CHAPTER III

EXPERIMENTS

3.1 Materials.

3.1.1 Preparation of Standards and Carriers. Carrier solution of Hg, Cu, Sb, Se, As and Ag in a concentration of 1 mg/cm^3 each, were prepared by dissolving the specpure grade oxide (Hg, Cu, Sb, As), acid (H_2SeO_3) or salt ($AgNO_3$) either in tri-distilled water or in dilute solution of A.R. grade nitric acid. Standard solutions with other concentrations were prepared by diluting appropriate amount of the stock solutions with tri-distilled water.

Tracer solutions were prepared by dilutimg the carrier solution of each element to a concentration of 100 μg/cm^3. Generally, 2-3 cm^3 of these solutions were separately subjected to neutron irradiation. The irradiated solutions were then diluted to give concentrations of 5 μg/cm^3 Sb, 10 μg/cm^3 Ag, 10 μg/cm^3 Se, 1 μg/cm^3 As, 5 μg/cm^3 Hg, and 5 μg/cm^3 Cu. These solutions were used in the tracer experiments from which optimum conditions for the separataion procedure were obtained.

The thermal neutron flux in the Thai Research Reactor I(TRR-I) at the irradiation position was about 6 x 10^2 n/cm^{2}s. Time of irradiation ranged from few minutes to few days depending on the half-life and the cross-section of the radio-nuclides of interest. Table 3-1 gives the list of isotopes used, their cross-sections, half-lives and energies.

Table 3-1 Isotopes used in tracer experiments

Element	Isotope	Crossection (barn)	Half life	Energy (8) (Kev)
Hg	Hg-203	4	46.9d	279.1
Ag	Ag-110m	3	253 d	657.8$^{@}$(100), 677.9(10), 706.4(20) 763.9(24), 818(8), 884.5(74), 937.2(23), 1383(22).
Se	Se-75	30	121 d	96.7(6), 121(28), 136(96), 264.6$^{@}$(100) 279.6(40), 400.7(20).
Sb	Sb-122	6	2.75d	546$^{@}$(100), 692.5(5), 1140(1), 1335(1).
Sb	Sb-124	3.3	60.9 d	602.6$^{@}$(100), 645.7(8), 722.8(10), 1325.5(2), 1436.8(2), 1690.7(1), 2090(7).
As	As-76	4.5	26.3 h	559.2$^{@}$(100), 657(14), 1228.8(25).
Cu	Cu-64	4.5	12.8 h	511.0$^{@}$(100),1345.5(100)

Note d = day, h = hour, @ = peak for calculation.

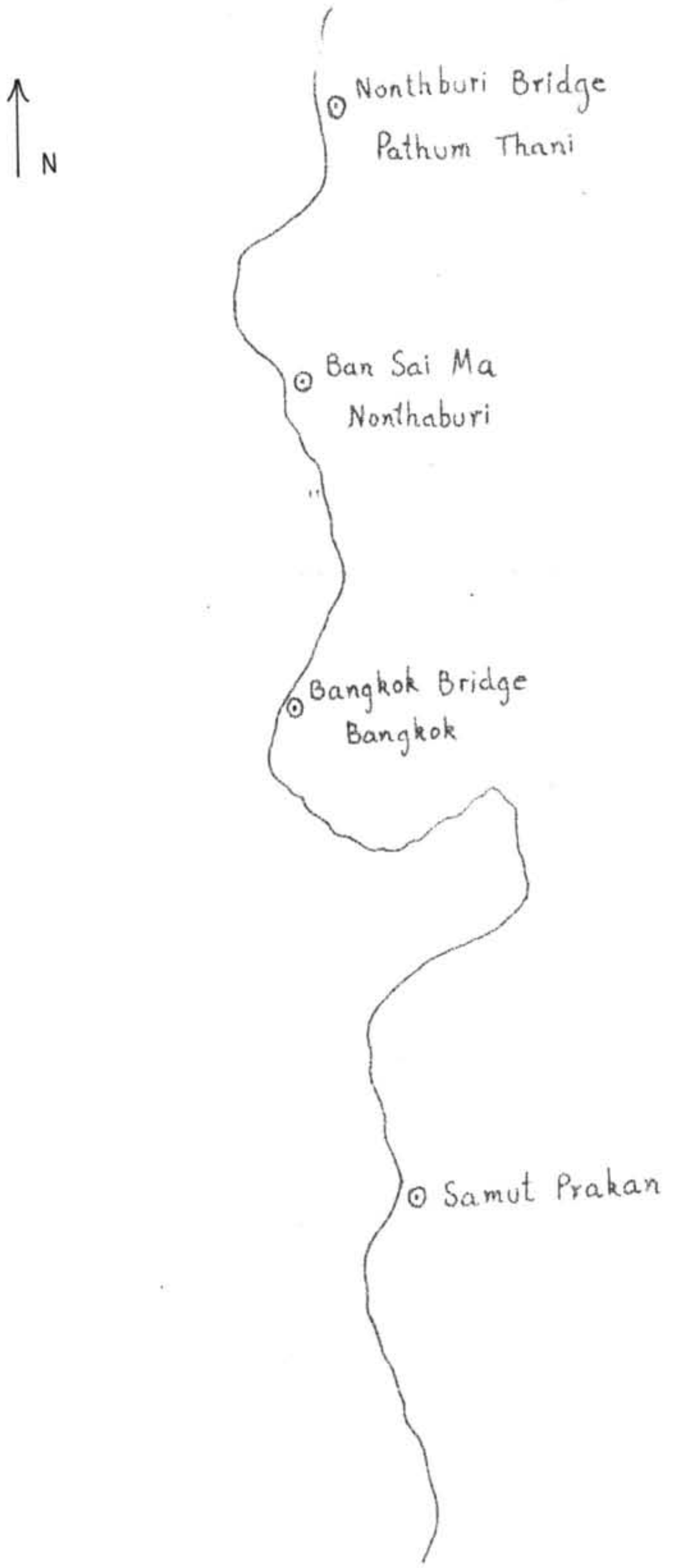

Fig. 3-1 Locations for sampling along the Chao Phya River

3.1.2 Sample Collection and Storage. Samples of surface water, at the depth of 1 metre from the surface, were collected from the middle of the Chao Phya River at the following locations: Nonthaburi Bridge (Pathum Thani), Ban Sai Ma (Nonthaburi), Bangkok Bridge (Bangkok) and Samut Prakan (Fig. 3-1). The sampling operations were performed on April 22, 1974 and June 5, 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 16 samples were obtained.

The samples, 4-5 dm^3 each, were separately stored in polyethylene bottles which were previously cleaned with concentrated nitric acid and distilled water. 10 cm^3 concentrated nitric acid were added per dm^3 of the water samples to avoid loss of the trace elements by adsorption on the container wall or on any suspended particals in the water solution(9). Each sample contained about 4-5g suspended materials which settled down after standing and the clear solution was used for analyses.

3.1.3 Reagents. Unless otherwise stated, all chemicals are of analytical reagent grade.

The additional reducing agent, $SnCl_2$ in hydrochloric acid, was prepared by adding 10 cm^3 concentrated hydrochloric acid to 4g $SnCl_2$(Lab Reagent). The solution was then warmed until all $SnCl_2$ dissolved, after which a small piece of tin metal was added. The solution thus prepared can be stored and used for one week.

A solution of 0.5 mol/l NaOH was prepared by dissolving 20g commercial grade NaOH per dm^3 deionized water.

A 0.1 % dithizone solution was prepared by dissolving 0.05 g dithizone in 50 cm^3 carbontetrachloride. The solution was prepared shortly before use.

Solutions of 2 % and 4 % NH_4SCN were prepared by dissolving 20 g and 40 g NH_4SCN (Lab. Reagent) respectively in $1dm^3$ of 0.05 mol/l sulphuric acid.

A 25 % hydroxylamine hydrochloride solution was prepared by dissolving 25 g $NH_2OH.HCl$ (Lab. Reagent) in 100 cm^3 deionized water.

0.015 mol/1,0.027 mol/l and 0.134 mol/l EDTA solutions at pH 4 to 5 were prepared by dissolving 0.56 g, 1.0 g and 5.0 g sodium salt of EDTA in 100 cm^3 deionized water respectively.

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

3.1.4 Preparation of Coated Materials. Two kinds of coating materials were used, dithizone and di(2-ethylhexyl) phosphoric acid (HDEHP). For the preparation of dithizone coated voltalef, 10 g of the solid support were mixed with 50 $cm^3$of 0.1% dithizone carbontetrachloride solution. The slurry was heated with constant agitation on a hot plate until the color of the material changed from dark green to light green which indicates that carbontetrachloride was all evaporated. The coated material was stored in a cool-dark place.

For the preparation of HDEHP coated voltalef, 20 g of the solid support was mixed with 10 cm^3 HDEHP in 20 cm^3 cyclohexane. The mixture was dried at 70°C until all cyclohexane was volatiled, after which was ready for use.

3.1.5 Preparation of Extraction Column. The columns 1 cm id. and 30 cm in height, were enlarged at the top with a ground glass joint that can be connected to a pressure pump and closed at the bottom with a glass stopcock. Glasswools were plugged at the bottom to hold the packing material and at the top to prevent disturbing the column when solutions were added. The column was first filled with 2 g of untreated voltalef and followed with 2 g of dithizone treated voltalef, thus making an efficient filling height of 16 cm. The flow rate was kept constant at 0.5 cm^3/min. throughout the work. After the column was packed, 2 cm^3 of carbontetrachloride was quickly drawn through the column by the application of vacumn. The column was then washed with 50 cm^3 0.1 mol/l HCl, followed by 100 cm^3 deionized water and was then ready for use.

Columns of anion exchangers were prepared by allowing a slurry of 2 g of Dowex 1 X 8, 100-200 mesh, in 2 mol/l HCl to run through glass columns with 1 cm diameter. The effective height was 5 cm.

3.2 Apparatus.

3.2.1 γ -Spectrometers. A well-type NaI(Tl) crystal detector which was connected to a Single Channel Analyzer from Nuclear Chicago (Model 181 A) and a 3" X 3" NaI(Tl) crystal detector (Fig. 3-3) which was connected to a 128 Channels Analyzer from Nuclear Data (Model ND-110, Fig. 3-2) were used in preliminary experiments. The spectrometers were calibrated before each measurement with standards from the Radiochemical Center Amersham, England.

A Ge(Li) detector which was connected to a 1024 Channels Analyzer from Nuclear Data (Model 2200) was used to measure the gamma spectra of samples after separation (Fig. 3-4 & 3-5). A typical energy calibration curve in the region mostly used is shown in Fig. 3-6.

3.2.2 Fraction Collector. A fraction collector from Gallenkamp which could turn automatically to the next tube position after collection of a selected number of drops was used. Fractions of 2 cm^3 were generally collected.

3.2.3 Vacuum Pump. A vacuum oil pump from A.H. Thomas Co. was used.

3.3 Distillation of Hydride. The method is based on the formation of easily volatile hydrides of Se, Te, As and Sb during the reaction of zinc and mineral acid. After the hydrides are distilled from the sample solution, the four elements can be separated from one another using appropriate absorbing solutions. The distillation apparatus is schematically shown in Fig. 3-7. The sample solution was filled in the reaction

