

CHAPTER III

EXPERIMENTS

3.1 Materials

3.1.1 Tracer Specification

In the recovery tests both on the preconcentration and chemical separation techniques, the radiotracers used were obtained either from the Radiochemical Centre, Amersham, England or locally produced by neutron irradiation of the very pure spec grade reagents in the high flux reactor of the Netherlands Energy Research Foundation. Their specifications were listed in table 3.1.

Table 3.1 Radiotracer Specification

Tracer	$T_{1/2}$	Chemical form	Specific activity
^{51}Cr	27.8 d	CrO_4^{2-}	20 mCi/mg.
^{60}Co	5.24 y	Co^{2+}	carrier free
^{65}Zn	245 d	Zn^{2+}	100 mCi/mg.
^{74}As	17.7 d	AsO_3^{2-}	carrier free
^{75}Se	120 d	SeO_3^{2-}	10 mCi/mg.
^{99}Mo	66 h	MoO_4^{2-}	3 $\mu\text{Ci}/\text{mg}$.

Table 3.1 (Cont.)

Tracer	$T_{1/2}$	Chemical form	Specific activity
^{115m}Cd	53 h	Cd^{2+}	0.2 mCi/mg.
^{125}Sb	2.77 y	SbCl_3	carrier free
^{187}W	23.8 h	WO_4^{2-}	0.05 mCi/mg.
^{197}Hg	66 h	Hg^{2+}	0.01 mCi/mg.

Each tracer was dissolved in an appropriate solvent and was diluted to a final activity of 1×10^4 cpm./100 μl . on counting with a 50 cm^3 NaI(Tl) crystal.

3.1.2 Inhome Standard Charcoal

The inhome standard charcoal was prepared by pipetting known amounts of mixed standards solution onto a very pure charcoal named "IXAN" which was artificially prepared [18]. After drying at 60°C for 2 hours, the charcoal was then remixed to obtain the homogeneity.

3.1.3 Standards Reference Materials

Since there is no standard Reference of water available at present, the test on the developed analytical procedures for reliability could only be done in some cases by using other types of standards eg. the biological standard "Orchard Leaves" from

the Bureau of Standards Reference Materials and a standard "Lake Sediment" from the International Atomic Energy Agency.

3.1.4 Iron Ring Neutron Flux Compactor

The pure iron rings of the average weight 25 ± 0.5 mg. were used as the neutron flux comparator in the irradiation of samples and standards in the reactor through out this study.

3.1.5 Membrane Filter

Two types of the Millipore membrane filter were used i.e., the $8 \mu\text{m}$. pore size diameter with 30 mm. diameter for preconcentration of trace elements from water sample and the $0.45 \mu\text{m}$ pore size diameter with 47 mm. diameter for the separation of the dissolved salts from suspended mater.

3.1.6 Sample Containers

Polyethylene bottles with scraw caps of capacity 1 litre were used to store filtrated and acidified water samples. The bottles were pre-cleaned with diluted nitric acid and finally double-distilled water.

3.1.7 Irradiation Containers Three types of container were used as follows :-

3.1.7.1 The polyethylene vials with snap caps of capacity $\frac{1}{2}$, $\frac{2}{3}$ and 1 ml. respectively. They would be packed in the outer vials with serew caps having the iron ring comparator mounted on top.

3.1.7.2 The polyethylene bottle (67 mm.i.d. x 115 mm. length) to contain the sample vials in 3.1.7.1 for long irradiation.

3.1.7.3 The polyethylene shutter (34 mm.i.d. x 120 mm. length) to contain the sample vials in 3.1.7.1 for short irradiation in Pneumatic rabbit system.

3.1.8 Counting Containers

3.1.8.1 Plastic bottle of capacity 5 ml. for tracer experiments.

3.1.8.2 Test tube of 16 mm.i.d. x 130 mm. length for irradiated samples.

3.1.9 Chemicals All chemicals used were of analytical grade.

3.1.9.1 Acid and base

- a. HCl (conc)
- b. HNO₃ (conc)
- c. NH₄OH (conc)

3.1.9.2 Demineralized water

3.1.9.3 Acid Al₂O₃

3.1.9.4 FeCl₃

3.1.9.5 As₂O₃

3.1.9.6 Acetone

3.1.9.7 Ammonium pyrrolidine dithiocarbamate (APDC)

3.1.9.8 Activated Charcoal

a) powder form of "Merck 2186" and a very pure home made "IXAN".

b) grain size 20-35 mesh of "Merck 9624".

