



**AUSTRALIAN ATOMIC ENERGY COMMISSION
RESEARCH ESTABLISHMENT
LUCAS HEIGHTS**

**AN IMPROVED METHOD FOR THE DETERMINATION OF
STRONTIUM-90 IN SOILS AND SANDS**

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**A. LAHOUD
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ABSTRACT

The method for the determination of strontium-90 in environmental materials used in this laboratory has been found to be subject to interference from the large concentrations of iron and aluminium in soil extracts. This report deals with the development of a suitable solvent extraction procedure that will remove iron and aluminium without itself interfering in the determination.

The method selected was the extraction of iron and aluminium acetylacetonates into chloroform at controlled values of pH. This procedure removed better than 95 per cent of both iron and aluminium and produced no undesirable complications. Normal recovery of strontium was better than 80 per cent.

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1. INTRODUCTION

Strontium-90 in environmental materials is determined at the A.A.E.C. Research Establishment using the method of Davis and Piper (1967). This method involves the ion-exchange separation of the strontium from calcium at elevated temperatures by carefully controlling the Ca:EDTA** molar ratio. The efficiency of this method is subject to interference from high concentrations of cations which form stable EDTA complexes at acid pH. The stability constants of some EDTA-metal complexes are shown in Table 1.

TABLE 1
STABILITY CONSTANTS OF EDTA-METAL COMPLEXES*

Cation	Log K	Cation	Log K
Na ⁺	1.7	Co ²⁺	15.4, 15.9, 16.1
Ag ⁺	7.2	Al ³⁺	15.5
Ba ²⁺	7.8	Cd ²⁺	16.1, 15.0
Sr ²⁺	8.6	Zn ²⁺	16.1, 15.3
Mg ²⁺	8.7	Pb ²⁺	17.6, 17.2, 17.7
Ca ²⁺	10.6	Ni ²⁺	18.2, 17.5, 17.4
Mn ²⁺	13.5	Cu ²⁺	18.4, 17.7, 18.8
Fe ²⁺	14.3	Th ⁴⁺	23.2
La ³⁺	15.1, 15.3	Cr ³⁺	24.0
Sc ³⁺	21.3	Fe ³⁺	25.1

* Table according to West and Sykes (1960)

In practice, it is found that the only cations occurring in sufficient quantities in the materials routinely sampled were Zn, found in oyster flesh ash in concentrations of about 2 per cent, and Fe and Al, found in soils, dirty sands and occasionally in vegetation. Zinc interference in oyster flesh is removed using the method of Lahoud and Piper (1967).

Digestion of soil with 5N HCl by boiling for 10 minutes generally extracts about 10 mg Fe and 2 to 3 mg Al/g soil ash. Dirty sands will produce smaller amounts depending on the proportion of mud included in the ash. It is necessary to remove the iron and aluminium at low values of pH because any precipitation of either will scavenge the strontium. The acetylacetone-chloroform extraction system appeared to be the most promising for the removal of both ions at low pH and investigations were confined to this system.

** Ethylenediaminetetraacetic acid

2. THE EXTRACTION OF IRON

2.1 Extraction of Fe³⁺ as a Function of pH

To each of eight 150 ml beakers was added 25 ml Fe³⁺ carrier solution (25 mg Fe³⁺/ml), 3 ml glacial acetic acid, 3 ml 30 per cent sodium acetate solution, and 5 ml standard Fe-59 tracer solution (~ 30,000 d.p.m./ml, where d.p.m. = disintegrations per minute). The pH was adjusted in each beaker to give respective values of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 and the volumes made to 50 ml. Aliquots of 10 ml were taken and each extracted twice for 2 minutes with 10 ml volumes of 50% V/V acetylacetone in chloroform, followed by an extraction with 10 ml chloroform. The combined organic phases were washed with 30 ml demin. water and the demin. water was added to the aqueous phase and made to 50 ml in a volumetric flask. A 5 ml aliquot was taken and counted in a γ well-scintillation counter to determine the removal of Fe-59. Results are shown in Figure 1. A pH of 1.5 or higher was found to give better than 99 per cent extraction of the iron.