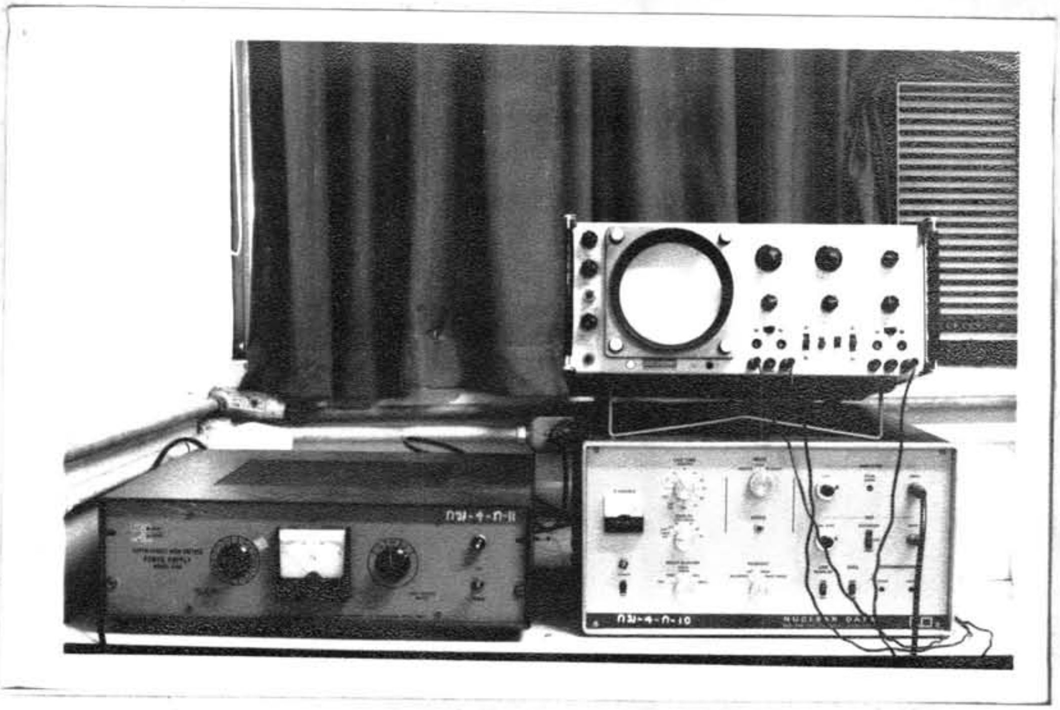

Fig. 3-2 The 128 channel analyzer and the printer

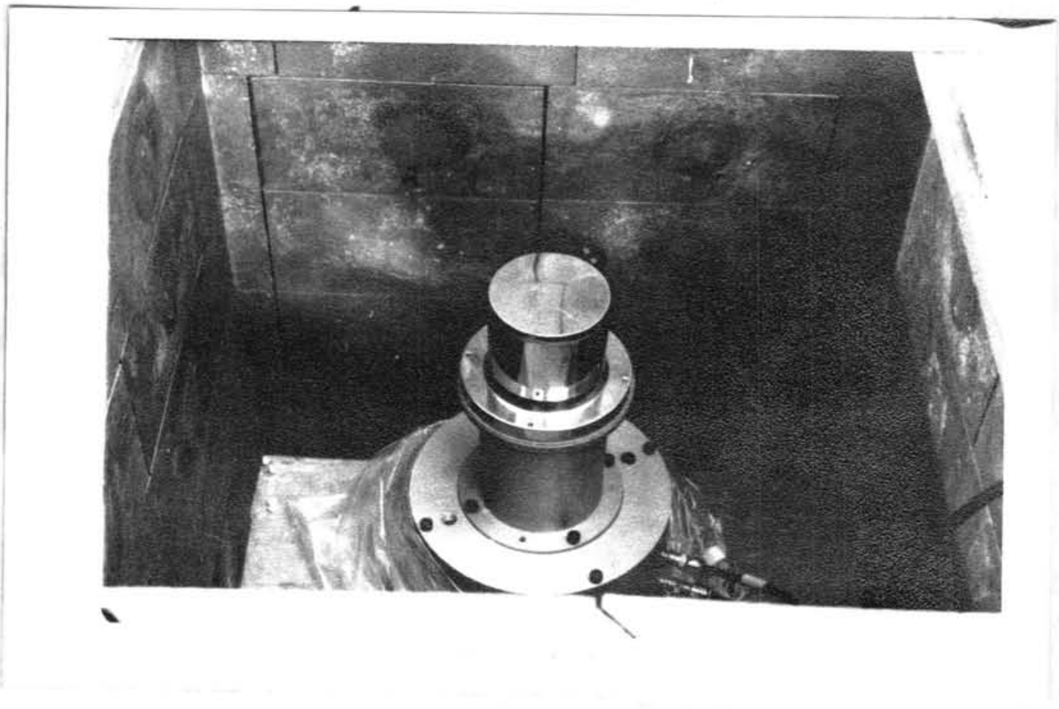

Fig. 3-3 The NaI(Tl) Detector with shielding

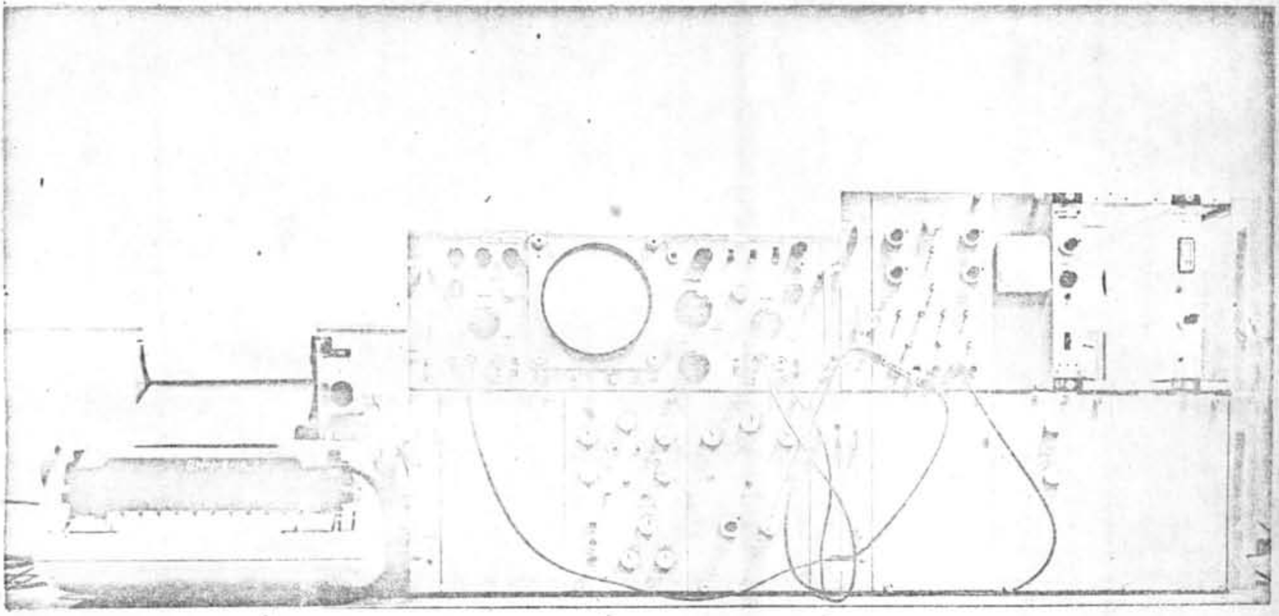

Fig. 3-4 The multichannel analyzer and the printer

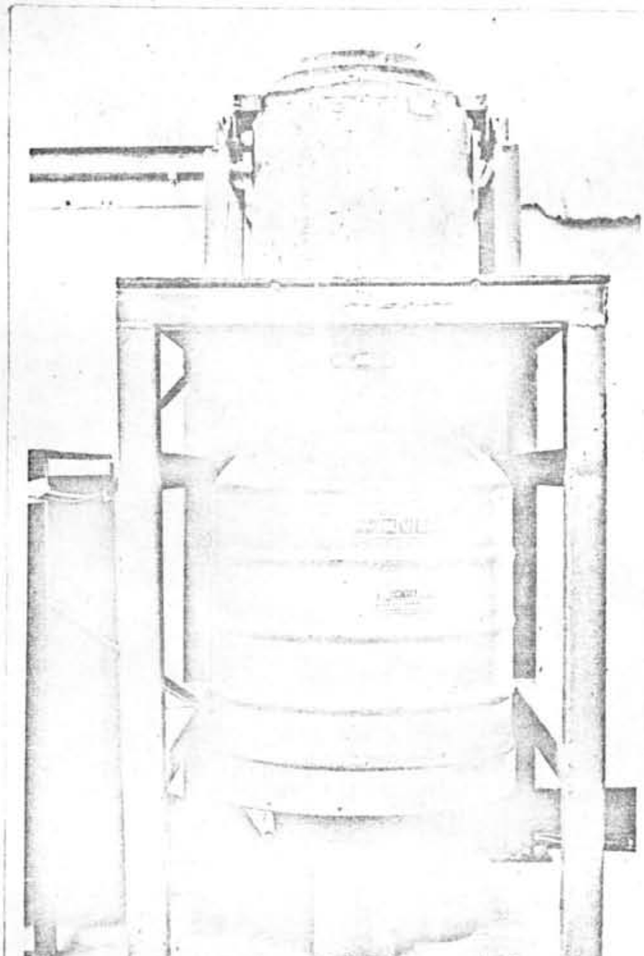

Fig. 3-5 The Ge(Li) detector with shielding and cooling system.

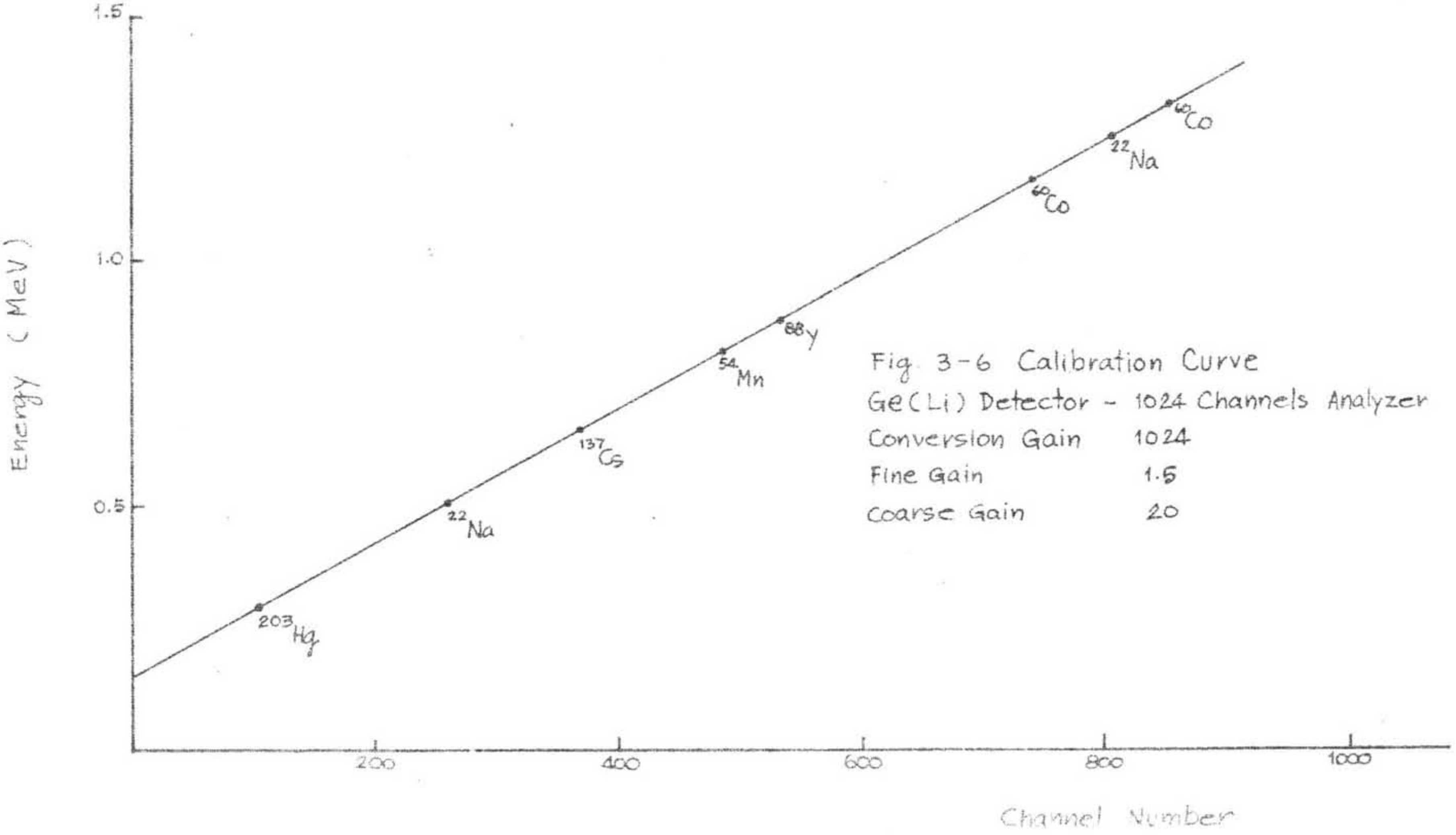

Fig. 3-6 Calibration Curve

Ge(Li) Detector - 1024 Channels Analyzer

Conversion Gain	1024
Fine Gain	1.5
Coarse Gain	20

A : Reaction flask
B : Spoon (Zn)
C : Reagent funnel
D : Water Bath
E : Trap A filled with 0.5 mol/l NaOH
F : Trap B filled with 9 mol/l $HCl+KClO_3$
G : Hot Plate

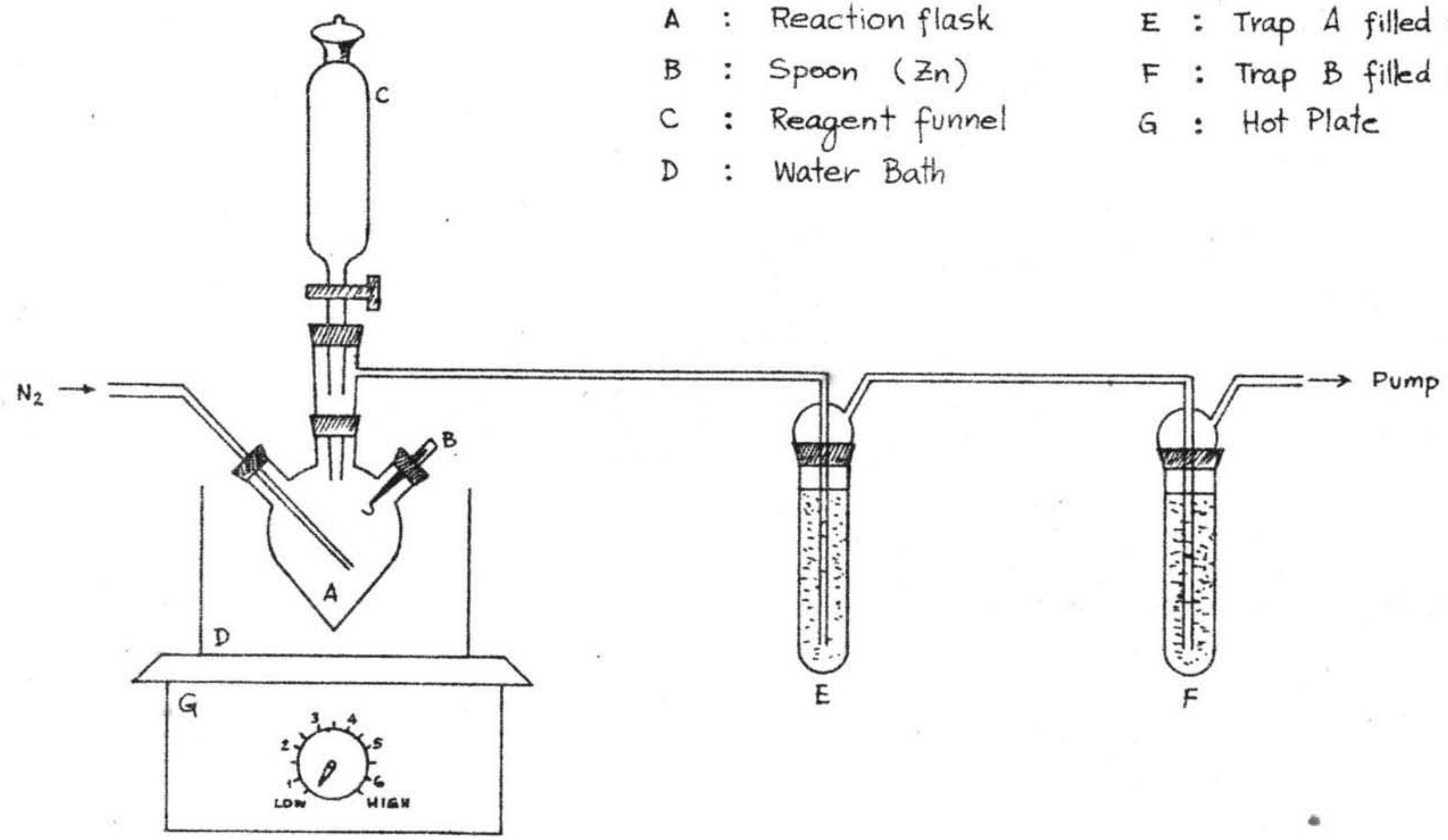

Fig. 3-7 Distilling Apparatus

flask A. B is a spoon in which zinc powders were put into before the performance of each experiment. The reducing agent, carrier and acid were added into the reaction flask A from the reagent funnel C. The whole system was dipped into a water bath for the control of the reaction temperature. By turning the spoon B, zinc fell into the sample solution and the reaction started. As the reaction took place, the reaction mass was stirred by bubbles of nitrogen gas which was also used as a carrier gas for the hydrides. The gas was pumped through E and F which were filled with 0.5 mol/l NaOH for trapping of SeH_2 and $KClO_3$ in 9 mol/l HCl for trapping of SbH_3 and AsH_3 respectively (10). The activity of the trapped solution was counted and compared to the activity of a standard stock solution containing equivalent of the element. The yield of distillation was calculated.