3.1.9.9 L-ascorbic acid

3.1.9.10 AgNO_3

3.2 Apparatus

3.2.1 Suction flask with radiochemical chimney (Satorius SM 16306) as shown in fig. 3.1.

3.2.2 The polyethylene column (VEMOR, Monvelle, Varese, Italy) as shown in fig. 3.2.

3.2.3 Micropipette with disposable tips (Gilson P 5000)

3.2.4 Polyethylene pincers

3.2.5 Polyethylene bucket with nylon string for sampling surface water.

3.2.6 Grabber with iron string mounted at the boat side for sampling of sediment.

3.2.7 A 50 rpm. rolling table

3.2.8 A pH meter (Seibold Wien type GDO)

3.2.9 Nitrogen gas pressurized teflon column filtering system as shown in fig. 3.3.

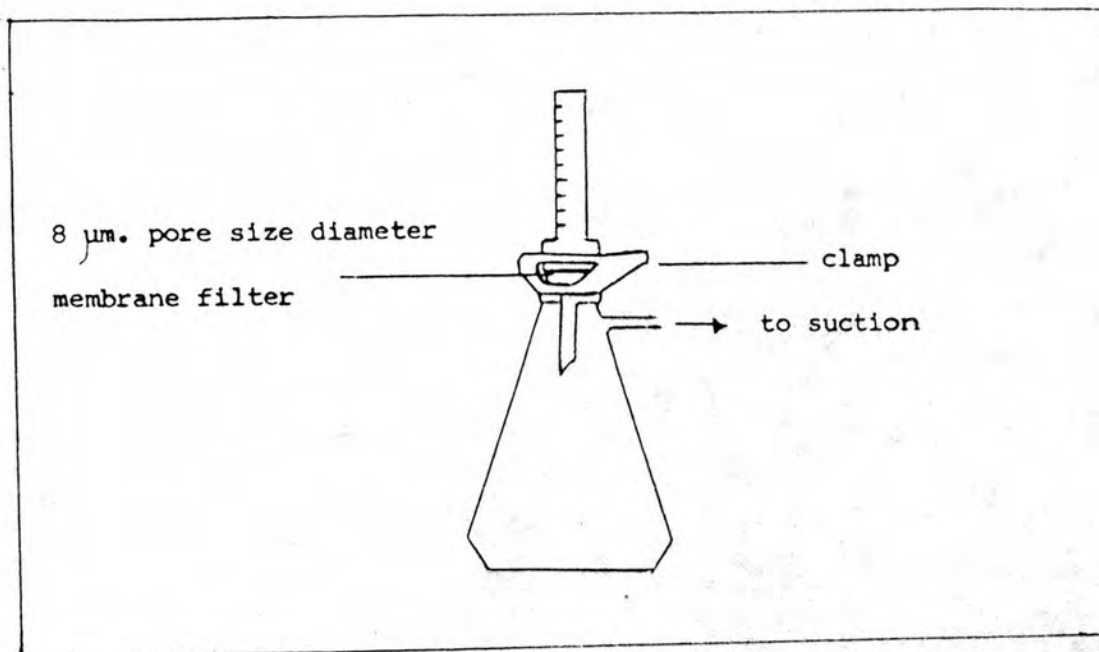