2.2 Extraction of Fe³⁺ as a Function of the Acetylacetone Concentration in Chloroform

To a 150 ml beaker was added 25 ml Fe³⁺ carrier solution (25 mg Fe³⁺/ml), 3 ml glacial acetic acid, 3 ml 30% sodium acetate solution, and 5 ml standard Fe-59 tracer solution (~ 30,000 d.p.m./ml), the solution adjusted to pH 2.5 and made to 50 ml in a volumetric flask. Aliquots of 10 ml were taken and each extracted twice with 10 ml portions of 5, 10, 25 and 50% V/V acetylacetone in chloroform respectively for 2 minutes each. Each solution was then washed with 10 ml chloroform and the organic phases combined and washed with 30 ml demin. water. The aqueous phase and the demin. water wash were placed in a 50 ml volumetric flask and diluted to volume. Aliquots of 5 ml were placed in polythene pill packs and counted on a γ well-scintillation counter to determine the removal of Fe-59. Results are shown in Figure 2. Better than 98 per cent extraction of iron took place with 10% acetylacetone.

2.3 Extraction of Fe³⁺ as a Function of the Fe³⁺ Concentration

Six solutions were prepared containing 5 ml of Fe-59 tracer, 3 ml glacial acetic acid, 3 ml of 30% sodium acetate solution, and containing 1.0, 5.0, 10.0, 12.5, 15.0 and 25.0 mg Fe³⁺/ml respectively. The pH of each was adjusted to 2.5. Each was extracted with an equal volume of 10% acetylacetone in chloroform for 2 minutes and washed with chloroform for 2 minutes. The organic extract and chloroform wash were combined and washed with an equivalent volume of demin. water and the water was added to the original aqueous phase in a 50 ml volumetric flask and made to volume. Aliquots were counted for Fe-59 to determine the removal of Fe-59. The results are shown in Figure 3. Better than 98 per cent of Fe was removed at concentrations up to 15 mg/ml.

2.4 Loss of Sr²⁺ During Extraction of Fe³⁺ as a Function of pH

Eight solutions were prepared containing 25 ml Fe³⁺ solution (25 mg Fe³⁺/ml), 5 ml Sr²⁺ carrier (5 mg/ml), 5 ml Sr-85 tracer, 3 ml glacial acetic acid, 3 ml 30% sodium acetate solution, and

each was made to about 45 ml. The pH was adjusted in each to give values of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 respectively, and volumes were adjusted to 50 ml. Each was extracted with 50 ml of 50% acetylacetone in chloroform followed by a 50 ml chloroform wash. The combination of wash and extractant was washed with 100 ml demin. water and the water wash was added to the original aqueous phase, evaporated to low volume and made to 50 ml in a volumetric flask. Aliquots were counted on a γ well-scintillation counter to determine the loss of Sr-85. Results are shown in Figure 4. Almost all of the Sr-85 was scavenged above pH 3.0, probably because of Fe(OH)₃ formation. No significant loss occurred between 0.5 and 3.0.

2.5 Effect of Fe³⁺ Extraction on Sr²⁺ Recovery from Ion Exchange

Six samples were prepared as follows:

Samples 1 and 2 contained 2.0 g Ca²⁺, 25 mg Sr²⁺, 5 ml standard Sr-85 tracer, 75 ml conc. HCl and 15 ml glacial acetic acid. Both solutions were prepared for ion-exchange (using the method of Davis and Piper) and then passed through the ion-exchange columns.

Samples 3 and 4 contained 2.0 g Ca²⁺, 25 mg Sr²⁺, 5 ml standard Sr-85 tracer, 75 ml conc. HCl, 15 ml glacial acetic acid, and 15 ml 30% sodium acetate solution. The pH was adjusted to 2.5 with 50% NH₄OH and each solution was extracted twice with an equal volume of 50% V/V acetylacetone in chloroform followed by a wash with an equal volume of chloroform. The combined organic extractant and wash were washed with an equal volume of demin. water and the aqueous phase added to the original aqueous solution. Each combined sample was then prepared for ion-exchange and treated in the same manner as samples 1 and 2.

Samples 5 and 6 were identical to samples 3 and 4 but contained 125 ml of Fe³⁺ carrier (25 mg Fe³⁺/ml). Each was extracted and passed through the ion-exchange columns in the same manner as samples 3 and 4.

All samples were eluted and the Sr-85 recovery determined in a γ well-scintillation counter. The results are shown in Table 2.