3.3.1 Distillation of SbH_3. The optimum conditions for the distillation of Sb were investigated using Sb-122 as tracer.

3.3.1.1 Effect of Amounts of Zinc on the Distillation of SbH_3. 1 cm^3 of the Sb-122 tracer solution containing 5μg Sb was pipetted into the reaction flask after which 1 cm^3 of the carrier solution was added and mixed. The reaction flask was dipped into a water bath which temperature was kept constant at 28°C. Nitrogen gas was allowed to pass through the system and the pump was turned on. The spoon B, containing zinc powders of various amount ranging from 0.4 g to 1.0 g was turned over to transfer the zinc metal into the reaction flask. 5 cm^3 of concentrated

Table 3-2 Effect of the amount of zinc on the distillation of SbH_3 (Conditions: 5 μg Sb-122, 1 mg carrier, 5 cm^3 HCl, no additional reducing agent, room temperature)

Expt No	Weight of zinc (g)	SbH_3 in Trap B (%)
1	0.4	80
2	0.6	78
3	0.8	82
4	1.0	85

Table 3-3 Effect of acid concentration on the distillation of SbH_3 (Conditions: 5 μg Sb-122, 1 mg carrier, no additional reducing agent, 0.4 g zinc, 20 cm^3 total volume, room temperature)

Expt No	Volume of conc. HCl (cm^3)	Total acid concentration (mol/l)	SbH_3 in Trap B (%)
1	5	3.0	46
2	10	5.4	48
3	14	8.2	54
4	20	10.5	51

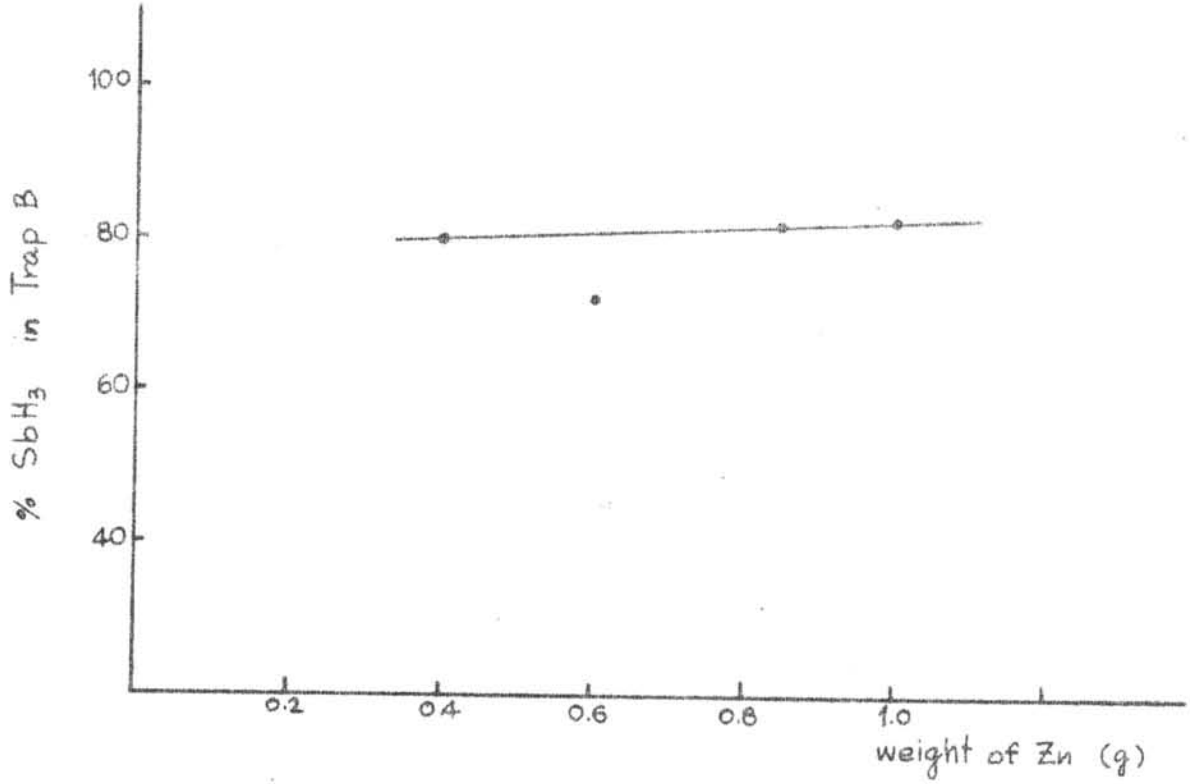

Fig. 3-8 Effect of the amount of Zn on the distillation of SbH_3

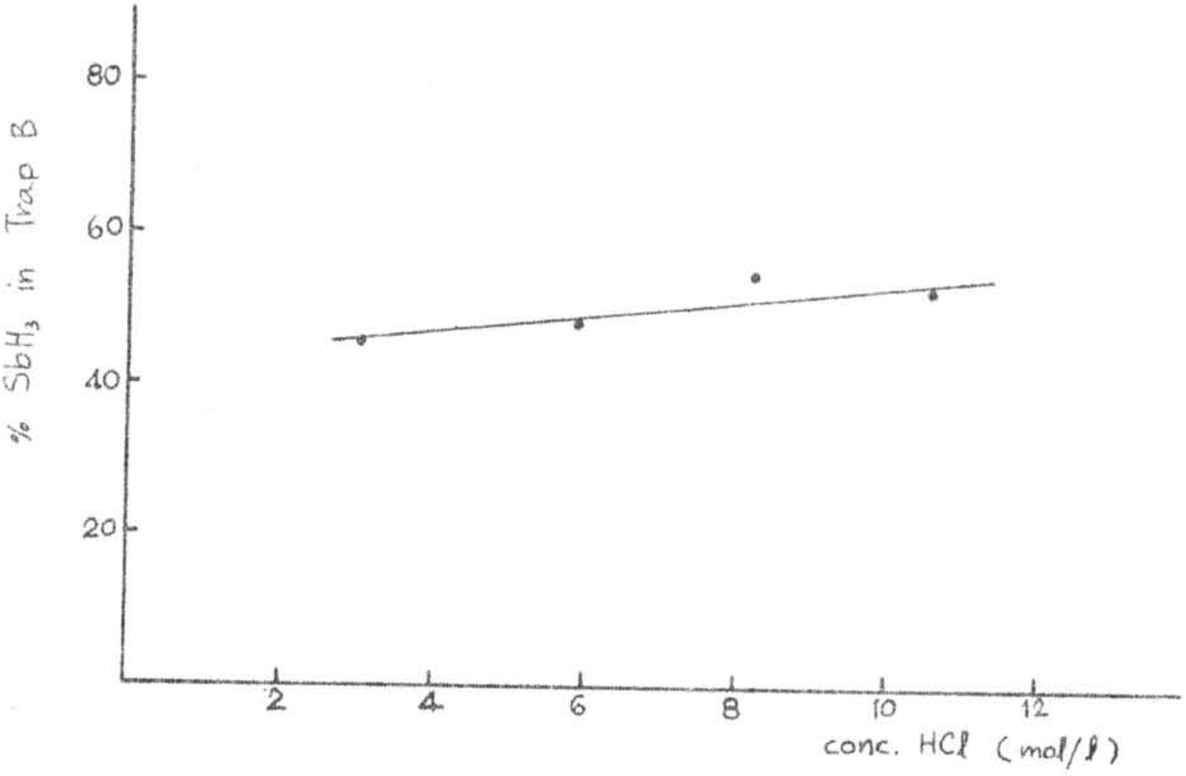

Fig. 3-9 Effect of concentration of acid on the distillation of SbH_3

hydrochloric acid from the reagent funnel C was added into the reaction mixture dropwise. Reaction started immediately and was allowed to continue for about 1 hour, after which the reaction apparently ceased. The Sb-activity in trap B was measured comparing to that of a standard solution. The chemical yields were calaulated and presented in Table 3-2. The weight of zinc used in each experiment versus the percent of SbH_3 recovered in trap B was plotted in Fig. 3-8. Under the conditions described above no significant difference was observed by varying the amount of zinc metal from 0.4 to 1.0 g.

3.3.1.2 Effect of Acid Concentration on the Distillation of SbH_3. Experiments were performed in the same manner as described in section 3.3.1.1 The amount of zinc was fixed at 0.4 g while the volume of acid was varied from 5 to 18 cm^3. The total volume of the reaction mass was kept constant at 20 cm^3 by the addition of water. This made the acid concentrations of the reaction mixtures vary from 3 mol/l to 10.5 mol/l. No difference was observed in the distillation yield of SbH_3 when the acid concentration was varied, as the results in Table 3-3 and the corresponding curve in Fig. 3-9 show.

3.3.1.3 Effect of Carrier on the Distillation of SbH_3. Since the concentration of Sb in the samples of interest is generally in trace-level, it is necessary to add inactive Sb into the reaction mass prior to each experiment. The optimum amount of carrier under the working conditions described in section 3.3.1.1 was checked by adding different amount of Sb

Table 3-4 Effect of the amount of carrier on the distillation of SbH_3 (Conditions: 5 μg Sb-122, no additional reducing agent, 5 cm^3 HCl, 0.4 g zinc room temperture)

Expt No	Amount of Carrier (mg)	SbH_3 in Trap B (%)
1	0.1	41
2	0.5	65
3	1.0	83
4	5.0	63
5	10.0	55

Table 3-5 Effect of temperature on the distillation of SbH_3 (Conditions: 5 μg Sb-122, 1 mg carrier, no additional reducing agent, 5 cm^3 HCl, 0.4 g zinc)

Expt No	Temperature (°C)	SbH_3 in Trap B (%)
1	28	83
2	50	90
3	70	73
4	97	85

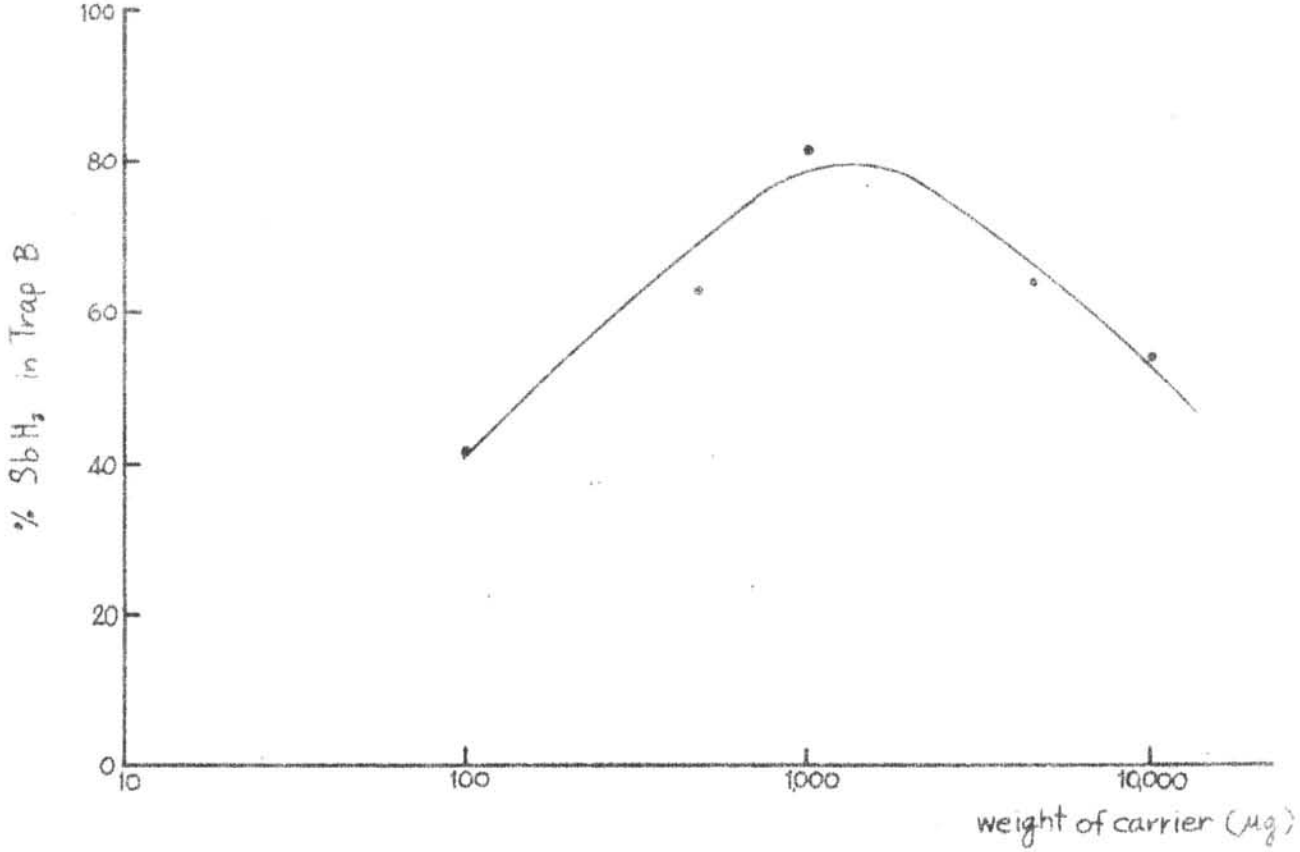

Fig 3 - 10 Effect of the amount of carrier on the distillation of SbH_3

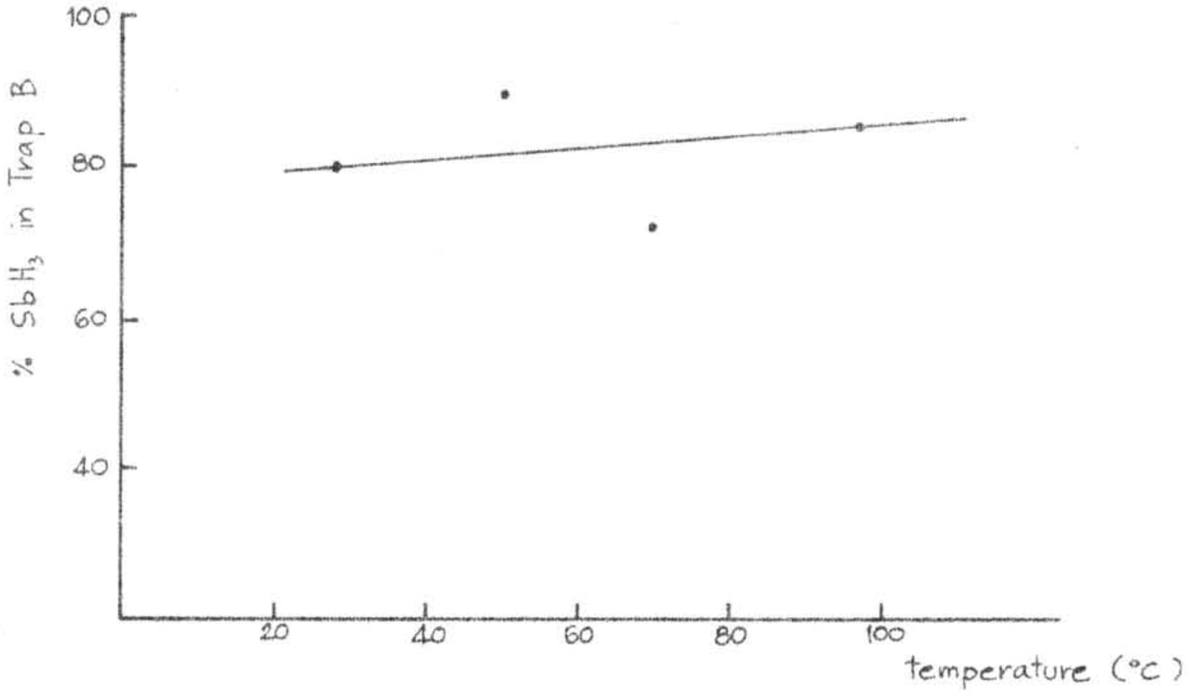

Fig. 3 - 11 Effect of temperature on the distillation of SbH_3

varying from 0.1 mg to 10 mg. The yield of SbH_3 was found to be maximum when 1 mg. of Sb carrier was added, as Table 3-4 and the corresponding curve in Fig. 3-10 show. It was observed that if the amount of carrier exceeds 1 mg. metallic Sb would preciptate. This might be caused by the fact that the volume of SbH_3 formed was large and the carrier gas was not able to sweep all of SbH_3 formed from the reaction flask immediately after it was formed. Sb(III) was further reduced to Sb metal by zinc.

3.3.1.4 Effect of Temperature on the Distillation of SbH_3. Experiments were performed by varying the temperature of the water bath from 28°C to 98°C while other parameters were kept similar to the conditions in section 3.3.1.1. From the results in Table 3-5, it is obvious that the bath temperature has no effect on the distillation of SbH_3. In other word, the distillation of SbH_3 could be performed at room temperature.

3.3.1.5 Effect of Additional Reducing Agent on the Distillation of SbH_3. From trial experiments, it was discovered that if $SnCl_2$ solution was added into the reaction mixture, Sb metal would precipitate and the distillation would not take place.

3.3.2 Distillation of SeH_2. Se-75 was used as tracer in the following experiments to determine the optimum conditions for the distillation of SeH_2.

3.3.2.1 Effect of Additional Reducing Agent on the Distillation of SeH_2. 1 cm^3 of the tracer solution containing 10 µg Se and 1 cm^3 of the carrier solution containing 1 mg of Se were added into the reaction flask. 0.4 g $SnCl_2$ in 1 cm^3 hydrochloric acid as additional reducing agent was added to the tracer and carrier solution. The reaction was allowed to take place at room temperature. Nitrogen gas was turned on for a few minutes after which 0.4 g of zinc metal was allowed to fall into the reaction flask by turning the spoon B down. Then 5 cm^3 of hydrochloric acid was added dropwise to the system from the reagent funnel C. The carrier gas carried the SeH_2 through trap A which contained 15 cm^3 0.5 mol/l NaOH. When the reaction stopped, the activity in trap A was counted and the recovery yield calculated. Another experiment was performed in the same manner, except that no additional reducing agent was added. The results in Table 3-6 indicate that $SnCl_2$ as additional reducing agent increased the chemical yield of SeH_2.