Fig. 3.1 Suction flask with radiochemical chimney

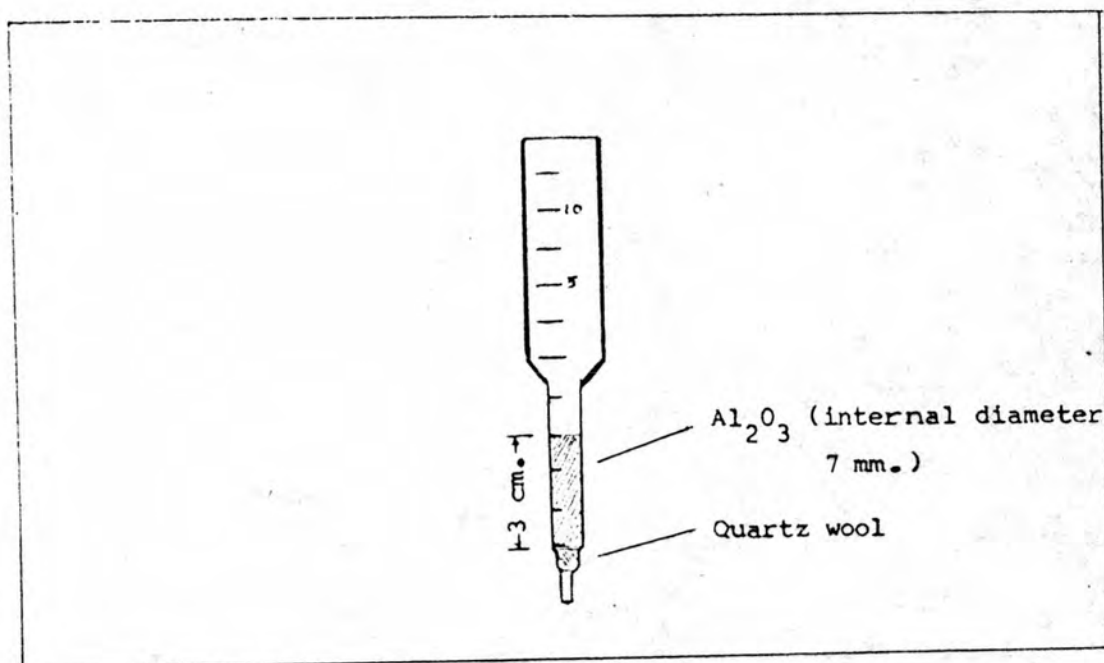


Fig. 3.2 Polyethylene column

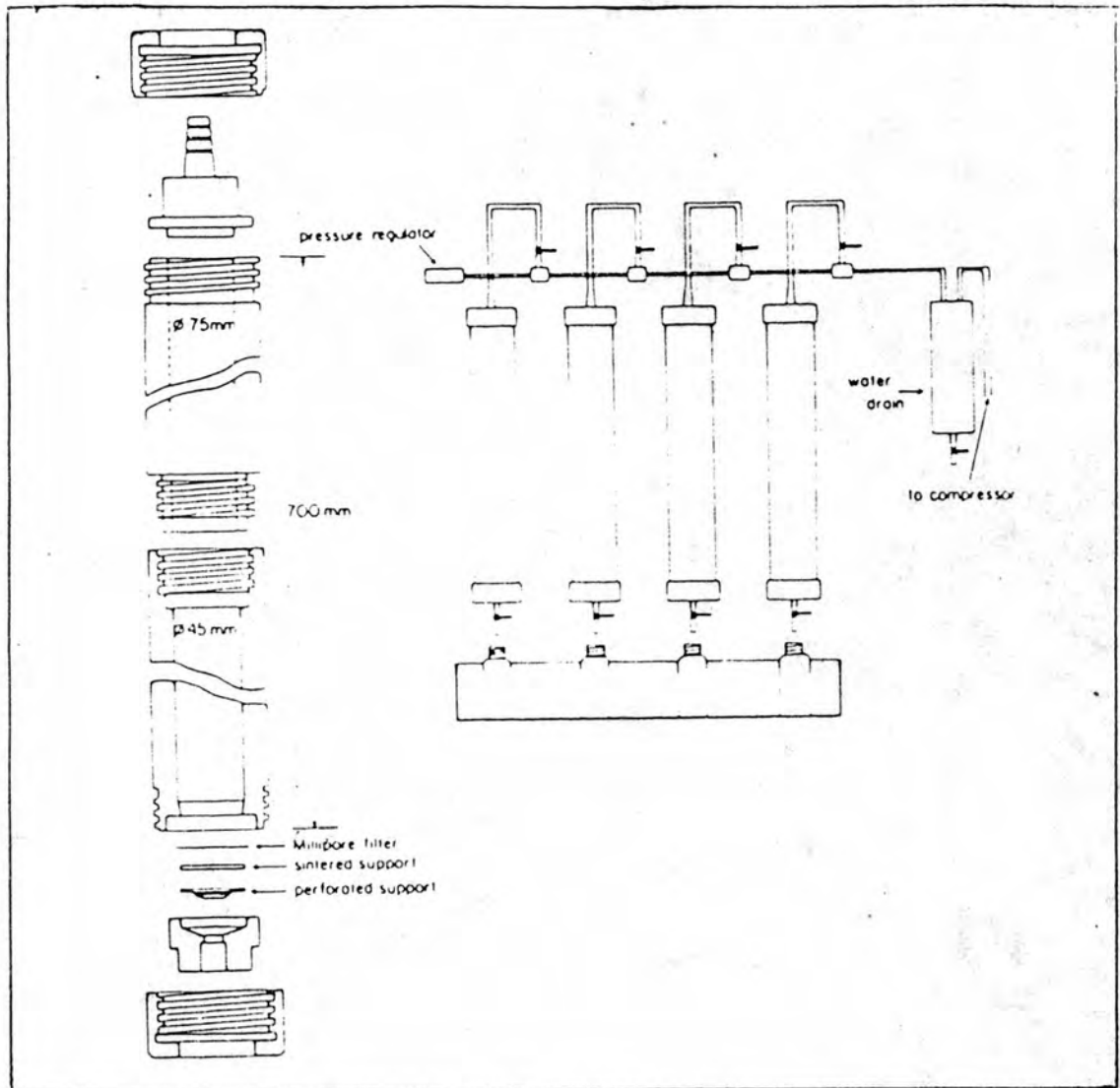


Fig. 3.3 Filtration system

3.2.10 A tube furnace combustion system for the separation of ^{197}Hg from interferential ^{82}Br as shown in fig. 3.4

3.2.11 A continuous flow centrifuge type "Junior 15000" was a Hereaus Christ product with teflon coated rotor and mounted in gimbals to be usable on a moving vessel for collection of size-fractionated suspended matter. The complete set composed of a speed controller and a teflon spoon. The apparatus was shown in fig. 3.5.