TABLE 2
EFFECT OF Fe³⁺ EXTRACTION ON RECOVERY OF STRONTIUM FROM ION EXCHANGE

Sample	Remarks	% Sr ²⁺ Recovered
1	No added Fe ³⁺ . No extraction	95.0
2	" " " " "	94.5
3	No added Fe ³⁺ . Extracted	97.7
4	" " " " "	93.8
5	3.125 g Fe ³⁺ added. Extracted	84.8
6	" " " " "	92.2

NOTE: It is apparent that, while the extraction itself does not interfere, some loss of Sr^{2+} has occurred in sample 5 due to slight emulsification. It was found that high iron concentrations produced emulsions which separated poorly and strontium was scavenged. The use of a more acid pH (between 1.5 and 2.0) eliminated this emulsion and the use of a general pH of 2.0 was decided upon, pH 1.5 being used where Fe concentration made it imperative.

3. THE EXTRACTION OF ALUMINIUM

3.1 Extraction of Al^{3+} as a Function of pH

To each of ten 150 ml beakers was added 25 ml Al^{3+} carrier (25 mg Al^{3+}/ml), 3 ml glacial acetic acid and 3 ml of 30% sodium acetate solution. The pH of each was adjusted to give the following range of values: 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5 and 5.0. Each solution was made to 50 ml in a volumetric flask. Then 10 ml aliquots were taken and extracted for 2 minutes with 10 ml 50% V/V acetylacetone in chloroform. The extraction was repeated and then the inorganic phase was washed with 10 ml chloroform. The combined organic phases were washed with 30 ml demin. water and the water added to the original solution. Aluminium was determined gravimetrically by precipitation with ammonia and ignition at 800 °C. The results are shown in Figure 5.

At pH 4.5 Al partially precipitated and at pH 5.0 complete precipitation occurred. The precipitate did not dissolve on extraction and was capable of scavenging Sr. The presence of the acetic acid and sodium acetate is necessary to buffer the solution, to prevent precipitation of the Al at a lower pH, and to provide a salting-out effect during extraction.

3.2 Extraction of Al^{3+} as a Function of Acetylacetone Concentration in Chloroform

A solution containing 50 ml Al^{3+} carrier (25 mg Al^{3+}/ml), 6 ml glacial acetic acid, 6 ml 30% sodium acetate solution and 25 ml demin. water was adjusted to pH 3.5 and made to volume in a 100 ml volumetric flask. Aliquots of 10 ml were taken and extracted twice with 10 ml aliquots of varying concentrations of acetylacetone in chloroform and each was then washed with 10 ml chloroform. The combined extractions and wash was washed with 30 ml demin. water which was then combined with the original solution. Aluminium retained in the aqueous phase was determined gravimetrically as the oxide after precipitating with NH_4OH and igniting to 800 °C.

The results are shown in Figure 6. Better than 95 per cent extraction occurs when the acetylacetone is 50% for a 12.5 mg/ml concentration of Al^{3+} (i.e. molar ratio of acetylacetone to Al^{3+} approximates 10 : 1 for equal volumes of inorganic and organic phases).

3.3 Extraction of Al^{3+} as a Function of Al^{3+} Concentration

Solutions were prepared containing 1.0, 5.0, 8.0, 10.0, 12.5, 15.0 and 25.0 mg Al^{3+}/ml respectively, as well as acetic acid and sodium acetate, the pH being adjusted to 3.5. Aliquots

were taken of each and were extracted with equal volumes of acetylacetone in chloroform where the concentration of acetylacetone was varied to give values of 5, 10, 25 and 50%. Each extraction was repeated and followed by a chloroform wash and Al^{3+} was determined as before in the aqueous phase. Results are shown in Figure 7. The amount of extracted Al^{3+} is not directly proportional to the amount of acetylacetone.

3.4 Loss of Sr^{2+} During Extraction of Al^{3+} as a Function of pH

Ten solutions were prepared containing 3 ml glacial acetic acid, 3 ml 30% sodium acetate solution, 25 ml Al^{3+} solution (25 mg Al^{3+}/ml), 5 ml Sr^{2+} carrier (5 mg Sr^{2+}/ml), 5 ml Sr-85 tracer, made to 50 ml with demin. water and having pH values of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5 and 5.0 respectively. Each was extracted twice with equal volumes of 50% V/V acetylacetone in chloroform and washed with chloroform. The organic phases were washed with demin. water which was added to the aqueous phase. Each was made to 100 ml in a volumetric flask and 5 ml aliquots were counted in a γ well-scintillation counter to determine the recovery of strontium. The results are shown in Figure 8. Loss of Sr was found to be less than 5 per cent in the pH range envisaged for the removal of the aluminium.

