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THE DETERMINATION OF STRONTIUM 90 IN ENVIRONMENTAL MATERIALS

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ABSTRACT

A method for determining strontium 90 in environmental materials is described. It consists of the ion-exchange separation of strontium from calcium at an elevated temperature by careful control of pH and the molar ratio of Ca:EDTA, followed by scavenging. Activity of the Sr-90 is determined by counting the yttrium 90 daughter. Recovery of strontium is determined with Sr-85 tracer. Typical recovery of strontium is 70-90 per cent.

Procedures are given for analysis of milk, vegetation, meat and fish, rainwater, and oyster shell and reference is made to analysis of oyster flesh, soil and effluent.

CONTENTS

1. INTRODUCTION

The method for the determination of strontium 90 in environmental samples reported here has been successfully used at the A.A.E.C.'s Research Establishment, Lucas Heights, for a number of years. Originally developed by Davis (1962) for grass and milk, it has been modified into a general method for a wide range of environmental and biological materials.

The method makes use of the different stability constants of the ethylene-diaminetetraacetic acid (EDTA) complexes of calcium and strontium to separate them by ion-exchange. The molar ratio of EDTA: calcium is important and the calcium content must be determined in advance. The separation takes place at elevated temperatures and requires a specially-designed column. Normal scavenging of the separated strontium follows. Strontium recoveries are determined by counting added Sr-85 tracer. Sr-90 is determined by counting the Y-90 daughter, using a low-level β counter. Recovery of Sr is typically 70-90 per cent.

This direct method is well suited to most environmental materials such as grass, milk, rainwater, fish, etc. However, interference by large quantities of iron, aluminium, and zinc, results in low yields. Consequently for Fe- and Al-rich soils and Zn-rich oyster flesh, the method is modified (Lahoud and Piper 1967 a, 1967 b).

2. REAGENTS

The reagents used are:

(1) Strontium carrier solution; approximately 5 mg Sr^{2+}/ml; dissolve 5.0g $SrCO_3$ in a slight excess of 5N HNO_3, adjust volume to 500 ml and standardise.

(2) Sr-85 solution; approximately 1,000 disintegrations per min. Sr-85/ml + 1 µg Sr^{2+}/ml in N/100 HNO_3.

(3) HCl; approximately 5N; dilute 250 ml conc. HCl to 500 ml with demin. water.

(4) HCL; approximately 3N; dilute 300 ml conc. HCl to 1 litre with demin. water.

(5) HCl; approximately 0.25 N; dilute 25 ml conc. HCl to 1 litre with demin. water.

(6) EDTA; Analar.

(7) EDTA; 0.05M; dissolve 18.6g in 1 litre demin. water, adjust pH to 4.8 using 40 per cent. NaOH, acetic acid.

(8) EDTA; 0.05M; dissolve 18.6g in 1 litre demin. water, adjust pH to 5.3 using 40 per cent. NaOH, acetic acid.

(9) NaOH; 40 per cent.

(10) Zeo-karb 225 resin, sodium form, 60-100 mesh, 12 per cent. D.V.B.

(11) Barium carrier solution; approximately 10 mg Ba^{2+}/ml; 7.1g $BaCO_3$ dissolved in a slight excess of 5N HNO_3; adjust volume to 500 ml.

(12) Sodium chromate solution; 30 per cent.

(13) Ammonium acetate solution; 50 per cent.

(14) Ferric ion carrier solution; approximately 5 mg Fe^{3+}/ml; 12g $FeCl_3$ dissolved in a slight excess of 5N HNO_3; adjust volume to 500 ml.

(15) Yttrium carrier solution; 10 mg Y^{3+}/ml; 6.4g spec. pure Y_2O_3 dissolved in a slight excess of 5N HNO_3; adjust volume to 500 ml with demin. water. Standardise.

(16) HNO_3; approximately 5N; dilute 165 ml conc. HNO_3 to 500 ml with demin. water.

(17) Acetic acid; approximately 6N; dilute 345 ml glac. acetic acid to 1 litre with demin. water.

(18) Oxalic acid; 8 per cent. solution.

(19) Sodium carbonate; saturated solution; dissolve 100g $Na_2CO_3.7H_2O$ in 500 ml warm demin. water; allow to cool.

(20) Oxalic acid; 0.1 per cent. solution.