3.3.2.2 Effect of the Amount of Zinc on the Distillation of SeH_2. By following the same process as described in section 3.3.2.1 with $SnCl_2$ as additional reducing agent, the effect of the amount of zinc used in the reaction was studied. Two series of experiments were performed. In the first series the volume of hydrochloric acid was fixed at 15 cm^3 and the weight of zinc varied between 0.56 g to 1.96 g. In the other series the volume of hydrochloric acid was fixed at 5 cm^3 while the weight of zinc was varied between 0.21 g and 0.58 g. The data-

Table 3-6 Effect of additional reducing agent on the distillation of SeH_2. (Conditions: 10 μg Se-75, 1 mg carrier, 15 cm^3 HCl, 0.4 g zinc, room temperature)

Expt No	Additional Reducing Agent	SeH_2 found in Trap A (%)
1	none	0
2	1 cm^3 $SnCl_2$ solution	10

Table 3-7 Effect of the amount of zinc on the distillation of SeH_2. (Conditions: 10 μg Se-75, 1 mg carrier, 15 cm^3 or 5 cm^{3*} HCl, 1 cm^3 $SnCl_2$ solution, 60°C.)

Expt No	Weight of zinc (g)	SeH_2 in Trap A (%)
1	0.56	28
2	0.74	33
3	0.98	41
4	1.45	53
5	1.61	49
6	1.96	51
7*	0.21	33
8*	0.31	49
9*	0.41	62
10*	0.50	61
11*	0.58	60

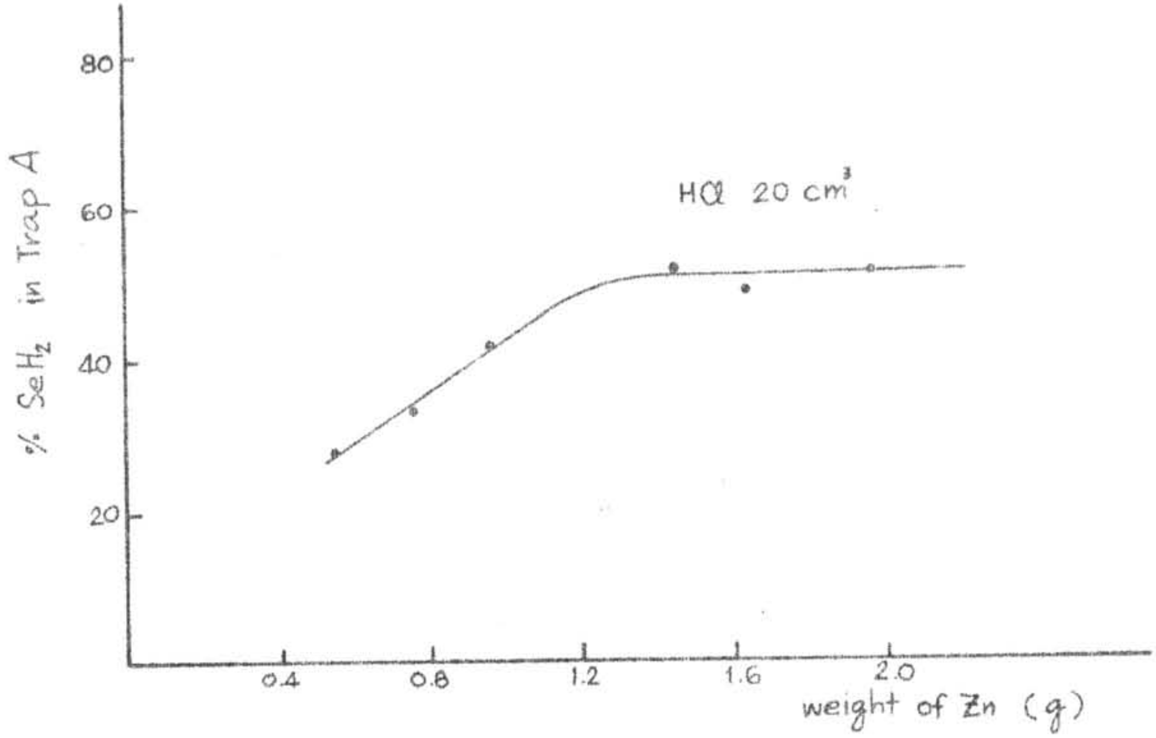

Fig. 3-12 Effect of amount of Zinc on the distillation of SeH_2

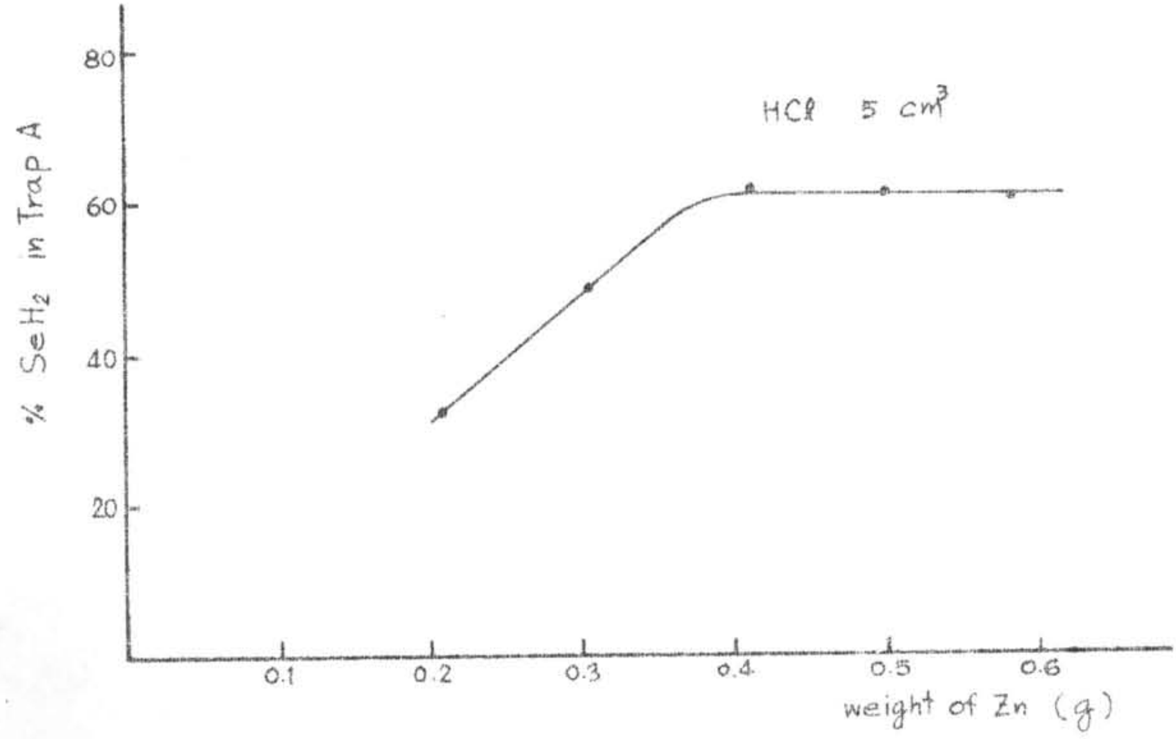

Fig. 3-13 Effect of amount of Zinc on the distillation of SeH_2

presented in Table 3-7, show that the optimum zinc to acid ratio which gave the highest chemical yield was approximately 1 : 12. No significant difference in the yield of SeH_2 was observed by increasing the weight of zinc. The amount of zinc was thus fixed at 0.4 g and the volume of hydrochloric acid at 5 cm^3 in all experiments performed. The yield of Se in trap A versus the amount of zinc was plotted in Fig. 3-12 and Fig. 3-13.

3.3.2.3 Effect of Time on the Distillation of SeH_2. The time required for the complete distillation of SeH_2 under the conditions stated in section 3.3.2.2 was investigated by varying the time of reaction from 30 minutes to 3 hours. The activity of Se-75 in trap A were counted and compared to the standard solution. From the results in Table 3-8 it could be observed that the reaction was complete after one hour. The recovery yields as a function of reaction time was plotted in Fig. 3-14.

3.3.2.4 Effect of Temperature on the Distillation of SeH_2. Experiments were performed to investigate the effect of temperature on the distillation of SeH_2. The mixture of 1 cm^3 of Se-75 tracer solution and 1 cm^3 of the additional reducing agent was first dipped into a water bath for a few minutes. The temperature of the bath was varied between 60°C to 100°C. The reaction proceeded in the usual manner. The results in Table 3-9 show that the chemical yield of SeH_2 increases with the increase of the bath-temperature.

Table 3-8 Effect of reaction time on the distillation of SeH_2. (Conditions: 10 μg Se-75, 1 mg carrier, 1 cm^3 $SnCl_2$ solution, 5 cm^3 HCl, 0.4 g zinc, 60°C)

Expt No	Reaction Time (hr)	SeH_2 in Trap A (%)
1	0.5	44
2	1.0	60
3	1.5	61
4	2.0	61
5	3.0	62

Table 3-9 Effect of temperature on the distillation of SeH_2. (Conditions: 10 μg Se-75, no carrier, 5 cm^3 HCl, 1 cm^3 $SnCl_2$ solution, 0.4 g zinc, 1 hr. reaction time)

Expt No	Temperature (°C)	SeH_2 in Trap A (%)
1	60	44
2	70	58
3	80	71
4	90	75
5	98	80

Table 3-10 Effect of the amount of carrier on distillation of SeH_2. (Condition: 10 μg Se-75, 5 cm^3 HCl, 1 cm^3 $SnCl_2$ solution, 0.4 g zinc, 1 hr. reaction time, 100°C)

Expt No	Amount of Carrier (mg)	SeH_2 in Trap A (%)
1	0	83
2	0.01	100
3	0.1	99
4	1.0	95