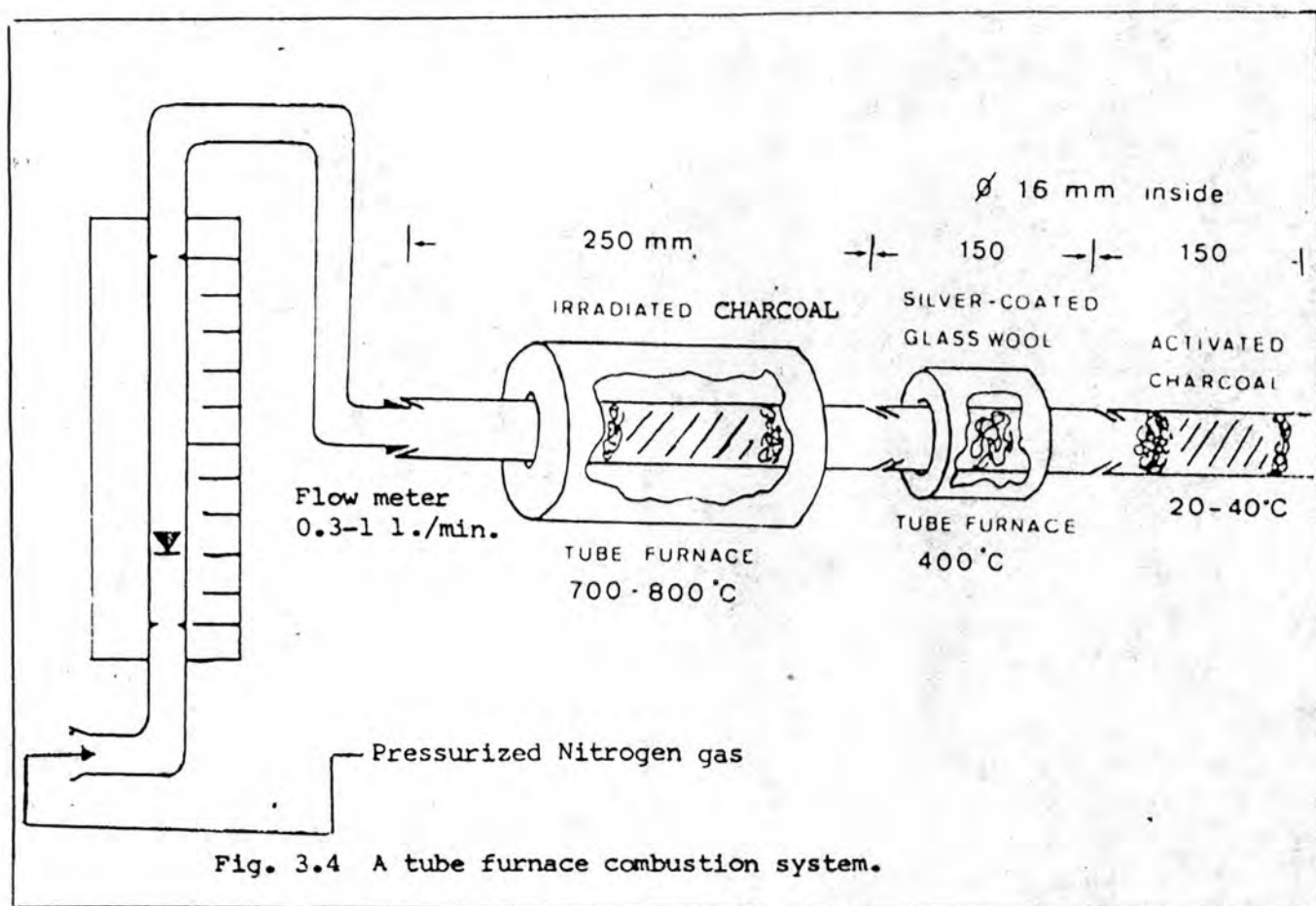


Fig. 3.4 A tube furnace combustion system.