(21) Phenolphthalein indicator solution; 0.5 per cent; dissolve 0.5g in 50 ml ethyl alcohol, add 50 ml demin. water.

(22) Methyl red indicator solution; 0.1 per cent; dissolve 0.1g methyl red indicator in a small amount of 10 per cent. NaOH and dilute to 100 ml with demin. water.

(23) Standard Sr-90/Y-90 solution; approximately 250 disintegrations per min./ml (accurately standardised).

(24) Ammonium hydroxide solution; carbonate-free; reagent grade NH_4OH (provided bottle is kept tightly stoppered).

(25) Carbon tetrachloride; commercial grade.

(26) NaCl; 3M; 176g NaCl dissolved in 500 ml demin. water and made to one litre.

3. ION-EXCHANGE COLUMN

3.1 Column Design

The design and dimensions of the column are shown in Figure 1. The reservoir, air bleed, and condenser are connected by appropriate adaptors and supported, with the column, by clamps to a Lablock frame. The reservoir is a 2 litre separating funnel with a B14 conical outlet and fitted with a Quickfit cone and stem MF 15/3B as a constant pressure head device.

The air bleed is a 50 cm x 4 mm glass tube fitted with an 12/5 BS spherical joint. The condenser is of the double jacketed type.

The column is maintained at 77°C by boiling carbon tetrachloride in a 250 ml spherical flask fitted to the base of the jacket and heated with an isomantle. VENTILATION MUST BE ADEQUATE, AS CARBON TETRACHLORIDE FUMES WHICH ESCAPE THE CONDENSER CAN BE DANGEROUS.

3.2 Column Preparation

(1) Add 30 ml of wet Zeo-karb 225 to the column. Stir to avoid bubbles.

(2) Add about 150 ml carbon tetrachloride to the 250 ml boiling flask and assemble apparatus, turn on heat and cooling water.

(3) When the CCl_4 is boiling and the column has reached a stable temperature, add 250 ml of demin. water to the separating funnel and run through the ion-exchange column at a flow rate of 1 ml/min.

(4) Convert resin to sodium form by passing 200 ml of 3M NaCl; discard effluent.

(5) Wash with 250 ml demin. water; discard wash.

(6) Condition column by running through 200 ml 0.05M EDTA, pH 4.8. Discard effluent.

The column is now ready for use.

4. PROCEDURE

4.1 Fresh Milk

PART A

1. Evaporate milk to dryness at 120°C in an air oven, then ash at 450°C until all carbon has been removed. Measure the ash/fresh volume ratio. (3 gallons of milk produces about 100g ash).

2. Determine the Ca content of the ash and weigh a sample of ash for Sr-90 analysis that contains 2.0g Ca into a 250 ml beaker.

3. Add accurately about 25mg Sr carrier (5.0 ml).

4. Add accurately 5.0 ml Sr-85 tracer solution (giving ≈ 5000 disintegrations per minute).

5. Add 150 ml 5N HCl, then digest on a hot plate.

6. Weigh 18.6g EDTA and dissolve, by mechanical stirring, in 1 litre demin. water contained in a 2 litre beaker. (EDTA: Ca equivalent ratio is 1:1).

7. Filter the digested solution and add the filtrate to the 2 litre beaker, add 15 ml glacial acetic acid and make volume to 2 litres.

8. Adjust pH to 4.8 using 40 per cent. NaOH. Stand for 5 minutes. If precipitate of $Fe(OH)_3$ is formed, remove by filtration and discard precipitate.

9. Pour the solution into the reservoir on top of the ion-exchange column and allow to run through at the rate of 1 drop/3-6 sec. (the time of elution should not be less than 18 h). IMPORTANT: Check COOLING WATER flow and CCl_4 level.

10. Retain effluent until Sr recovery has been determined.

11. Elute with 600 ml 0.05M EDTA solution, pH 5.3, discard eluant (containing trace Ca).

12. Elute with 250 ml water to remove EDTA; discard eluant.

13. Elute with 350 ml 0.25N HCl to remove Mg, Na; discard eluant.

14. Elute with 250 ml 3N HCl, collect eluant in a 400 ml beaker and evaporate to dryness under infra-red.

15. Run two further aliquots of 50 ml 3N HCl through the column, add to the first Sr^{2+} eluant and evaporate to dryness.