3.5 Effect of Al^{3+} Extraction on Sr^{2+} Recovery from Ion Exchange

Six samples were prepared as follows:

Samples 1 and 2 contained 2.0 g Ca^{2+} , 25 mg Sr^{2+} , 5 ml standard Sr-85, 75 ml conc. HCl and 15 ml glacial acetic acid. Both solutions were prepared for ion exchange using the method of Davis and Piper and passed through the ion-exchange columns.

Samples 3 and 4 contained 2.0 g Ca^{2+} , 25 mg Sr^{2+} , 5 ml standard Sr-85 tracer, 75 ml conc. HCl, 15 ml glacial acetic acid and 15 ml of 30% sodium acetate solution. The pH was adjusted to 3.5 with 50% NH_4OH and each solution extracted twice with an equal volume of 50% acetylacetone in chloroform followed by a wash with an equal volume of chloroform. All organic phases were combined for each sample and washed with an equal volume of demin. water. The aqueous wash was added to the original solution and the combined solution was prepared and absorbed on ion exchange in a similar manner to Samples 1 and 2.

Samples 5 and 6 were similar to samples 3 and 4 except for the addition of 125 ml of Al^{3+} solution (25 mg Al^{3+}/ml), and were treated in the same manner.

All samples were eluted from the columns and Sr-85 determined in a well-scintillation counter to determine Sr^{2+} recovery. The results are shown in Table 3. Excellent recoveries were recorded, with no apparent problems.

TABLE 3

EFFECT OF Al^{3+} EXTRACTION ON RECOVERY OF STRONTIUM FROM ION EXCHANGE

Sample	Remarks	% Sr^{2+} Recovered
1	No added Al^{3+} No extraction	95.0
2	" " " " "	94.5
3	No added Al^{3+} . Extracted	97.5
4	" " " " "	98.1
5	3.125 g Al^{3+} added. Extracted	93.7
6	" " " " "	93.0

4. RECOVERIES OF Sr^{2+} FROM SOILS AND SANDS

4.1 Sulphate-carbonate Precipitation Method

Normally, soil and sand cannot be analysed by the ion-exchange method owing to the large interferences, so that typical recoveries without the extraction step are non-existent. The method previously used for these samples was the method of sulphate-carbonate precipitation as follows: 500 g samples were used, to which was added 400 mg Sr^{2+} carrier, 5 ml Sr-85 tracer and 250 ml 1:1 HCl. This was boiled, filtered and the filtrate diluted to 2 litres. $SrSO_4$ was precipitated by heating the solution with 100 ml conc. H_2SO_4 and the addition of 50 to 100 ml ethyl alcohol to the cooled solution and allowed to stand. The precipitate was filtered, washed with 50% alcohol, and transferred to a 250 ml beaker in 20 ml demin. water. The solution was heated on a hot plate, saturated with Na_2CO_3 and digested for 30 minutes. The precipitate was filtered on sintered glass and washed with warm water, the filtrate being discarded. The $SrCO_3$ was dissolved in 1:1 HCl, evaporated to dryness, dissolved in water and counted for Sr-85.

Typical recoveries from this method averaged 70 per cent but varied widely between 40 and 90 per cent with occasional recoveries of 30 per cent.

4.2 Solvent-extraction Ion-exchange Method

Two samples of soil of 250 g each were boiled for 30 minutes with 25 mg Sr^{2+} carrier, 5 ml standard Sr-85 tracer and 250 ml of 1:1 HCl. When cool, the solution was filtered and evaporated to approximately 200 ml and 15 ml glacial acetic acid and 15 ml of 30% sodium acetate solution were added. The pH was adjusted to 2.5 and the solution made to approximately 250 ml. It was then extracted twice with 50% V/V acetylacetone in chloroform (250 ml aliquots) and washed with 250 ml chloroform. The combined organic extracts were washed with 750 ml demin. water in a 2 litre separating funnel. The combined aqueous phases were then evaporated to 200 ml, pH

adjusted to 3.5, made to 250 ml and extracted twice with 250 ml aliquots of 50% V/V acetylacetone in chloroform followed by a 250 ml chloroform wash. The organic phases were combined and washed with 750 ml water which was then added to the original solution. The volume was made up to 2 litres and a sample analysed for Ca. The required amount of EDTA was added to give a 1:1 mole ratio with the Ca and the sample was run through an ion-exchange column according to the method of Davis and Piper. Sr^{2+} was eluted and Sr-85 was determined in a well-scintillation counter.