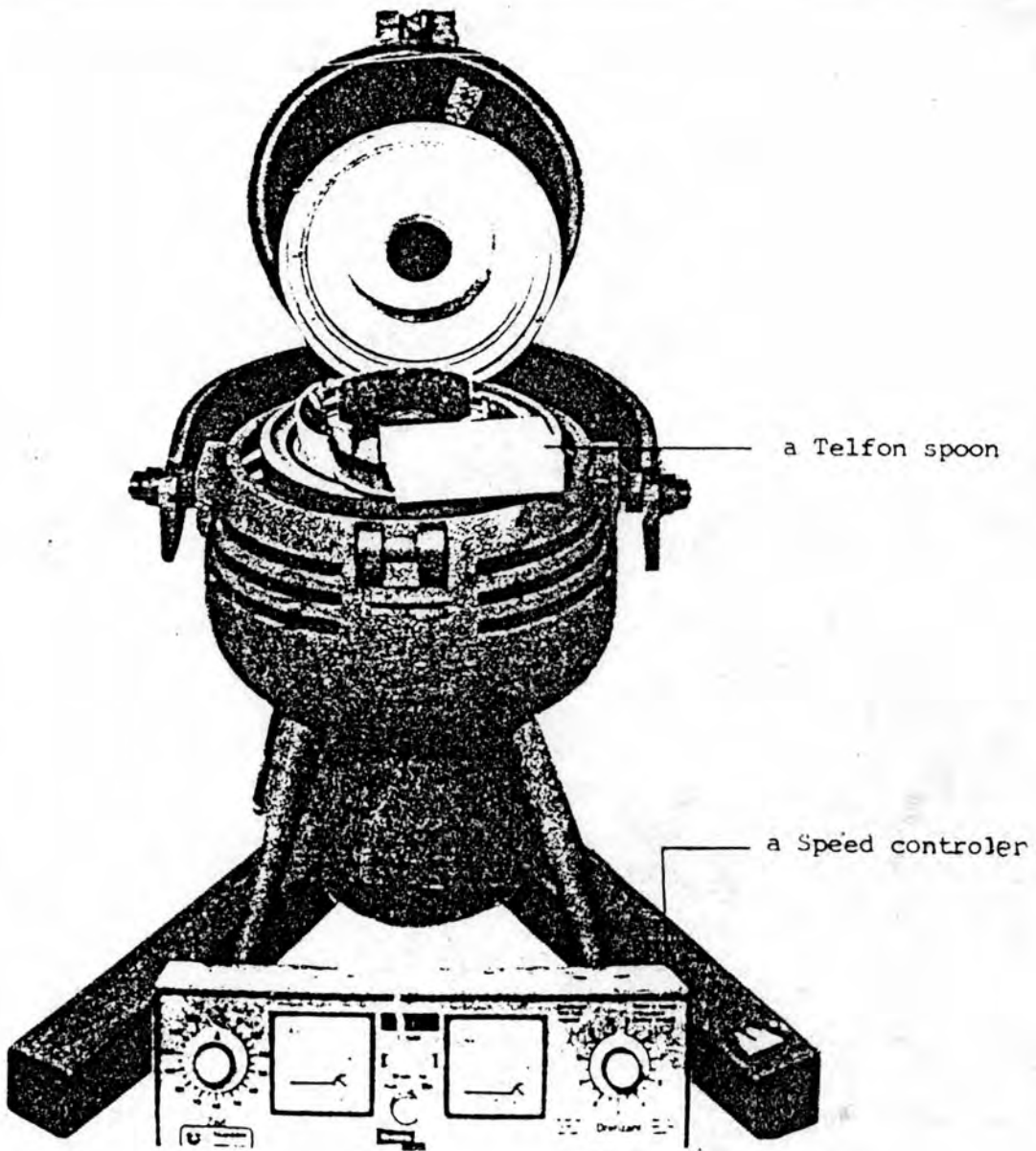


Fig. 3.5 A continuous flow centrifuge mounted in gimbals.



3.2.12 Counting equipment

3.2.12.1 A 3x3 in. Well-type NaI(Tl) detector connected to a single-channel analyser.

3.2.12.2 A 88 cm³ coaxial Ge(Li) detector (of FWHM 1.9 keV at 1332 keV and efficiency 14.7%) connected to a multichannel analyser.

3.2.13 An Oceanographic salinity and temperature measuring bridge (Swith gear Model MC 5/2)

3.2.14 An oxygen meter with salinity correction on the read out scale (Yellowshpring model 57)

3.2.15 Irradiation Facilities

The High Flux Reactor (HFR) of 45 MW of the Netherlands Energy Research Foundation (ECN) was used through out this experiment. It contains some useful facilities as following :-

3.2.15.1 The Pneumatic rabbit system 1 with 5×10^{13} n . cm⁻². sec⁻¹ thermal neutron flux.

3.2.15.2 The Poolside rotating facility with 2×10^{12} n . cm⁻². sec⁻¹ thermal neutron flux.

3.2.16 The ship

The ship for the sampling trip was offered by the Netherland Institute of Sea Research (NIOZ), Texel, the Netherlands.

3.3 Procedure

3.3.1 Recovery test on the preconcentration techniques

3.3.1.1 Co-precipitation of As with Fe(OH)₃

The influence on the co-precipitation yield of the following parameters was studied, using the carrier-free ⁷⁴As tracers :-

3.3.1.1.1 The acidity

The procedure consisted of the following steps :-

1. Spike 100 μ l. of the carrier-free ⁷⁴As tracer to 50 ml. water sample.
2. Add to obtain 10 μ g./l of As carrier and 40 mg./l of Fe³⁺.
3. Adjust the pH to a desired value by adding appropriate amount of HNO₃ or NH₄OH.
4. Stir 10 minutes using a magnetic stirrer.
5. Settle down the precipitation by allowing to stand for \gg $\frac{1}{2}$ hour.
6. Collect the precipitate on a 8 μ m. membrane filter mounted on a suction flask with radiochemical chimney (Fig. 3.1) and put it in the counting tube.

7. The same amount of ^{74}As tracer was spiked on a membrane filter mounted in a counting tube to be used as the comparison standard.

8. The count rate of 596 keV photo peak was measured by a 88 cm^3 coaxial Ge(Li) detector for 1 minute counting time.

9. Repeat steps 1-8 at various desired pH value.

3.3.1.1.2 The Fe^{3+} concentration

After the pH was adjusted to optimum value as obtained in 3.3.1.1.1, the same procedure of 3.3.1.1.1 was applied with varying the concentration of Fe^{3+} .

3.3.1.1.3 The sample volume

The procedure in 3.3.1.1.1 was adapted by varying the sample volume between 50-500 ml. at optimum pH value.

3.3.1.1.4 The As-concentration

The procedure in 3.3.1.1.1 was employed by varying the concentration of As-carrier at the optimum pH.

3.3.1.1.5 The stirring time

The procedure in 3.3.1.1.1 was repeated by varying the stirring time between 1-10 minutes at the optimum pH.