16. Add 2 or 3 drops 5N HCl to the dry residue in the 400 ml beaker and wash carefully into a 5 ml polythene pill pack.

17. Dilute to 5 ml with demin. water and determine γ activity by counting in a well-scintillation counter. Calculate the percentage recovery of Sr by comparing the activity with that of a 5.0 ml aliquot of the Sr-85 tracer, correcting both for background (averaging at least two background counts of 1000 seconds each).

18. If the percentage recovery of Sr-85 is less than 60 per cent. the column must be reconditioned and the sample recombined with the initial effluent and run

through the column again.

19. Record the percentage recovery of Sr.

PART B

1. If recovery is satisfactory, transfer solution from pill pack to a 40 ml centrifuge tube, make volume to about 20 ml and heat in a water bath.

2. Precipitate R_2O_3 by making alkaline with CO_2-free NH_4OH, cool to room temperature, and centrifuge.

3. Filter the solution through a Whatman No. 541 filter paper into another centrifuge tube. Discard the precipitate.

4. Add 1 ml of saturated Na_2CO_3 solution, heat to about 80°C in a water bath for 5 minutes, cool to room temperature, and centrifuge.

5. Add 1 drop of Na_2CO_3 solution and if no precipitate appears discard supernate.

6. Add 5N HCl dropwise to dissolve precipitate, add 5 ml demin. water, about 10 mg Ba carrier and 2 drops methyl red indicator.

7. Neutralize carefully by adding conc. NH_4OH dropwise, then add 1 ml 50 per cent. ammonium acetate solution and 1 ml 6N acetic acid (pH should now be between 4.5 and 5.0; check using pH paper).

8. Dilute to 20 ml, heat in a water bath and slowly add 1 ml 30 per cent. sodium chromate solution with gentle stirring, cool to room temperature, centrifuge and filter into another tube. Discard precipitate.

9. Make alkaline by adding conc. NH_4OH dropwise (colour changes from orange to greeny-yellow).

10. Add 1 ml of saturated Na_2CO_3 solution, digest in a water bath for 5 minutes, cool to room temperature, centrifuge and discard supernate (after checking with 1 drop Na_2CO_3 solution).

11. Add 5 ml methanol to the precipitate and wash; centrifuge, and discard methanol.

12. Dissolve the precipitate by adding 5N HNO_3 dropwise, adjust volume to 10 ml, make alkaline with conc. NH_4OH and add 1 ml of saturated Na_2CO_3 solution, heat in a water bath for 5 minutes, cool, and centrifuge. Discard supernate.

13. Dissolve the $SrCO_3$ precipitate by adding 5N HNO_3 dropwise, then adjust volume to 20 ml.

14. Add 0.25 ml of 10 vol. H_2O_2 (2 drops of 100 vol.), heat in a boiling water bath to expel CO_2.

15. Prepare a standard by adding accurately about 15 pCi of Sr-90/Y-90 solution, using a micro-pipette, into a 40 ml centrifuge tube, along with an accurate amount of Sr carrier ($\approx$ 25 mg), 5 ml of Sr-85 solution, diluting to 10 ml, adding H_2O_2, and treating in the same fashion as the sample.

16. Add to both sample and standard 5 mg Fe^{3+} carrier and 1 mg Y carrier.

17. Make alkaline by adding CO_2-free NH_4OH dropwise, centrifuge hot, and filter, using Whatman No. 541 filter paper, into a 25 ml volumetric flask containing an accurate amount of Y carrier (about 10 mg) and 1 ml 5N HCl; make to volume.

18. Take a 5.0 ml aliquot and place in a 5 ml polythene pill pack, count as before to determine Sr recovery. Record this value as the overall Sr recovery.

19. Transfer both the solution used for counting and the solution in the volumetric flask to a 100 ml bottle and store for 14 days. (Volume should be not more than 25 ml).

PART C

1. After at least 14 days, transfer solution to a 40 ml centrifuge tube, heat in a water bath and make alkaline by adding CO_2-free conc. NH_4OH dropwise. Note time of separation.

2. Cool to room temperature, centrifuge, and transfer supernate back to bottle.

3. Dissolve the precipitate in a minimum amount of 5N HCl added dropwise, adjust volume to 20 ml and reprecipitate by adding CO_2-free NH_4OH as before; cool to room temperature, and centrifuge, transfer supernate to bottle as before.