The Sr^{2+} recoveries obtained were:

Sample 1 85.8%

Sample 2 81.6%

These figures are very acceptable recoveries and require only 25 mg Sr^{2+} compared to 400 mg Sr^{2+} for the sulphate-carbonate method. There is every reason to believe that these figures would be obtained consistently and because the method is new, may represent the lower limits of the recovery of Sr^{2+} as the results in Sections 2 and 3 indicate.

NOTE: Acetylacetone can be reclaimed from organic solutions by distillation. Chloroform distils first, followed by a water-acetylacetone mixture. Pure acetylacetone distils next at a temperature of about 140 °C.

5. THE METHOD

5.1 Reagents

- (1) Strontium carrier solution; approx. 5 mg Sr^{2+} /ml; dissolve 5.0 g $SrCO_3$ in a slight excess of 5N HNO_3 , adjust volume to 500 ml and standardise.
- (2) Strontium-85 solution; approx. 1000 d.p.m. Sr-85/ml + 1 μ g Sr^{2+} /ml in N/100 HNO_3 .
- (3) HCl; approx. 5N; dilute 250 ml conc. HCl to 500 ml with demin. water.
- (4) HCl; approx. 3N; dilute 300 ml conc. HCl to 1 litre with demin. water.
- (5) HCl; approx. 0.25N; dilute 25 ml conc. HCl to 1 litre with demin. water.
- (6) Sodium acetate solution; 30%.
- (7) Acetylacetone; A.R.
- (8) Chloroform; A.R.
- (9) EDTA; Analar.
- (10) EDTA; 0.05M; dissolve 18.6 g in 1 litre demin. water, adjust pH to 4.8 using 40% NaOH, acetic acid.
- (11) EDTA; 0.05M; dissolve 18.6 g in 1 litre demin. water, adjust pH to 5.3 using 40% NaOH, acetic acid.
- (12) Sodium chromate solution; 30%.
- (13) NaOH; 40%.

- (14) Zeo-karb 225 resin, sodium form, 60-100 mesh, 12% D.V.B.
- (15) Barium carrier solution; approx. 10 mg Ba^{2+} /ml; dissolve 7.1 g $BaCO_3$ in slight excess 5N HNO_3 ; adjust volume to 500 ml with demin. water.
- (16) Ammonium acetate solution; 50%.
- (17) Ferric ion carrier solution; approx. 5 mg Fe^{3+} /ml; dissolve 12 g $FeCl_3$ in a slight excess of 5N HNO_3 , adjust volume to 500 ml with demin. water.
- (18) Yttrium carrier solution; 10 mg Y^{3+} /ml; dissolve 6.4 g spec. pure Y_2O_3 in slight excess of 5N HNO_3 , adjust volume to 500 ml with demin. water. Standardise.
- (19) HNO_3 ; approx. 5N; dilute 165 ml conc. HNO_3 to 500 ml with demin. water.
- (20) Acetic acid; glacial; A.R. grade.
- (21) Acetic acid; approx. 6N; dilute 345 ml glacial acetic acid to 1 litre with demin. water.
- (22) Oxalic acid; 8% solution.
- (23) Oxalic acid; 0.1% solution.
- (24) Sodium carbonate; saturated solution; dissolve 100 g $Na_2CO_3 \cdot 7H_2O$ in 500 ml demin. water, allow to cool.
- (25) Phenolphthalein indicator solution; 0.5%; dissolve 0.5 g in 50 ml ethyl alcohol, add 50 ml demin. water.
- (26) Methyl red indicator solution; 0.1%; dissolve 0.1 g methyl red indicator in a small amount of 10% NaOH and dilute to 100 ml with demin. water.
- (27) Standard Sr-90/Y-90 solution; approx. 250 d.p.m./ml (accurately standardised).
- (28) NH_4OH solution; carbonate-free; reagent grade NH_4OH provided bottle is kept tightly stoppered.
- (29) Carbon tetrachloride; commercial grade.
- (30) NaCl; 3M; dissolve 176 g NaCl in 500 ml demin. water and make to 1 litre.

5.2 Equipment

- (1) Jacketed ion-exchange column as described by Davis and Piper (1967).
- (2) Filter stick (HASL Manual 1959).
- (3) Sample mount (Davis and Piper 1967).