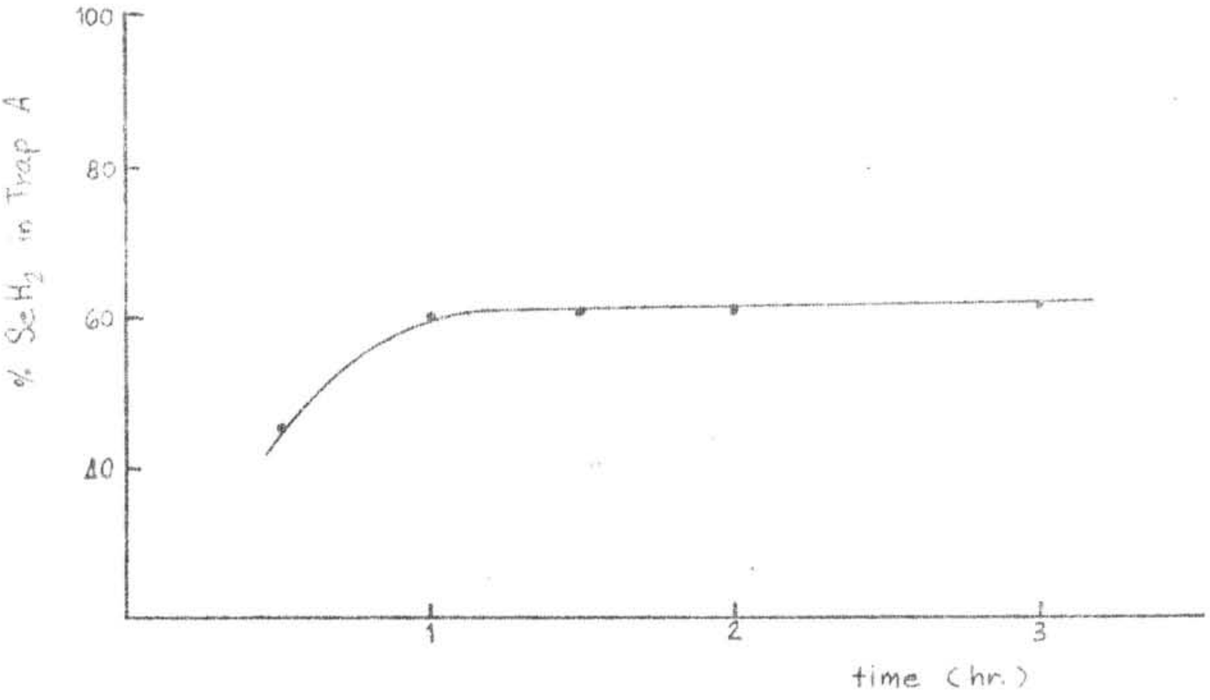

Fig. 3-14 Effect of reaction time on the distillation of SeH$_2$

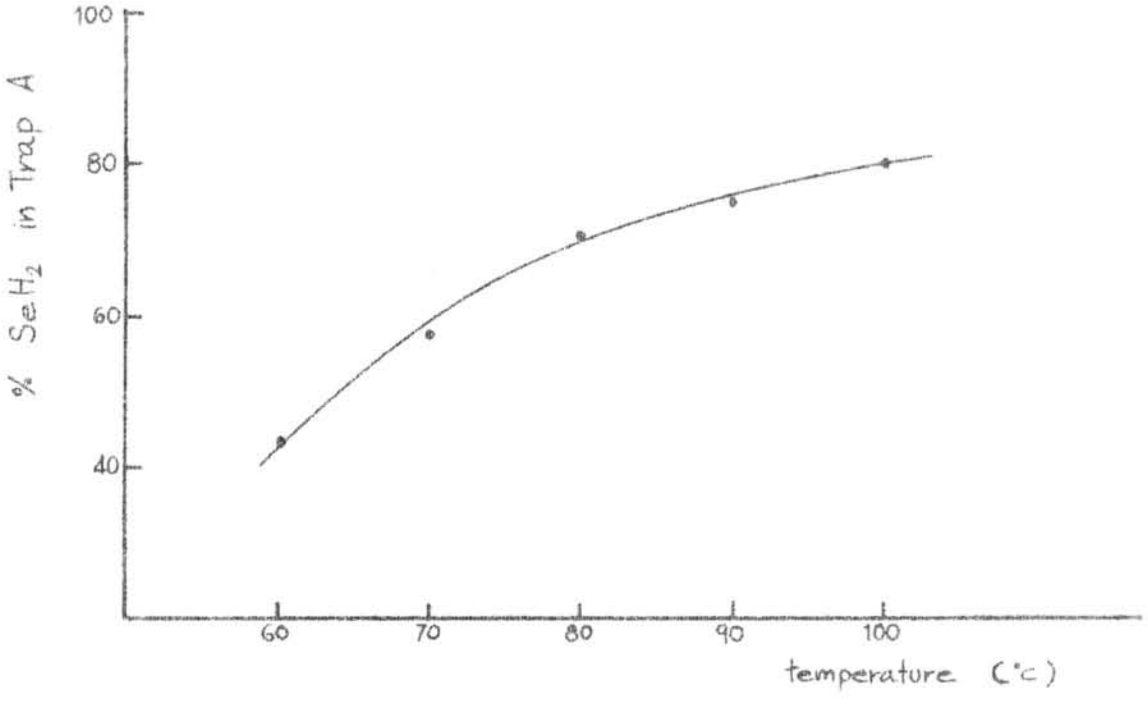

Fig. 3-15 Effect of temperature on the distillation of SeH$_2$

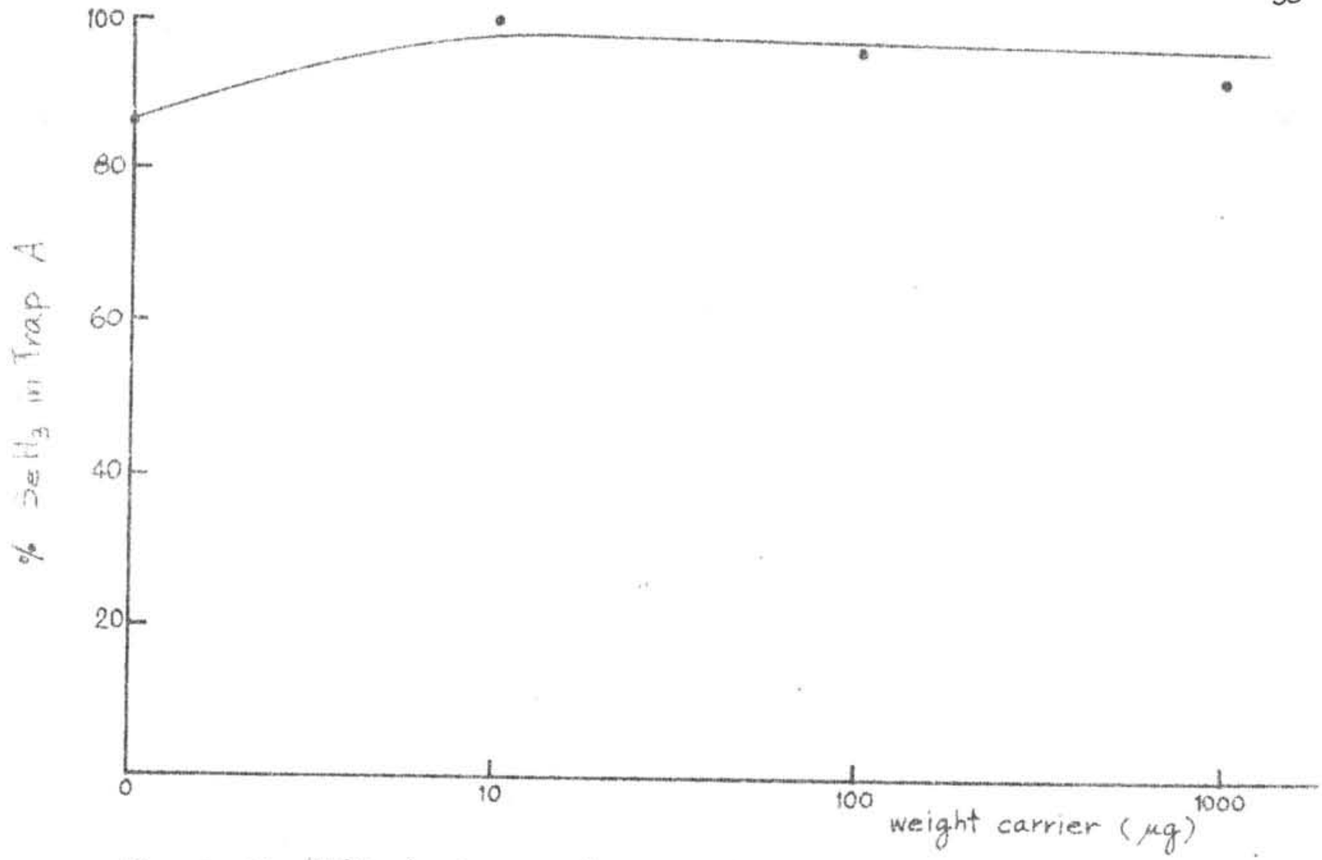

Fig. 3-16 Effect of amount of carrier on the distillation of SeH$_2$

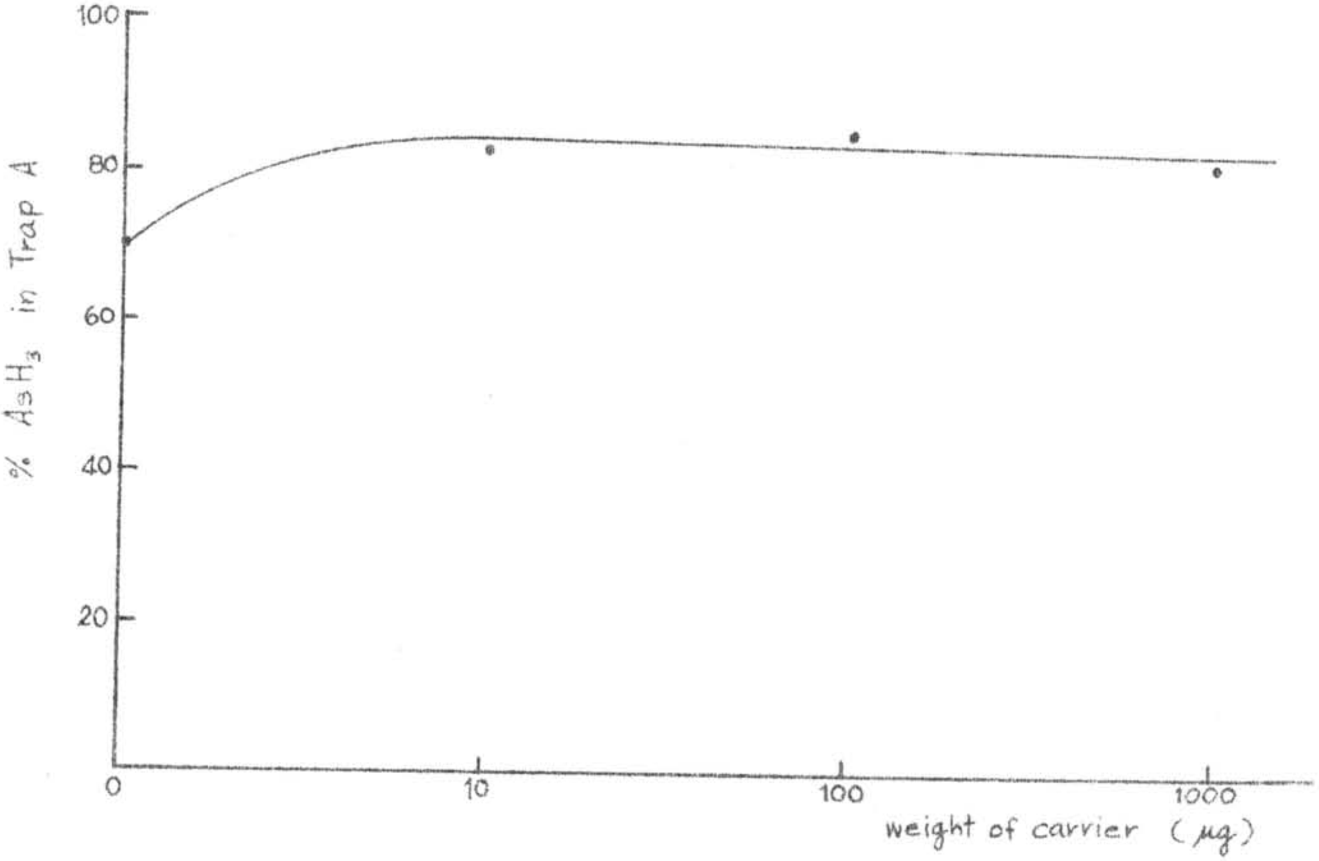

Fig. 3-17 Effect of amount of carrier on the distillation of AsH$_3$

3.3.2.5 Effect of Carrier on the Distillation of SeH_2. It is necessary to add inactive Se into the sample before distillation since the concentration of Se in fresh water is usually very low. To investigate the appropriate amount of inactive Se used as carrier a series of experiments was performed. The amount of Se-carrier was varied from 0 to 1 mg. The chemical yields of SeH_2 were calculated and presented in Table 3-10. It could be observed that better results were obtained with the addition of carrier. No significant difference was observed by varying the amount of carrier from 10 μg to 1 mg.

3.3.3 Distillation of AsH_3. The generation of AsH_3 using zinc and hydrochloric acid was long known as an effective method for the determination of minute amount of arsenic. Since from the study of the distillation of SeH_2 and SbH_3 some conditions for the distillation such as amount of zinc, volume of acid etc., were already investigated, only the studies on the effect of $SnCl_2$ as additional reducing agent and the effect of carrier were performed. As-76 was used as tracer.

3.3.3.1 Effect of Additional Reducing Agent on the Distillation of AsH_3. Two experiments were performed, with and without the addition of $SnCl_2$. In both experiments, 1 cm^3 of a As-76 trace solution containing 1 μg As, and 1 cm^3 of the As carrier solution containing 100 μg As were used. The volume of acid was fixed at 5 cm^3 and the amount of zinc was 0.4 g. The distillation was performed as usual in a water bath whose

Table 3-11 Effect of additional reducing agent on the distillation of AsH_3. (Condition: 1 μg As-76, 0.1 mg carrier, 5 cm^3 HCl, 0.4 g zinc, 1 hr. reaction time, 100°C)

Expt No	Addition Reducing Agent	AsH_3 in Trap B (%)
1	None	10
2	1 cm^3 $SnCl_2$ Solution	81

Table 3-12 Effect of the amount of carrier on the distillation of AsH_3. (Conditions: 1 μg As-76, 1 cm^3 $SnCl_2$ solution, 0.4 g zinc, 5 cm^3 HCl, 1 hr. reaction time, 100°C)

Expt No	Amount of carrier (mg)	AsH_3 in Trap B (%)
1	0	70
2	0.01	83
3	0.1	86
4	1.0	82

temperature was kept constant at 100°C. The AsH_3 and the carrier gas were bubbled through trap A and trap B. The activities of AsH_3 dissolved in trap B, were counted and compared to the activities of a standard solution. The yield of AsH_3 when $SnCl_2$was added was about 4 times higher as the results in Table 3-11 indicate.

3.3.3.2 Effect of Amount of Carrier on the Distillation of AsH_3. The distillations were performed as described in section 3.3.3.1. $SnCl_2$ was added as the additional reducing agent. The amount of carrier was varied from 0 to 1 mg. The results in Table 3-12 indicate that the chemical yield of AsH_3 was higher when carrier was added. Since no significant difference was observed in increasing the amount of carrier from 10μg to 1 mg, 10μg of carrier was used for the distillation of AsH_3 through out the study.

3.3.4 Separation of As from Sb. After distillation, both AsH_3 and SbH_3 were trapped in a solution of 9 mol/l HCl+ $KClO_3$. Since Sb(V) in 9 mol/l HCl could be extracted by HDEHP and As(V) not, a log K_D value of +3.5 for Sb(V) comparing to -1 for As(V)(11), the separation of the two ions could be performed easily. The extraction could be performed rapidly by filtering the solution through a layer, 15 mm. in diameter, of the quasi-solid solvent, HDEHP coated voltalef. Experiments were carried out to investigate the amount of extracting material for a complete extraction of Sb(V).

Table 3-13 Extraction of Sb(V) on HDEHP-Voltalef layer

Expt No	Weight of HDEHP coated Voltalef (g)	Sb found in filtrate (%)
1	2	7
2	3	0
3	4	0
4	6	0
5	8	0

1 cm^3 of the Sb-122 tracer solution containing 5 μg Sb was mixed with 1 cm^3 of the Sb-carrier solution containing 1 mg Sb. The mixture was filtered through a layer of HDEHP coated voltalef with a weight varied between 2g to 8g. The layer was washed with 10 cm^3 9 mol/l HCl. The filtrate together with the washed solution was subjected to measurement. From the results in Table 3-13 it is clear that 3g of coated material was sufficient to extract 1mg antimony completely. Since no significant difference in separation time was observed by using 3 or 4g of coated material, 4g was generally used in the present study. The time for complete separation of amtimony from arsenic was approximately 5 sec.

3.3.5 Adsorption of Hg, Ag and Cu on Dithizone Column.

The completeness of the adsorption of Hg, Ag and Cu on dithizone coated voltalef column from a 0.1 mol/l HNO_3 was first checked. 1 cm^3 of each tracer solution was pipetted into 10 cm^3 0.1 mol/l HNO_3 and the solution was passed through a column previously prepared as described in 3.1.6 at a flow rate of 0.5 cm^3/min. The column was then washed with 30 cm^3 0.1 mol/l HNO_3. The filtrate together with the washed solution was counted for characteristic gamma energy of each element and compared to that of the standard solutions with known concentrations and activities. The NaI-single channel analyzer which was set at the appropriate gain and base level was used for this purpose. It was found that, under the stated conditions the three elements would be completely adsorbed.

3.3.6 Elution of Hg. Since the mercury-dithizone complex could be destroyed by 6 mol/l HCl, this was chosen as eluant for Hg. An elution experiment was performed by allowing 6 mol/l HCl to pass through a column with adsorbed Hg at a flow-rate of 0.5 cm^3/min. The eluant was collected in 2 cm^3 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 and presented in Table 3-14. From the elution curve in Fig. 3-18 it could be observed that 90 % of the total activity could be eluted with 14 cm^3 6 mol/l HCl.

3.3.7 Elution of Ag. Efforts were made to check the suitability of dilute NH_4SCN solution as eluant for Ag from dithizone coated voltalef column. Ag was adsorbed on a column in the same manner as described in section 3.3.5. 2 % and 4 % NH_4SCN in 0.05 mol/l H_2SO_4 were allowed to pass through the column with a flow rate of 0.5 cm^3/min. The activities of all fractions, 2 cm^3 each, were measured and the percent elution calculated. The results are tabulated in Table 3-15 and the elution curves are given in Fig. 3-19 and Fig. 3-20. 4 % NH_3SCN as eluting agent gives sharper elution curve. The elution of 10 μg Ag was complete by the use of 10 cm^3 4 % NH_4SCN solution.

Table 3-14 Elution of Hg with 6 mol/l HCl

Fraction No*	Elution of Hg with 6 mol/l HCl	
	Elution %	Accumulative Elution %
1	0.21	0.21
2	0.13	0.34
3	8.40	8.74
4	46.73	55.47
5	21.79	77.26
6	7.26	84.52
7	2.46	86.98
8	1.54	88.98
9	0.95	89.47
10	0.65	90.12
11	0.40	90.52
12	0.27	90.79
13	0.37	91.16

*1 fraction = 2 cm^2

Table 3-15 Elution of Ag with 2 % and 4 % NH_4SCN

Fraction* No	Elute with 2 % NH_4SCN		Elute with 4% NH_4SCN	
	Elution (%)	Accumulative Elution (%)	Elution (%)	Accumulative Elution (%)
1	0	0	0.91	0.91
2	16.02	16.02	71.99	72.90
3	28.02	44.04	16.28	89.18
4	7.30	51.34	7.97	97.15
5	4.49	55.83	4.70	101.85
6	3.34	59.17	2.13	103.98
7	1.80	60.97	1.14	105.12
8	1.59	62.56	0.97	106.09
9	1.31	63.87	0.76	106.85
10	1.29	65.16	0.55	107.40
11	0.85	66.01	0.41	107.81
12	0.87	66.88	0.28	108.09
13	0.83	67.71	0.28	108.37
14	0.77	68.48		
15	0.68	69.16		
16	0.64	69.80		
17	0.65	70.45		