4. Add 5N HCl dropwise to dissolve precipitate, heat in a water bath and add 20 ml of 8 per cent. oxalic acid solution, cool to room temperature, centrifuge, and discard supernate.

5. Prepare a blank (for background determination) by adding a similar amount of yttrium carrier to a centrifuge tube and adding 20 ml of 8 per cent. oxalic acid solution, heat in a water bath for 5 minutes, cool to room temperature, centrifuge, and discard supernate.

6. Wash blank, standard and samples with about 20 ml of 0.1 per cent. oxalic acid (using stirring rod).

7. Place a 1 inch diameter Whatman No. 5 filter paper on the special filter stick (HASL Manual 1959) and wash with water, using vacuum filtration.

8. Filter the solution, wash with demin. water, and finally with methanol.

9. Transfer the filter paper to the special mount (Figure 2) and dry under the infra-red lamp.

10. Transfer the mounting disc to the low-background β-counter and count for at least six separate hours until at least 65 hours have elasped. Note the time of the mid-point of each count with respect to time elapsed since separation of the Y-90 from the parent Sr-90.

11. Weigh a porcelain crucible to constant weight after igniting at 800°C.

12. Transfer the filter paper with precipitate from the planchette to the crucible and ignite at 800°C for 1 hour.

13. Cool and weigh to constant weight.

14. Calculate yttrium recovery (mg Y_2O_3 x 0.787 = mg Y).

15. Using the decay tables for Y-90 (Table 1) determine the count rate at zero time (time of separation).

CALCULATIONS

Co: Count rate in counts per minute at zero-time, obtained by multiplying the actual count (corrected for background) by a decay factor depending on time elapsed between separation and count.

E: Per cent. efficiency of counter (from standard).

Y: Per cent. yttrium recovery.

Ca: Per cent. Ca in ash.

Sr: Per cent. Sr recovery overall, obtained from Sr-85 count.

Ash: Weight in grams of ash used.

$$\mu\mu Ci \ \text{Sr-90/g Ca} = \frac{Co}{2.22} \times \frac{100}{E} \times \frac{100}{Y} \times \frac{100}{Sr} \times \frac{100}{Ca} \times \frac{1}{Ash} \ .$$

Note: If recovery of Y is below 90 per cent, a correction factor must be applied for β absorption efficiency.

4.2 Powdered Milk

1. Weigh out 1000g and ash in furnace at 450°C until all carbon has been destroyed. Determine ash/F.W.

2. Determine Ca content of the ash and weigh a sample of ash for Sr-90 analysis that contains 2.0g of Ca into a 250 ml beaker.

3. Proceed as for fresh milk from step 3 of Part A in Section 4.1.

4.3 Vegetation (Grass, wood, leaves, seaweed, vegetables)

1. Weigh the fresh sample and dry sample in an air oven at 110°C. Weigh the dried sample.

2. Ash in furnace at 450°C until carbon has been destroyed. Weigh the ash and determine the ash/F.W. and ash/D.W.

Note: Normally ash/D.W. is only determined on grass, seaweed, or wet samples.

3. Determine the Ca content of the ash and weigh 10g into a 250 ml beaker (Use 2.5g ash for grass).

4. Add accurately about 25 mg Sr carrier.

5. Add accurately 5.0 ml Sr-85 solution.

6. Add sufficient conc. HCl to cover ash, then digest on hot plate to dryness; cool.

7. Add 150 ml 5N HCl; heat to dissolve residue.

8. Weigh out sufficient EDTA to give an EDTA: Ca molar ratio of 2:1. (18.6g EDTA per g Ca).

9. Dissolve the EDTA in about 1 litre demin. water in a 2 litre beaker.

10. Transfer the sample quantitatively to the 2 litre beaker.

11. Add 15 ml glac. acetic acid, make to 2 litres with water.

12. Proceed according to step 8, Part A of the method for fresh milk.

4.4 Fish, Crabs and Meat

1. Weigh fresh sample and ash at 450°C in a furnace until all carbon is removed. Weigh ash and record ash/F.W.

2. Determine Ca content of the ash and weigh a quantity of the ash containing 2g Ca into a 250 ml beaker.

3. Proceed according to step 3, Part A of the method for fresh milk.

4.5 Oyster Flesh

This can be treated identically to fish and meat, but yields will be very low (50 per cent.) due to interference by zinc in the complexing of the Ca with EDTA.

