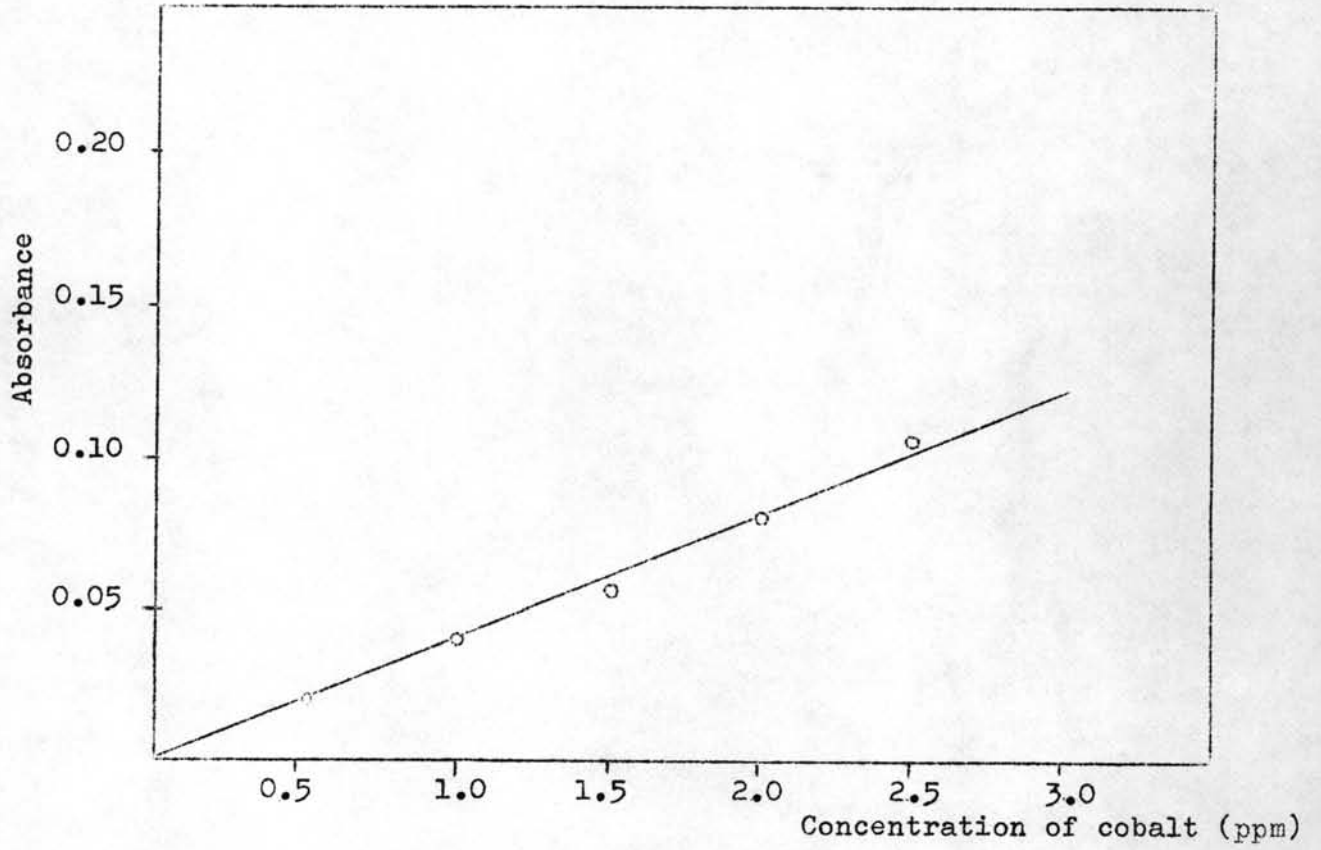


Fig 3-16 Calibration curve for cobalt

Table 3-11 The detection limit of Ag, Hg, Cu, Pb, Cd
and Co

Element	detection limit (ppm)
Ag	0.033
Hg	8.421
Cu	0.072
Pb	0.383
Cd	0.027
Co	0.098