* 1 Fraction = 2 cm^3

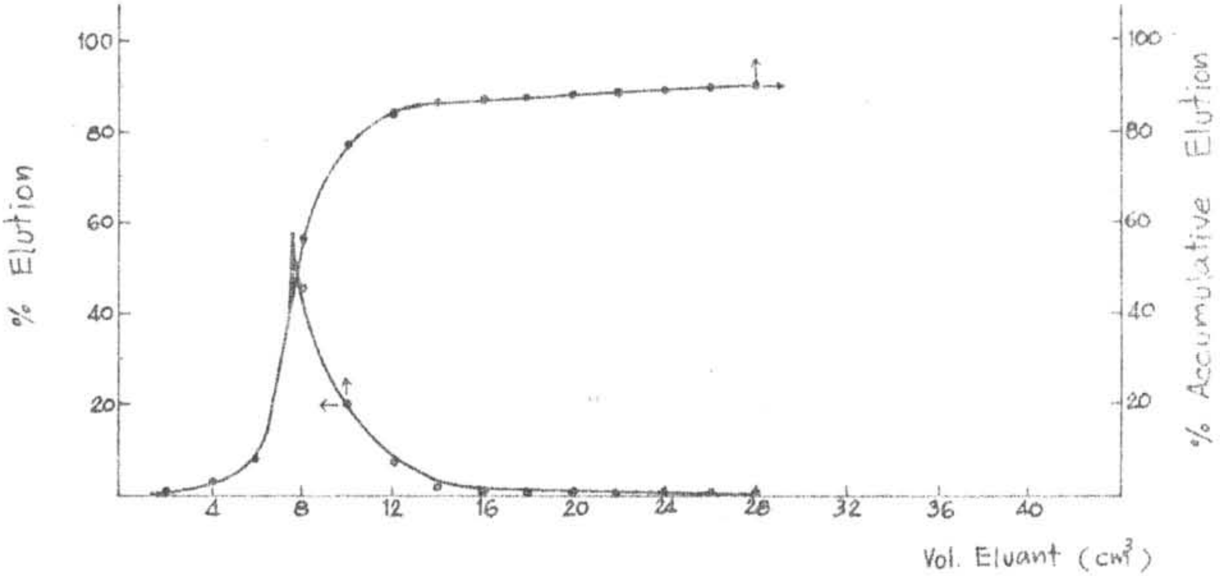

Fig. 3-18 Elution of Hg with 6 mol/l HCl

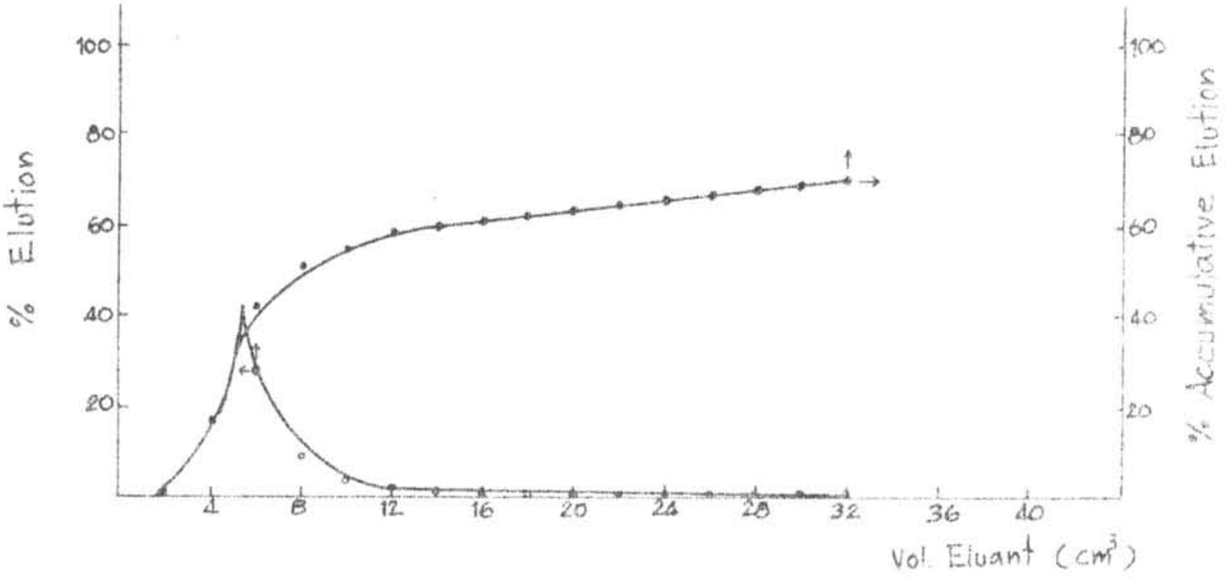

Fig. 3-19 Elution of Ag with 2 % NH_4CNS

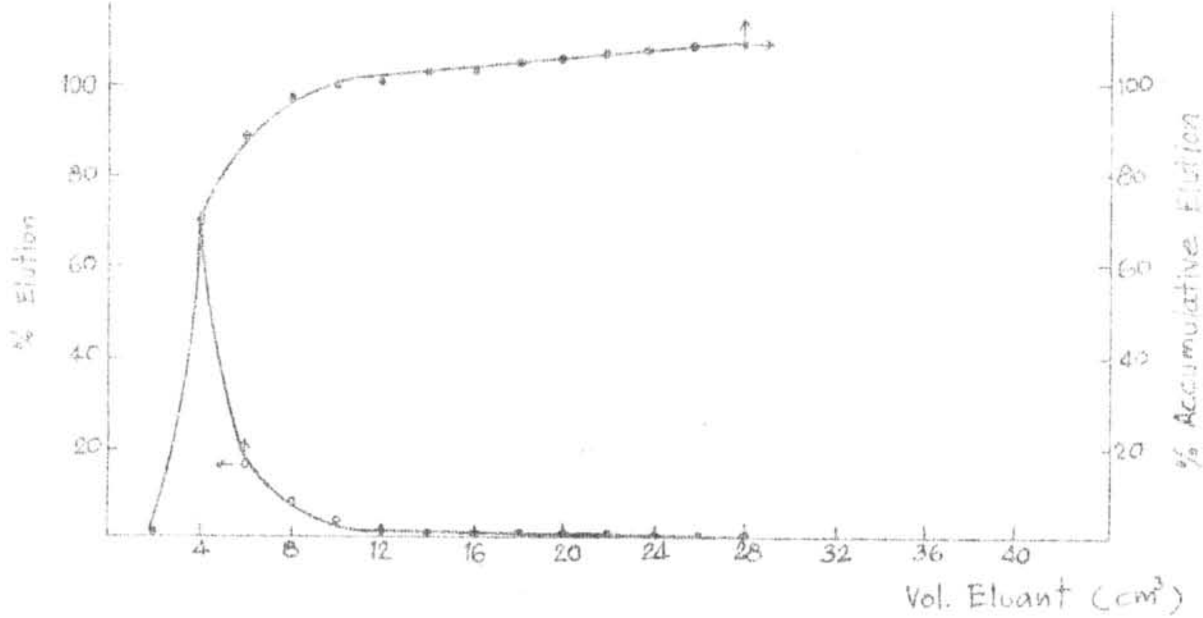

Fig. 3-20 Elution of Ag with 4 % NH_4CNS

3.3.8 Elution of Cu. Experiments were performed to elute Cu from the column with 0.015 mol/l, 0.027 mol/l and 0.134 mol/l EDTA as eluting agents. Since all three solutions gave poor eluting yield, 6 mol/l and 9 mol/l HCl were chosen. The results in Table 3-16 and the elution curves in Fig. 3-21 and Fig. 3-22 show that Cu could be quantitatively removed from the column by HCl of both concentrations. The retention time, the time measured from start of elution to peak maximum, is much shorter in the case of 9 mol/l HCl.

3.3.9 Separation of Cu from Hg. From the results in section 3.3.6 and 3.3.8, one could observe that by using 6 mol/l HCl as eluting agent copper starts to remove from the column after about 80 % of Hg has been eluted. Attempts were made to achieve a better separation of Hg and Cu with 6 mol/l HCl as eluting agent by varying the ratio of treated to untreated voltalef. For this purpose two columns were prepared. One column contained 2g of untreated and 2g of treated voltalef. The other column contained 3g of treated and 1g of untreated voltalef. A solution containing 5μg Cu and 5μg Hg in 10 cm^3 0.1 mol/l HNO_3 was allowed to pass through the columns. Elution was performed in the same manner as already discribed. The activities of all fractions were counted by the NaI-single channel analyzer spectrometer immediately after the elution was ended. The activities thus obtained corresponded to the total activities of Cu and Hg. Two weeks later, after which the activities of Cu all decayed, the fractions were recounted for the

Table 3-16 Elution of Cu with 6 and 9 mol/l HCl

Fraction* No	Elute with 6 mol/l HCl		Elute with 9 mol/l HCl	
	Elution (%)	Accumulative Elution (%)	Elution (%)	Accumulative Elution (%)
1	0	0	0	0
2	0	0	0	0
3	0	0	0	0
4	2.09	2.09	31.97	31.97
5	0	2.09	31.22	63.19
6	5.53	7.62	11.25	74.44
7	19.41	27.04	6.23	80.67
8	31.20	58.23	3.90	84.57
9	17.93	76.16	1.58	86.15
10	8.48	84.64	1.12	87.27
11	2.70	87.34	0.65	87.92
12	1.26	88.60	0.56	88.48
13	0.48	89.08	0.56	89.04
14	0.12	89.20	0.56	89.60
15	0.22	89.20	0.56	89.60
16	0.22	89.42	0.09	89.69

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* 1 Fraction = 2 cm^3

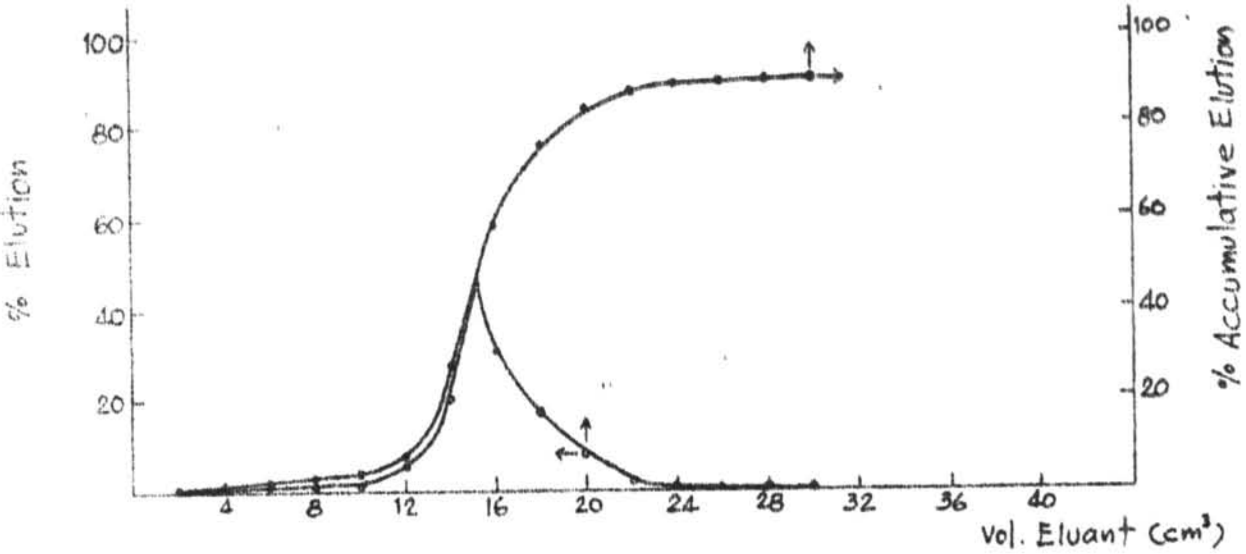

Fig. 3-21 Elution of Cu with 6 mol/l HCl

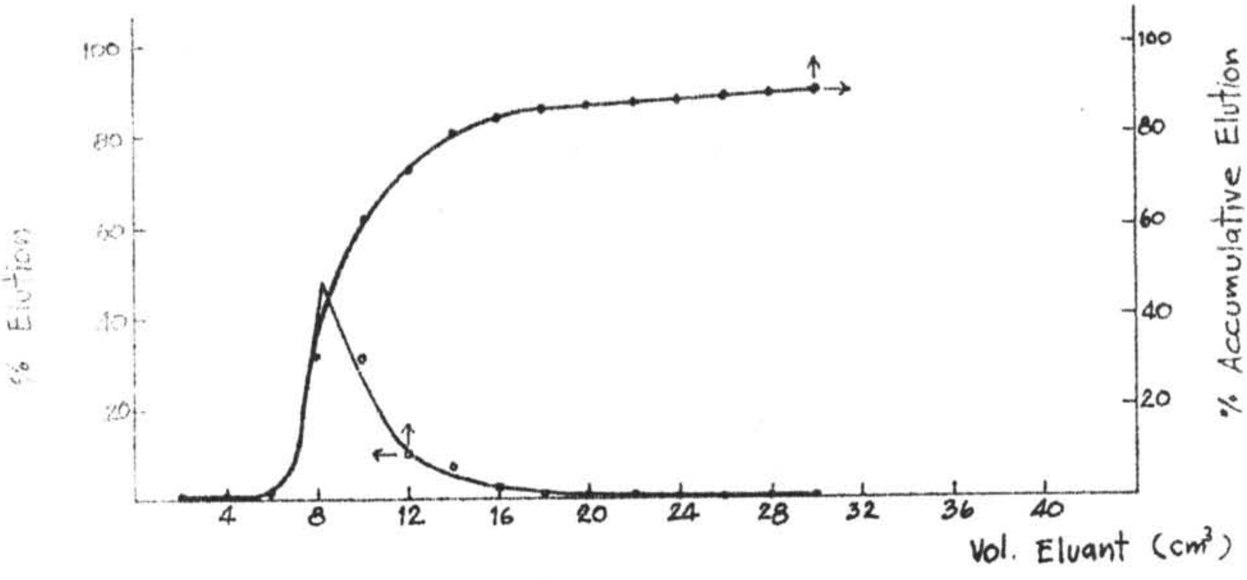

Fig. 3-22 Elution of Cu with 9 mol/l HCl

Table 3-17 Separation of Cu and Hg from dithizone-Voltalef columns with different ratios of treated to untreated material (Eluant: 6 mol/l HCl)

Fraction* No	Ratio of Treated-untreated Voltalef = 2 : 2				Ratio of Treated-untreated Voltalef = 3 : 1			
	Hg		Cu		Hg		Cu	
	Elution %	Accumulative Elution %	Elution %	Accumulative Elution %	Elution %	Accumulative Elution %	Elution %	Accumulative Elution %
1	0	0	0.18	0.18	0	0	0	0
2	7.9	7.9	0.23	0.41	3.79	3.79	0	0
3	5.84	13.74	0.71	1.12	17.42	21.21	0	0
4	57.43	71.17	0.40	1.52	5.30	26.51	0	0
5	16.83	88.00	2.03	3.55	21.97	48.48	0	0
6	26.70	144.70	26.90	30.45	34.09	82.57	0	0
7	6.93	121.63	51.44	61.89	9.09	91.66	7.55	7.55
8	0	121.63	19.17	81.06	8.33	99.99	22.77	80.32
9	0	121.63	7.35	88.41	6.06	106.05	31.65	61.97
10			2.94	91.35	3.03	109.08	16.58	78.55
11			1.17	92.52	0	109.08	6.83	85.38
12			0.23	92.75	0	109.08	2.70	88.08
13			0.58	93.33			1.50	89.59
14			0.42	93.75			0.81	90.40
15			0.32	94.07			0.55	90.95
16			0.27	94.34			0.31	91.26