An improved method (Lahoud and Piper 1967 a) is recommended to overcome this problem.

4.6 Oyster Shell

1. Clean oyster shells of organic matter and dry in air oven at 110°C. Weigh the shell and ash at 450°C in a furnace. Grind and weigh ash and record ash/D.W.

2. Determine Ca and weigh an amount of ash containing 2g Ca into a 250 ml beaker.

3. Proceed according to step 3 of Part A in the method for fresh milk.

4.7 Rainwater

1. Add accurately about 25 mg Sr carrier and 5.0 ml of Sr-85 tracer solution to the total sample and evaporate to dryness in a 250 ml beaker.

2. If the sample leaves a large residue then it should be passed through the ion-exchange column to remove interfering ions. Follow the procedure as for milk, Part A, step 5. (Section 4.1).

If the sample contains a large soil content, with a large iron contamination, the method for soil (Lahoud and Piper 1967 b) should be used.

If the residue is small and reasonably colourless, dissolve in the minimum volume of HCl, transfer to a 38 ml centrifuge tube and proceed from part B of the method for fresh milk.

4.8 Soil and Sand

High Fe and Al contents of these materials interfere in the complexing of Ca with EDTA and must be removed. An improved method (Lahoud and Piper 1967 b) is recommended.

4.9 Effluent

Various considerations must be introduced in the analysis of effluent. An improved method (McClellan and Oh 1965) is recommended.

5. REFERENCES

Davis, P. S. (1962). - Application of low background counting methods to the estimation of β-active nuclides in biological materials. (M.Sc. Thesis - University of New South Wales, January, 1962).

HASL Manual of Standard Procedures, (1959). - NYO-4700, page G-02-09-01.

Lahoud, A., and Piper, N. R. (1967 a). - An improved method for the determination of Sr-90 in oyster flesh. A.A.E.C. report in preparation.

Lahoud, A., and Piper, N. R. (1967 b). - An improved method for the determination of Sr-90 in soils and sands. A.A.E.C. report in preparation.

McClellan, N. A., and Oh, P. W. (1965). - A.A.E.C. Unpublished report.

TABLE 1

YTTRIUM-90 DECAY FACTORS - 1 TO 100 HOURS (0.5 HOUR STEPS)

($t_{\frac{1}{2}}$ OF Y-90 TAKEN AS 64.4 HOURS)