3.3.1.2 Adsorption of APDC-chelates of Co, Cd, Cr(VI), Mo, Sb, W, Zn and Hg on activated charcoal

The influence by various parameters on the adsorption yield of APDC-chelates of these elements concerned was studied, using radiotracers :-

3.3.1.2.1 Acidity

The procedure consisted of these following steps :-

1. Spike 100 μ l. of the radiotracer concerned to 100 ml. of sea water (32% salinity).
2. Adjust the pH to the desired value by adding appropriate amount of HNO_3 or NH_4OH .
3. Add to obtain 100 mg./l APDC and add 40 mg. activated charcoal powder.
4. Stir the solution for 20 minutes on a magnetic stirrer.
5. Collect the charcoal fraction by filtration through a 8 μ m. membrane filter mounted on a suction flask with radiochemical chimney. Transfer to a counting tube.
6. By comparison with an aliquot of the tracer solution, the photopeak of the nuclide concerned was measured with either NaI(Tl) detector or Ge(Li) detector.

7. Repeat steps 1-6 at various desired pH value.

3.3.1.2.2 APDC concentration

The procedure in 3.3.1.2.1 was adapted by varying the concentration of APDC at the obtained optimum pH value.

3.3.1.2.3 Amount of Charcoal

The procedure in 3.3.1.2.1 was repeated by varying the amount of charcoal at the optimum pH.

3.3.1.2.4 The sample volume

The procedure in 3.3.1.2.1 was used by varying the sample volume at the optimum pH.

3.3.1.2.5 The stirring time

The procedure in 3.3.1.2.2 was employed by varying the stirring time at the optimum pH.

3.3.1.2.6 The salinity

The procedure in 3.3.1.2.1 was adapted by varying the salinity of water sample using the mixture at various ratio of sea water with demineralized water.



3.3.1.3 Adsorption of elemental Se on activated charcoal

The influence of various parameters on reduction of SeO_3^{2-} to elemental Se by L-ascorbic acid and adsorption on activated charcoal was studied using radiotracer :-

3.3.1.3.1 Acidity

The procedure consisted of the following steps :-

1. Spike 100 μl . of ^{75}Se tracer to 100 ml. water sample.
2. Add 500 mg. L-ascorbic acid to the solution and adjust to a desired pH value.
3. Add 10 mg. of activated charcoal and stir for 10 minutes.
4. Collect the charcoal fraction by filtration through a 8 μm . membrane filter mounted on a suction flask with radiochemical chimney.
5. Count the 402 keV photopeak of ^{75}Se in the charcoal fraction in comparison with a standard tracer aliquots.
6. Repeat steps 1-5 at various desired pH value.

3.3.1.3.2 Concentration of L-ascorbic acid

At optimum pH value, the procedure in 3.3.1.3.1 was adapted by varying the amount of ascorbic acid.

3.3.1.3.3 Amount of charcoal

The procedure in 3.3.1.3.1 was repeated by varying the amount of charcoal, using the optimum pH and L-ascorbic acid concentration.

3.3.1.3.4 Reaction time of reduction

The stirring time was varied to find the appropriate time in which the highest yield could be obtained.

3.3.1.3.5 The sample volumes

The sample volume was varied, using the condition obtained from 3.3.1.3.1 to 3.3.1.3.4.

3.3.1.3.6 The Salinity

At the optimum conditions, the influence of salinity was tested by using various ratio of sea water - demineralized water mixture.

3.3.2 Recovery test on the chemical separation

3.3.2.1 Adsorption of ^{76}As on acid Al_2O_3

From 3.3.1.1, As in $\text{Fe}(\text{OH})_3$ precipitate will be converted to ^{76}As by thermal neutron activation. Since ^{59}Fe will be occurred and resulting high radiation burden thus prevention the direct spectroscopic measurement of the ^{76}As peak, the chemical separation was necessary to solve this problem.

The procedure as described by Giradi et.al.[19] was modified as following :-

1. The optimum condition obtained in 3.3.1.1 was repeated until the filtrate was collected and then dried at 60°C for $\frac{1}{2}$ hour.
2. Dissolve the precipitate in 1.5 ml. conc. HNO_3 on a hot flame.
3. Dilute the solution to 4 N HNO_3 and passed through a column of Al_2O_3 (fig. 3.2). The flow rate was about 0.25 ml./min.
4. Wash the column two times with 5 ml. 4 N HNO_3 and dry it with acetone.
5. Collect the Al_2O_3 fraction in a counting tube.
6. Count the ^{74}As photo peak in the Al_2O_3 fraction in comparison with the same amount of standard tracer solution which was spiked on the same amount of Al_2O_3 in another tube.

3.3.2.2 Separation of ^{197}Hg from ^{82}Br interference

The charcoal fraction obtained from the Hg-preconcentration may probably contains some amount of Br, thus will cause the interference of ^{82}Br on the concened spectrum of ^{197}Hg . The chemical separation is therefore necessary to solve this problem.

The procedure as described by Kosta and Byrne [20] was modified as following :-

1. Irradiated the standard Reference material Lake sediment SL-1 with a standard charcoal of known Hg-content for 2 hours in a $2 \times 10^{12} \text{ n.cm}^{-2} \text{ sec}^{-1}$ thermal neutron flux.
2. After 1-3 days decay time, the sample and standard were burned in the apparatus shown in fig. 3.4. A stream of N_2 gas was passed through the system at 0.6-0.8 l/min. The temperature of the furnaces were kept at 800°C and 400°C respectively.
3. After 5 minutes, the charcoal fraction at the out let end was counted for the recovery yield of ^{197}Hg .