*1 Fraction = 2 cm*

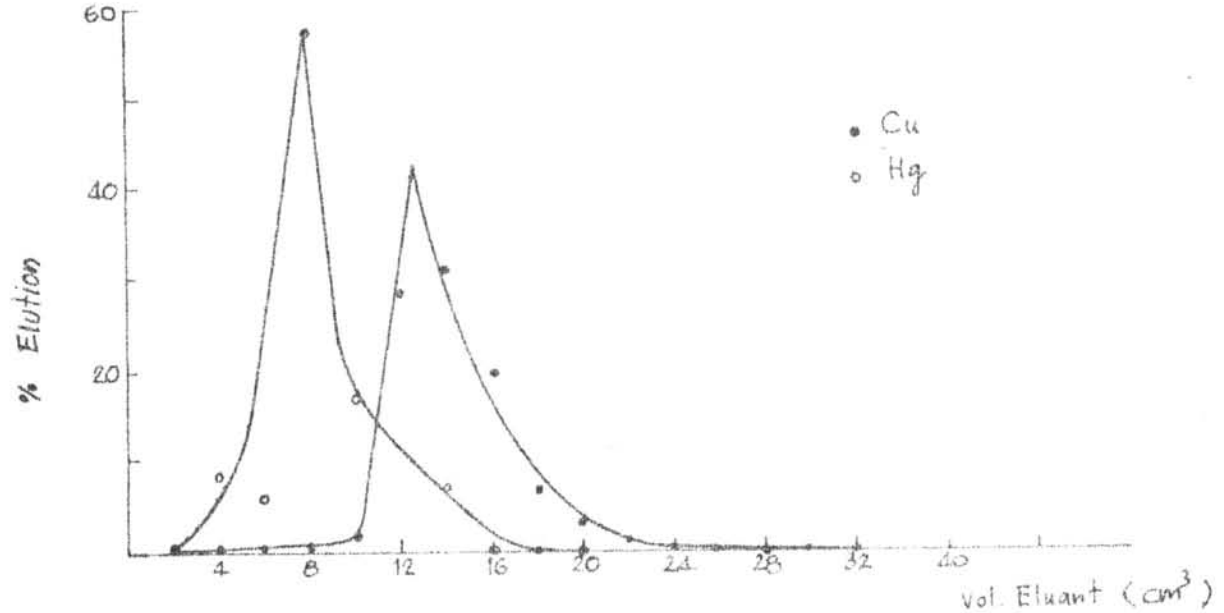

Fig. 3-23 Elution of Hg + Cu 6 mol/l HCl, column 2:2

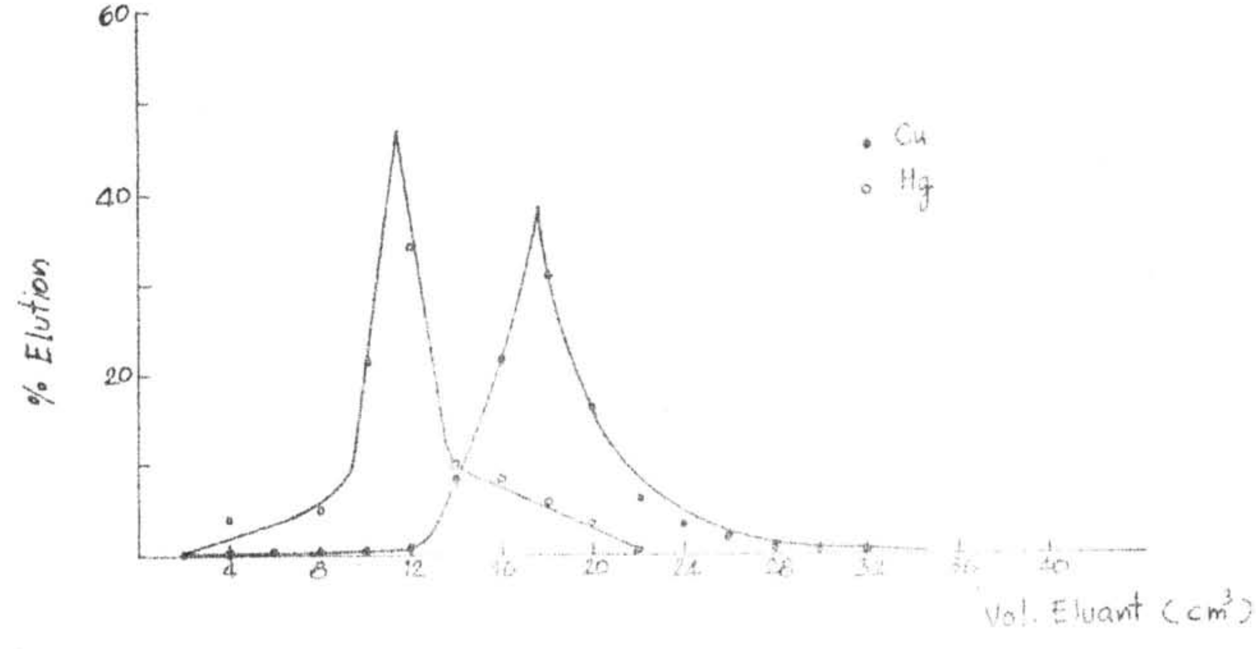

Fig. 3-24 Elution of Hg + Cu 6 mol/l HCl, column 3:1

activities of Hg. The results which are tabulated in Table 3-17 show no difference between the two variations. The elution curves are given in Fig. 3-23 and Fig. 3-24.

Since the separation of Cu and Hg from the dithizone coated voltalef column using 6 mol/l HCl gives no sharp separation and the separation time is generally very long, separation via anion-exchange was therefore tried. In dilute solution of HCl copper remains in the form of cation (Cu^{+2}) and would not be adsorbed on anion exchanger. Mercury forms anion complex ($HgCl_4^=$) in dilute HCl and is adsorbed on anion exchanger with a log K_D value of 4.2 (12). To separate Cu from Hg, the two elements were first eluted from the dithizone-voltalef column with 20 cm^3 9 mol/l HCl. The effluent was diluted with water to give a 2 mol/l HCl solution. A few drops of 28 % H_2O_2 were added to assure that both elements were in the higher oxidation state. When oxygen ceased to evolve, the solution was passed through a column of Dowex 1 X 8. The column was washed with 15 cm^3 2 mol/l HCl and 15 cm^3 deionized water respectively. The activities of the filtrate was counted and was found to contain only Cu. Hg was totally adsorbed on the column.

3.3.10 Separation Scheme. From the results in section 3.3.2 to section 3.3.9 a separation scheme for the separation of Hg, Cu, As, Se and Sb from fresh water samples could be drawn. This is presented in Fig. 3-25. The resason for dropping out Ag from the analytical scheme is given in section 3.4.2

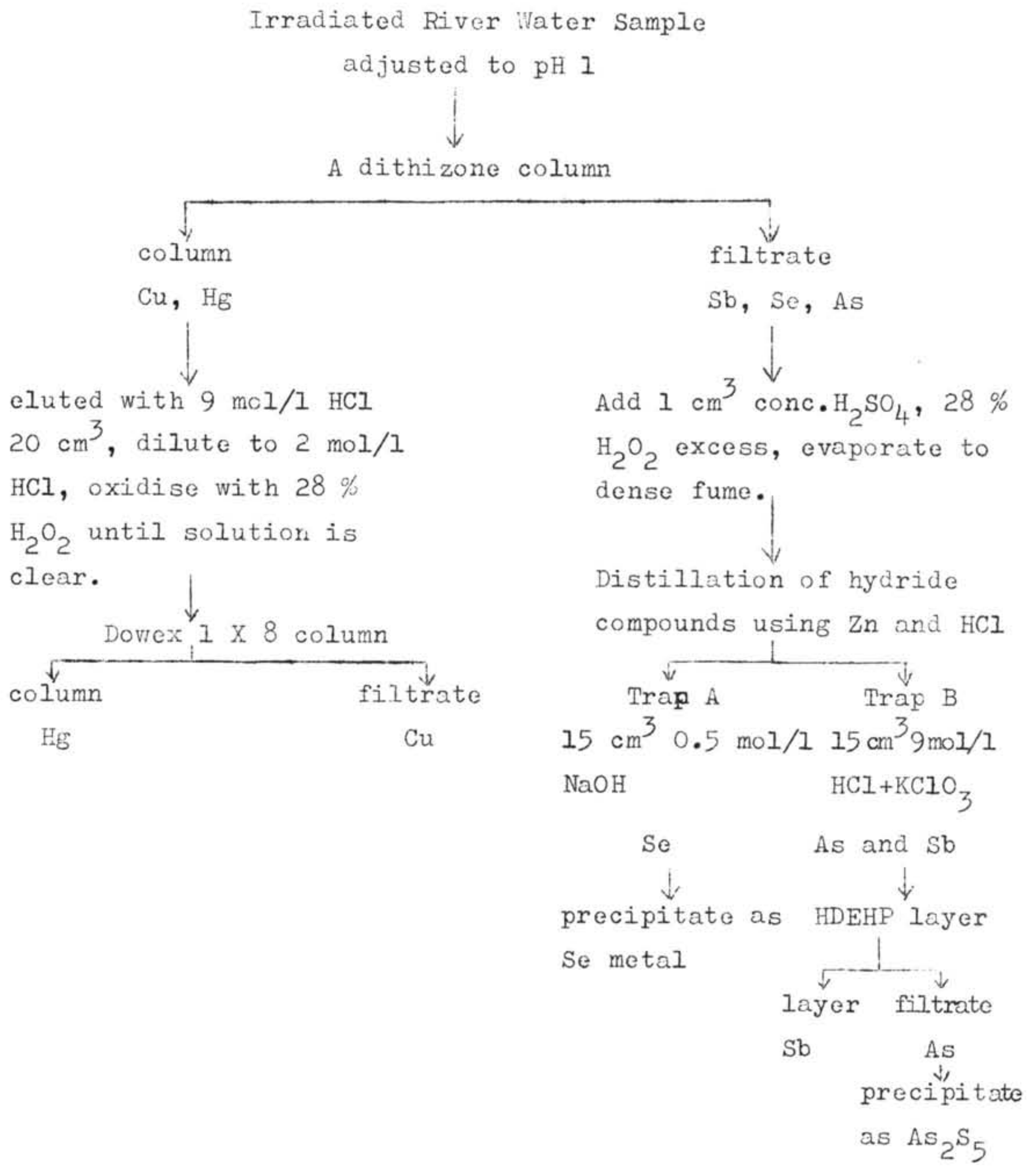

Fig. 3-25 Separation scheme for the quantitative analysis of Hg, Cu, Sb, Se and As in surface water.

3.4 Sample processing.

3.4.1 Preparation of Samples for Irradiation. Since the elements of interest are present in the samples in minute amount, preconcentration is required. This was performed by evaporating 100 cm^3 of the samples under an infrared lamp to dryness. The temperature during evaporation did not exceed $70^{\circ}C$ so that no loss of the easily volatile elements would occur. The residue was dissolved in 1 cm^3 concentrated HNO_3 and transferred into a polyethylene vial. The evaporating dish was rinsed with small amount of tridistilled water and was added into the vial. The total volume did not exceed 5 cm^3.

The sample vials were heat-sealed and subjected to irradiation in the reactor core. The irradiation time was usually 12 hours.

3.4.2 Radiochemical Separation. The irradiated sample was transferred from the container into a beaker. The vial was washed with 1 cm^3 concentrated HCl and 4 cm^3 deionized water respectively. The solution was adjusted to pH 1 by addition of dilute solution of NaOH, after which the separation scheme in Fig. 3-25 was followed. The solution was passed through a column of dithizone-voltalef at a flow rate of 0.5 cm^3/min. Cu, Hg, Ag and some fraction of Sb were retained on the column where as Se and As were completely removed and found in the filtrate. 100 cm^3 1 mol/l HCl was required to remove all of the antimony which was adsorbed on the column. The increase in molarity of the washed solution, 1 mol/1 HCl instead of 0.1 mol/1 HNO_3 as stated in section 3.3.5, did not interfere the adsorption of Cu and Hg since their complexes could only be destroyed if the molarity of the HCl is higher than 3. The only drawback is that Ag would be washed down from the column into the filtrate. Extra separation procedure was essential to separate Ag from other elements in the filtrate. This had not been tried in the present investigation. The quantitative analysis of Ag was thus dropped out. Cu and Hg were eluted from the column by 20 cm^3 9 mol/1 HCl. It was then diluted to 2 mol/1 HCl after which a few drops of 28 % H_2O_2 were added. The solution was passed through a column of Dowex 1 X 8 and the column was washed with 15 cm^3 2 mol/1 HCl and 15 cm^3 deionized water respectively. The resin in the column was transferred to a polyethylene bottle and counted for Hg.

The filtrate containing only Cu was evaporated to almost dryness and was transferred to a polyethylene bottle and counted for Cu.

The filtrate from the dithizone column was transferred into the reaction flask of the distillation apparatus (Fig.3-5). 1 cm^3 concentrated H_2SO_4 was added into the solution and the mixture was heated to remove any nitrate that may be present. During the time of evaporation, 28 % H_2O_2 was added occasionally to keep the ions of Se, As and Sb remain in the higher oxidation state. The solution was evaporated to dense fume. After cooling, 1 cm^3 of the Sb carrier solution containing 1 mg of the element was added to the reaction flask. It was then dipped into a water bath which temperature was kept constant at 100°C. After 0.4 g zinc powder was added into the reaction flask by turning down the spoon B, 5 cm^3 hydrochloric acid were added dropwise from the reagent funnel C while nitrogen gas was bubbled through the system. The reaction started and the SbH_3 was carried through trap A and absorbed in trap B with the help of a vacuum pump. After 1 hour the pump and nitrogen gas were turned off. Carrier solutions of As and Sb, 1 cm^3 each, were added into the reaction flask. 1 cm^3 of $SnCl_2$ solution was added from funnel C and nitrogen gas and the pump were turned on. Another 0.4 g of zinc was added to the system after which 5 cm^3 hydrochloric acid were added dropwise. The generated gas (AsH_3 and SeH_2) was carried through the system and absorbed either in trap A (SeH_2) or trap B (AsH_3). After about 1 hour the reaction stopped. The solution in trap A was transferred into a beaker. Se carrier (4 mg) were added and the solution was made to dilute acid solution by addition of HCl. Se was then precipitated as Se metal by the addition of 4 cm^3 25 % $NH_2OH.HCl$. The solution was warmed on a water bath until the precipitation was complete. The precipitate was filtered and washed with deionized water and ethanol. After drying at room temperature it was counted for Se. The solution in trap B which contained As and Sb was sucked through a HDEHP layer to separate As from Sb. The layer, after washing with 20 cm^3 9 mol/l HCl, was transferred into a polyethylene bottle and counted for Sb, 2 mg of As were added into the filtrate and the washed solution as carrier and As was precipitate as As_2S_5 by adding excess amount of saturated solution thioacetamide. The precipitate was filtered and washed with 25 cm^3 4 mol/l HCl, deionized water and ethanol respectively. After drying, it was counted for As.

3.4.3 Counting Techniques. The activities of the fractions which contained Cu, Hg, As, Sb and Se were measured by the Ge(Li) detector. The counting intervals were usually 4000 s. A mixed standard solution containing all the element of interest, 1 μg each, was irradiated together with the samples and processed in the same manner. The activities of Cu, Hg, As, Sb and Se separated from the mixed standard solution were measured and used as reference for calculation.

3.5 Data Processing. The content of each element in a sample was calculated by the equation:

$$\frac{W_1}{W_2} = \frac{A_1 \pm \sigma_1}{A_2 \pm \sigma_2}$$

where

W_1 = Weight of the element in sample
W_2 = Weight of the element in standard
A_1 = Photopeak area of the element in sample
A_2 = Photopeak area of the element in standard
σ_1 = Standard deviation for A_1
σ_2 = Standard deviation for A_2

The photopeak area was determined by Covell's method (4). Fig. 3-26 shows a typical gamma ray pulse height distribution curve. Co is the channel which gives the heighest count rate in the peak and n channels are counted off on both sides of Co. The area above the base line may then be expressed by the formula:

$$\text{Area} = \sum_{m=-n}^{+n} A_m - (n+\tfrac{1}{2})(A_{-n} + A_{+n})$$

where

A_m = number of counts in the m^{th} channel
A_{-n} = number of counts in the channel C_{-n}
A_{+n} = number of counts in the channel C_{+n}

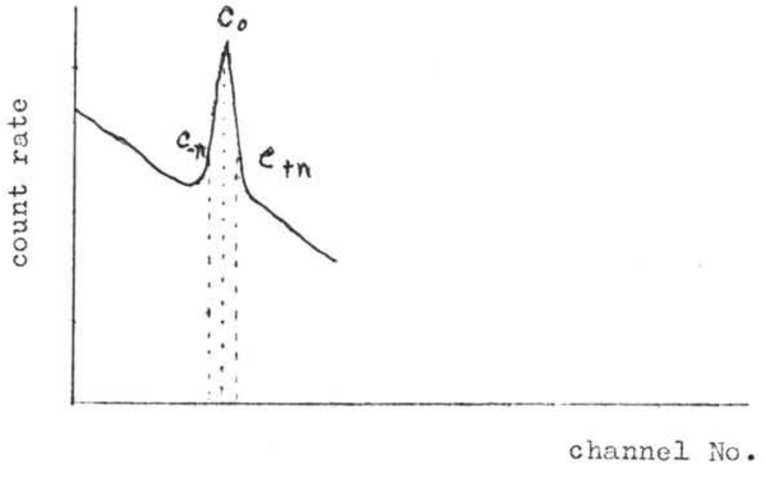

Fig. 3-26 Gamma ray pulse height distribution curve.