Time	Factor	Time	Factor	Time	Factor	Time	Factor	Time	Factor
1.0	1.011	25.5	1.316	50.0	1.713	74.5	2.229	99.0	2.903
1.5	1.016	26.0	1.323	50.5	1.722	75.0	2.242	99.5	2.917
2.0	1.022	26.5	1.330	51.0	1.732	75.5	2.253	100	2.934
2.5	1.028	27.0	1.338	51.5	1.741	76.0	2.266		
3.0	1.033	27.5	1.345	52.0	1.750	76.5	2.278		
3.5	1.039	28.0	1.352	52.5	1.760	77.0	2.291		
4.0	1.044	28.5	1.359	53.0	1.769	77.5	2.302		
4.5	1.050	29.0	1.367	53.5	1.778	78.0	2.315		
5.0	1.055	29.5	1.374	54.0	1.788	78.5	2.328		
5.5	1.061	30.0	1.381	54.5	1.798	79.0	2.341		
6.0	1.067	30.5	1.389	55.0	1.807	79.5	2.352		
6.5	1.073	31.0	1.396	55.5	1.818	80.0	2.364		
7.0	1.078	31.5	1.404	56.0	1.827	80.5	2.378		
7.5	1.084	32.0	1.411	56.5	1.837	81.0	2.392		
8.0	1.090	32.5	1.419	57.0	1.847	81.5	2.405		
8.5	1.096	33.0	1.427	57.5	1.857	82.0	2.416		
9.0	1.102	33.5	1.434	58.0	1.866	82.5	2.430		
9.5	1.108	34.0	1.442	58.5	1.877	83.0	2.443		
10.0	1.114	34.5	1.450	59.0	1.887	83.5	2.457		
10.5	1.119	35.0	1.457	59.5	1.897	84.0	2.469		
11.0	1.126	35.5	1.465	60.0	1.907	84.5	2.482		
11.5	1.132	36.0	1.473	60.5	1.918	85.0	2.497		
12.0	1.138	36.5	1.481	61.0	1.928	85.5	2.510		
12.5	1.144	37.0	1.489	61.5	1.938	86.0	2.523		
13.0	1.150	37.5	1.497	62.0	1.949	86.5	2.536		
13.5	1.156	38.0	1.505	62.5	1.959	87.0	2.551		
14.0	1.162	38.5	1.513	63.0	1.970	87.5	2.565		
14.5	1.169	39.0	1.522	63.5	1.981	88.0	2.578		
15.0	1.175	39.5	1.530	64.0	1.991	88.5	2.592		
15.5	1.181	40.0	1.538	64.5	2.002	89.0	2.606		
16.0	1.188	40.5	1.546	65.0	2.013	89.5	2.620		
16.5	1.194	41.0	1.554	65.5	2.023	90.0	2.635		
17.0	1.200	41.5	1.563	66.0	2.034	90.5	2.648		
17.5	1.207	42.0	1.571	66.5	2.046	91.0	2.663		
18.0	1.213	42.5	1.580	67.0	2.057	91.5	2.677		
18.5	1.220	43.0	1.589	67.5	2.067	92.0	2.693		
19.0	1.227	43.5	1.597	68.0	2.079	92.5	2.705		
19.5	1.233	44.0	1.605	68.5	2.090	93.0	2.720		
20.0	1.240	44.5	1.614	69.0	2.101	93.5	2.736		
20.5	1.247	45.0	1.623	69.5	2.113	94.0	2.751		
21.0	1.254	45.5	1.632	70.0	2.124	94.5	2.765		
21.5	1.260	46.0	1.641	70.5	2.136	95.0	2.780		
22.0	1.267	46.5	1.649	71.0	2.147	95.5	2.796		
22.5	1.275	47.0	1.659	71.5	2.159	96.0	2.810		
23.0	1.280	47.5	1.667	72.0	2.170	96.5	2.824		
23.5	1.287	48.0	1.676	72.5	2.182	97.0	2.840		
24.0	1.295	48.5	1.686	73.0	2.194	97.5	2.856		
24.5	1.302	49.0	1.694	73.5	2.206	98.0	2.872		
25.0	1.309	49.5	1.703	74.0	2.218	98.5	2.887		