3.3.3 Neutron activation analysis

3.3.3.1 Neutron irradiation

The irradiation were performed in the High Flux Reactor in two positions as following :-

3.3.3.1.1 The Pneumatic rabbit system

The irradiation for short and intermediate lived radionuclides was usually done in the Pneumatic rabbit system of flux $5.10^{13} \text{ n.cm}^{-2} \text{ sec}^{-1}$.

In this study, this facility was selected for the irradiation of As co-precipitate with $\text{Fe}(\text{OH})_3$. The irradiation time used was 20 minutes.

3.3.3.1.2 The Pool side rotating facility

The irradiation for rather long lived radionuclides was usually done in this facility at flux 2×10^{12} n, cm^{-2}, sec^{-1} . In this study, the irradiation time used for the preconcentrated trace elements on activated charcoal was 12 hours and 6 hours for the solid sediment and particulate samples respectively.

In both irradiations, the neutron flux gradient was corrected by using iron ring comparator mounted on top of each sample-vial in the same container.

3.3.3.2 The Gamma ray spectroscopy

The measurement on the gamma ray spectra was accomplished at fixed position next to the top of a 87.5 cm^3 Ge(Li) detector (FWHM 1.9 keV at 1332 keV, efficiency 14.7%). The typical counting times were 1000 and 3000 seconds respectively.

The iron flux monitors were counted separately in a 3x3 inch well-type NaI(Tl) detector coupled with a multichannel analyser. The area under the 1292 keV photo peak of ^{59}Fe was calculated and normalized against previously count-rates for a certain standard irradiation time.

The spectra were processed by a computer programme, which accounted for the partial overlap of photo peaks, applied the pulser correction for pile-up, introduced weights and flux factors and correction for decay.



The concentration were determined using the gamma-lines mentioned in table 3.2.

Table 3.2 The gamma-lines used for calculations.

Nuclide	Energy of the gamma-line in keV.	The decay time
^{76}As	559.3	12 hr.
^{187}W	685.7	1-3 d
^{197}Hg	77	1-3 d
$^{115\text{m}}\text{Cd}$ (In)	336	12 hr.
^{124}Sb	1691.2	10-15 d
^{60}Co	1173.2	10-15 d
^{51}Cr	320	10-15 d
^{75}Se	401	10-15 d
$^{99\text{m}}\text{Mo}$ (Tc)	140.5	10-15 d
^{65}Zn	1115	10-15 d
^{59}Fe	1291.6	10-15 d

3.3.4 The Reliability test on the developed techniques

A Standard Biological Reference Material named as Orchard leaves (SRM 1571) was used instead of Standard Reference of Water which is not available to check on the reliability of the developed techniques. The analytical scheme used was as following :-

1. Preparation of samples by drying, weighing and encapsulation.
2. Irradiation for 12 hours at $2 \times 10^{12} \text{ n cm}^{-2} \text{ sec}^{-1}$ and cooling for 12 hours.
3. Destruction with a saturated $\text{Mg}(\text{NO}_3)_2$ solution.
4. Dissolved in 6 N HCl and diluted to 150 ml.
5. Separation of trace elements by adsorption on activated charcoal.
6. Adsorption of ^{76}As on Al_2O_3 column.
7. Counting of the charcoal fractions and the Al_2O_3 on Ge(Li) detector respectively.
8. Counting of the iron flux monitor on a NaI(Tl) detector.
9. Calculation using the computer programme.

3.3.5 Some applications of the developed techniques

3.3.5.1 The determination of arsenic in tap-canal- and sea-water

The samples collected around the Netherland Energy Research Foundation were analysed using the spiked demineralized water samples as comparison standards.

3.3.5.2 Leaching behaviour of some trace elements from an alkaline ash in contact with sea water

The leachates of various solid to liquid ratios of an alkaline ash in sea water mixing in different contact times were analysed to verify whether retention mechanisms as found in the fresh water leaching of the ash [23] are present in sea water as well. The analytical procedure consisted of the following scheme :-

1. Determine the total concentrations of some elements content in the ash by INAA.
2. Prepare 12 aliquots in the following solid to liquid ratios of the ash : sea water :- $1/100$, $1/20$, $1/5$ and $1/1$.
3. Roll the mixtures for $1/2$, 5 and 50 hours respectively on a rolling table.
4. After allowing the mixtures stand for a few minutes, filter them through a $0.45 \mu\text{m}$ membrane filter.
5. Measure the pH of each filtrated solution and then store them at pH 1.5 in polyethylene bottles.
6. By using the developed techniques, the elemental concentration of As, Sb, Mo, W, Cr(VI), Se, Co and Hg in the leachates were analysed.

3.3.5.3 The determination of some trace elements in water and related samples from the Western Scheldt estuary

A trip has been arranged during Sept. 27 to Oct.8 1982 in the Western Scheldt estuary in the Netherlands for the study concerning water pollution problem. The sampling places are presented in fig. 3.6.