The net standard deviation which results from the division of A_1 by A_2 can be calculated from the equation:

$$\frac{A_1 \pm \sigma_1}{A_2 \pm \sigma_2} = \frac{A_1}{A_2} \pm \frac{1}{A_2^2} \left(A_1^2 \sigma_2^2 + A_2^2 \sigma_1^2 \right)^{\frac{1}{2}}$$

Therefore the weight of each element in a sample can be determined by the equation:

$$W_1 = \left[\frac{A_1}{A_2} \pm \frac{1}{A_2^2} \left(A_1^2 \sigma_2^2 + A_2^2 \sigma_1^2 \right)^{\frac{1}{2}} \right] W_2$$

A program was written for the calculation of the concentrations (W_1) from the data obtained. A small computor, PDP 8/e, was avialable for this purpose.

3.6 Limit of Quantitative Determination.

The limit of quantitative determination for all elements under investigation was studied. Single standard solution, containing 10 $\mu g/cm^3$ of each element were irradiated in the reactor for 12 hours. From the single standard solution, solutions containing 1, 0.5, 0.25, 0.05 and 0.025 $\mu g/cm^3$ of each element were prepared. Mixed standard solutions were prepared by mixing single standard solution of the same concentration. The separation scheme (Fig. 3-25) was followed to separate the elements in the mixed standard solution. The radioactivities of all fractions were measured by by the solid state detector. The relation between the concentration and the activity was poltted in Fig. 3-27 to 3-31 .

From these data the detection limits, the concentrations which gave no linear response to the activities, were found and presented in Table 3-18

Table 3-18 Minimum determinable concentrations of Hg, Cu, Sb, Se and As as measured by Ge(Li) detector.

Element	min. determinable conc. in (ppb.)
Hg	0.5
Cu	0.25
Sb	0.25
Se	0.25
As	0.25

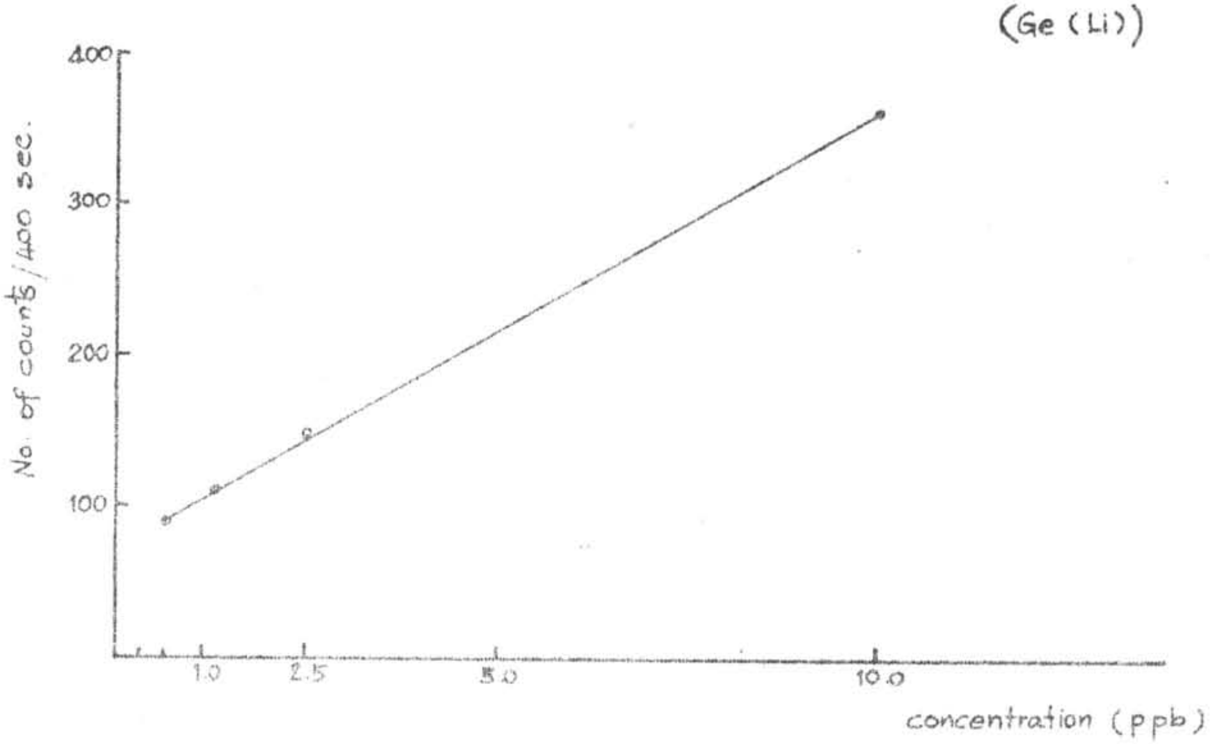

Fig 3-27 The relation between tha concentration and the activity of Hg.

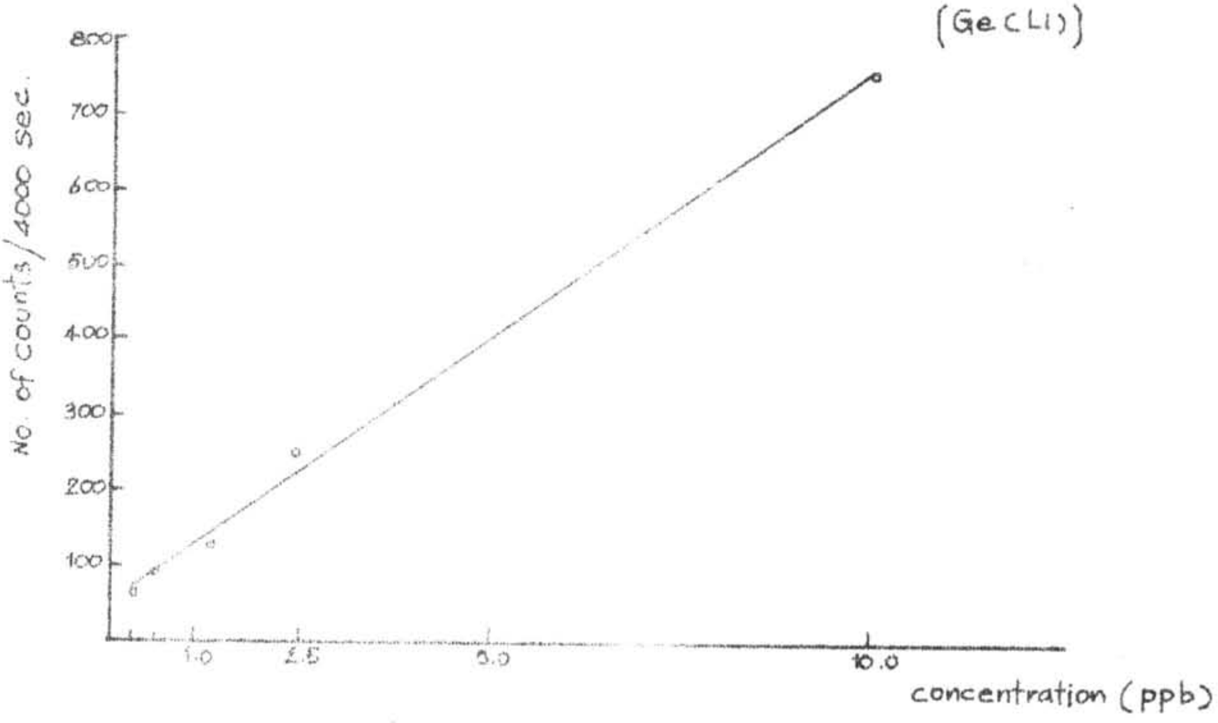

Fig. 3-28 The relation between the concentration and the activity of Cu

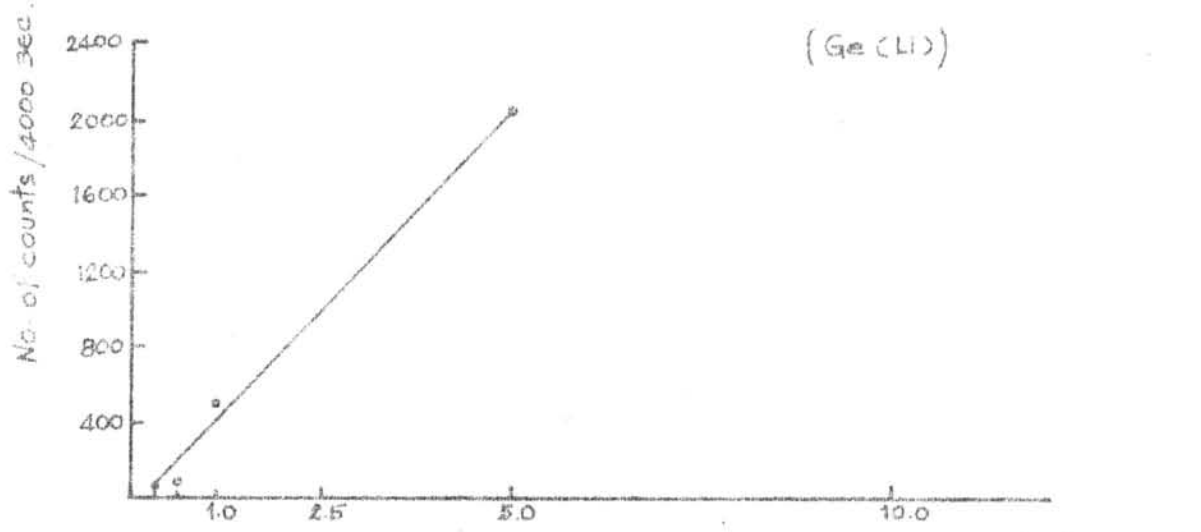

Fig. 3-29 The relation between the concentration and the activity of Sb.

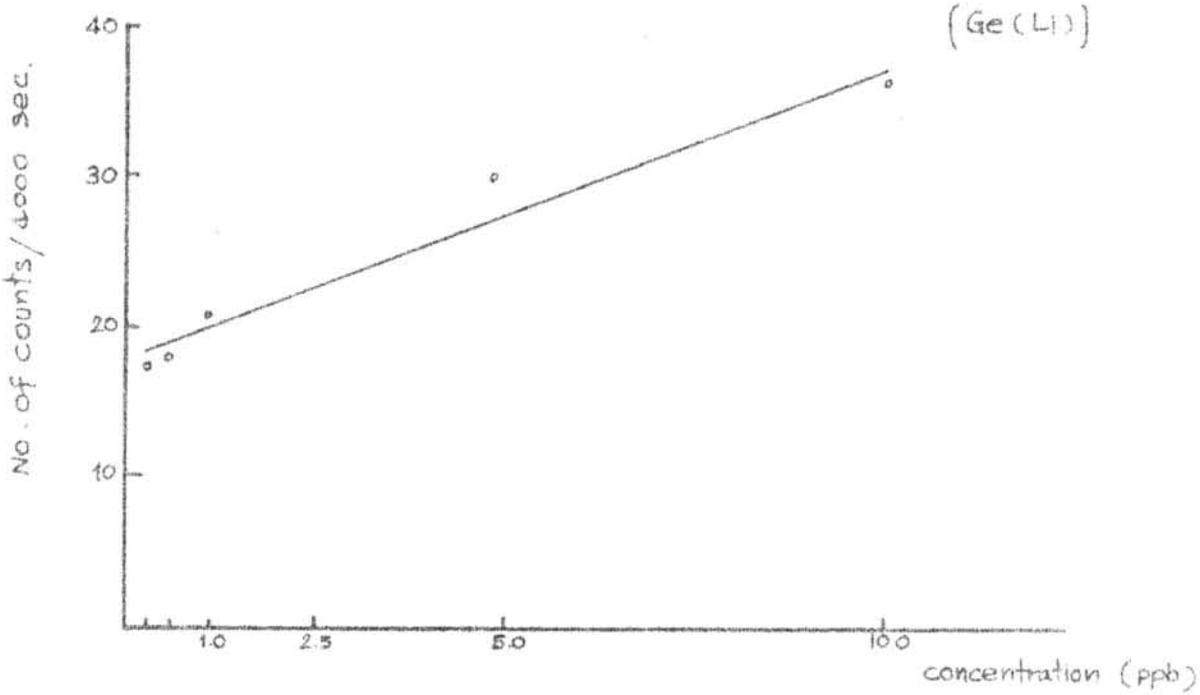

Fig. 3-30 The relation between the concentration and the activity of Se.

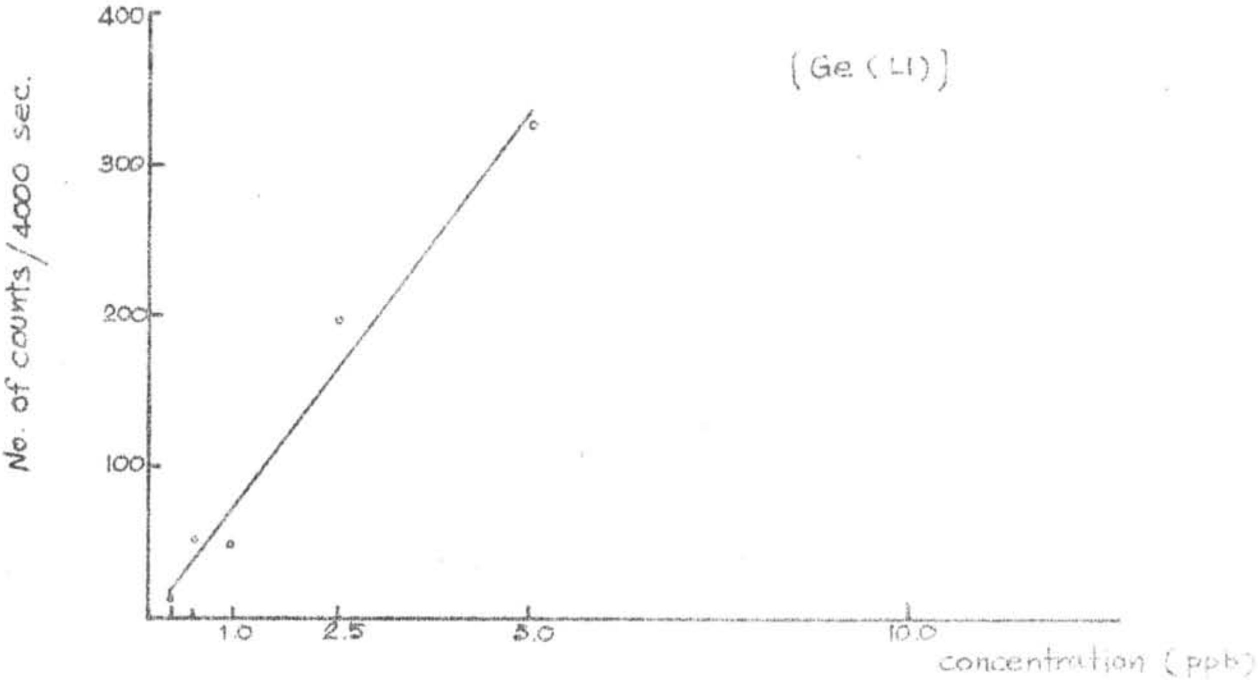

Fig. 3-31 The relation between concentration and the activity of As.