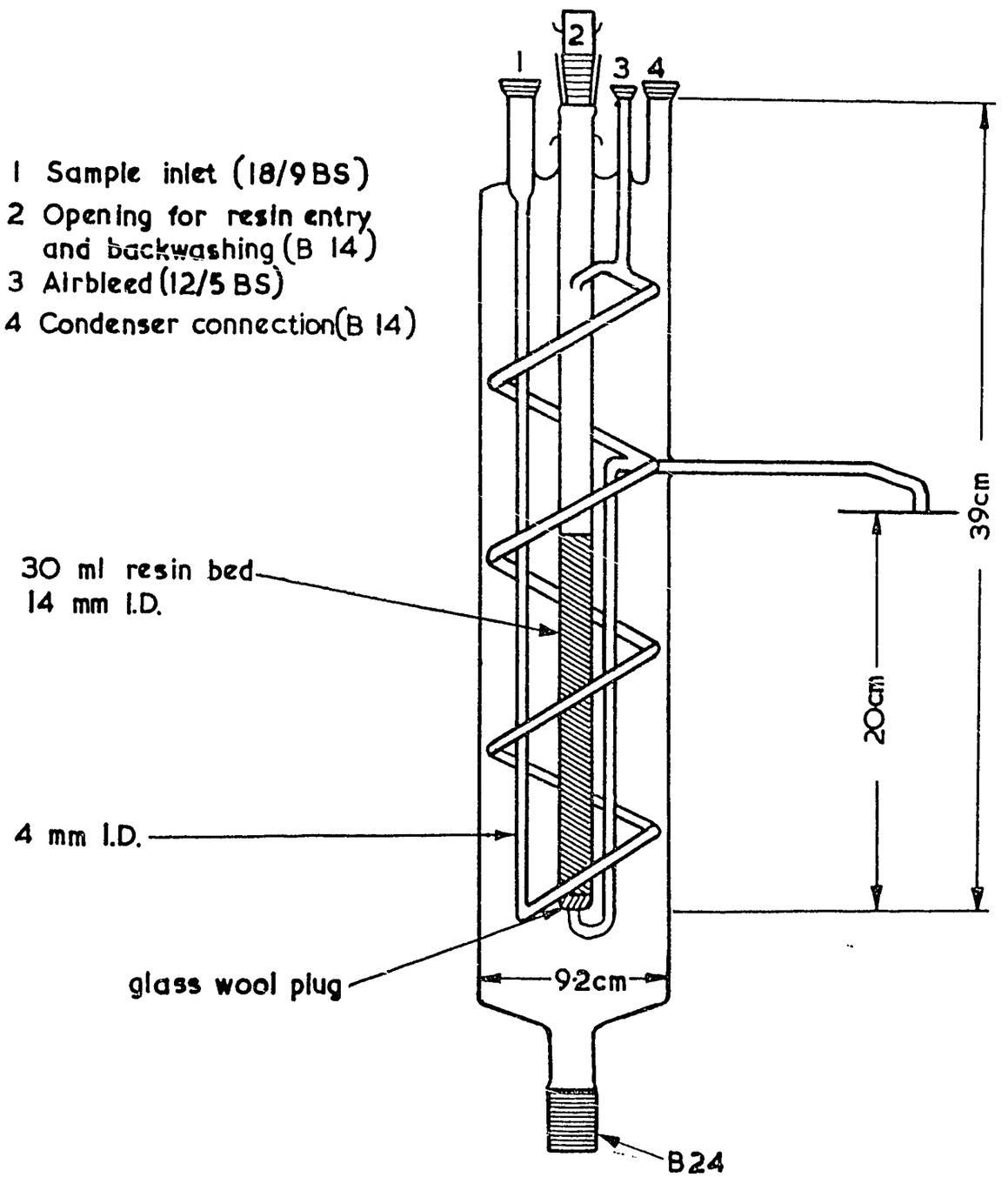
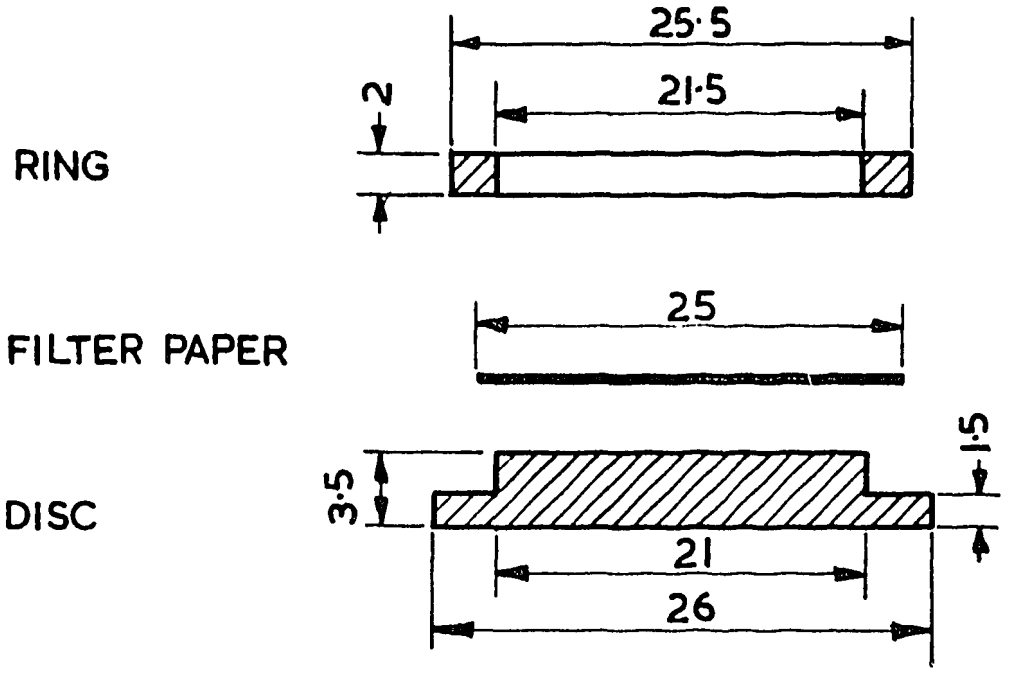


FIGURE 1. JACKETED ION-EXCHANGE COLUMN DESIGNED FOR DEGASSING AND PRE-HEATING OF SAMPLE



MATERIAL: STAINLESS STEEL

DIMENSIONS IN mm

FIGURE 2. MOUNTING DISC