Sampling techniques and sample preparation :-

The water sample

The surface water samples were collected with a polyethylene bucket with a nylon string. Simultaneously, some physical properties of the water eg. acidity, salinity, temperature and oxygen content were measured. The suspended matter was eliminated by filtration of the samples in the apparatus mentioned in 3.2.9. Two aliquots of 500 ml. filtrated samples were simultaneously preconcentrated on boat as the Metal-APDC chelates of Sb, Mo and W which were sorbed on activated charcoal. Half a litre of the filtrated sample was stored at pH 1.5 in a polyethylene bottle for the further determination of As content at the laboratory.

The sediment

The sediment samples were grabbed at the same sites. About 5 gm. of each sample was kept in a polyethylene vial to be freeze-dried in the laboratory. INAA, was used for the analysis on the total elemental content.

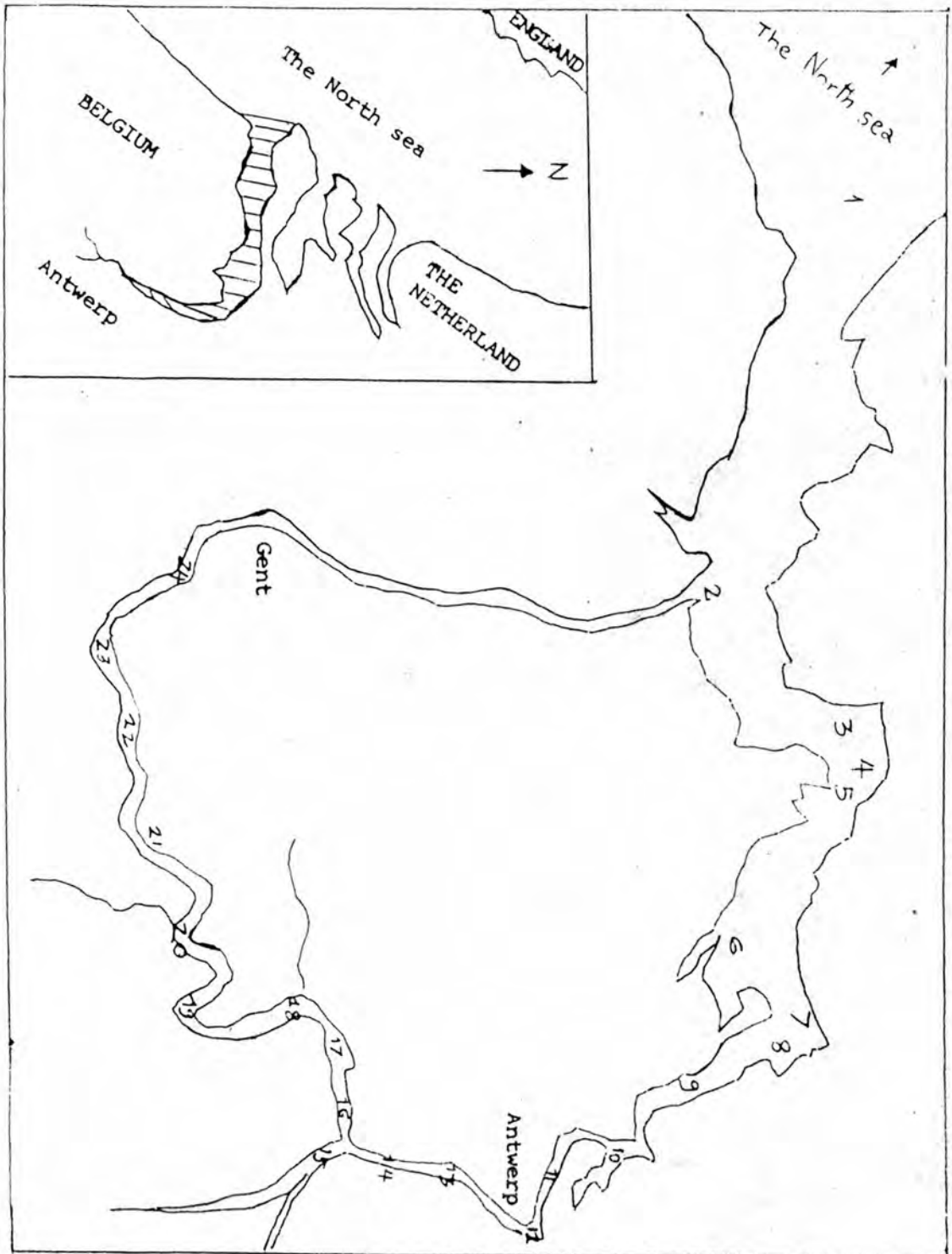


Fig. 3.6 The sampling stations in the Western Scheldt estuary.

The suspended matter

About 200 litres of the surface water sample at the same of each sampling site was pumped and centrifuged by the apparatus mentioned in 3.2.11. Up to 2 gm. of sample could be obtained and then divided in to four fractions of different grain sized using a teflon spoon. The samples were kept in the polyethylene vial with snap caps to be freeze dried. INAA was used for the analysis on the total elemental content.