5.3 Procedure for Soil

Part A

1. Dry soil sample in an air oven at 110 to 120 °C.
2. Sieve the dried sample through a ¼ inch mesh sieve, breaking up large sods and removing stones retained by sieve.

3. Weigh about 1300 g of soil and ash at 450 °C for 24 hours. Weigh ash and record ash/dry weight.
4. Grind ash in a hammer mill and take 250 g soil for analysis.
5. Add accurately about 25 mg Sr^{2+} carrier (5.0 ml).
6. Add accurately 5.0 ml Sr-85 tracer solution.
7. Add 250 ml of 5N HCl and boil on hot plate for 30 minutes with stirring; cool.
8. Filter solution through a porosity-4 sintered glass filter under vacuum. Wash residue with demin. water and discard residue.
9. Evaporate filtrate to approx. 200 ml under infra-red.
10. Add 15 ml glacial acetic acid and 15 ml of 30% sodium acetate solution.
11. Adjust pH to 2.0 with NH_4OH and make up to 250 ml.
12. Extract for 2 minutes with 250 ml of 50% V/V acetylacetone in chloroform in a 1 litre separating funnel. Drain off organic layer into a 2 litre separating funnel.
13. Repeat extraction with 250 ml of 50% V/V acetylacetone in chloroform. Add organic phase to the 2 litre separating funnel.
14. Wash aqueous phase with 250 ml chloroform. Add chloroform wash to 2 litre separating funnel.
15. Wash the combined organic phases with 750 ml demin. water, transfer aqueous phase to a 2 litre beaker and add the original soil extract solution. Discard organic phase (see Note in Section 4.2).
16. Evaporate on a hot plate to about 200 ml and transfer to a 400 ml beaker with washings.
17. Adjust pH to 3.5 with NH_4OH and adjust volume to 250 ml.
18. Extract for 2 minutes with 250 ml of 50% V/V acetylacetone in chloroform in a 1 litre separating funnel. Drain off organic layer into a 2 litre separating funnel.
19. Repeat extraction with 250 ml of 50% V/V acetylacetone in chloroform. Add organic phase to the 2 litre separating funnel.
20. Wash the aqueous phase with 250 ml chloroform. Add chloroform wash to the 2 litre separating funnel.
21. Wash the combined organic phases with 750 ml demin. water. Transfer aqueous phase to a 2 litre beaker and add the original soil extract solution. Discard organic phase (see Note in Section 4.2).
22. Boil the solution for 10 minutes on a hot plate to remove chloroform; cool.
23. Transfer solution to a 2 litre volumetric flask and make to volume with demin. water.
24. Take a 50 ml aliquot and determine Ca content of solution.

25. Transfer remainder of solution to a 2 litre beaker and add sufficient solid EDTA to give an EDTA:Ca molar ratio of 1:1.

26. Bring EDTA into solution and adjust pH to 4.8 using 40% NaOH.

27. Pour the solution into the reservoir on top of the ion-exchange column and allow to run through at the rate of 1 drop every 3 to 6 seconds (the time of elution should not be less than 18 hours).

IMPORTANT: Check COOLING WATER flow and CCl_4 level.

28. Retain effluent until Sr recovery has been determined.

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

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

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

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

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

34. 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.

35. Dilute to 5 ml with demin. water and determine γ activity by counting in a well-scintillation counter. Calculate the per cent recovery of Sr^{2+} by comparing the activity with that of a 5.0ml aliquot of the Sr-85 tracer, correcting both for background (the average of at least two 1000 second counts).

36. If the recovery of Sr-85 is less than 70 per cent, the column must be reconditioned and the sample recombined with the effluent and run through the column again.

37. Record the per cent recovery of Sr.

Part B

1. If recovery is satisfactory, transfer solution from pill pack to a 40 ml centrifuge tube, make volume up 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 further precipitate appears, discard supernate.

6. Add 5N HCl drop by drop 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 of 50% 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 of 30% 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 green-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 one 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 2 drops of 100 vol. H_2O_2 , 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 (~ 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 up 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 contents of the pill pack and 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 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 CO₂-free NH₄OH as before; cool to room temperature, centrifuge, and 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% 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 8% 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% 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 sample mount and dry under infra-red.

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 elapsed. 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 Y₂O₃ x 0.787 = mg Y).

15. Correct each sample count for Y-90 decay and determine the count rate at zero time (time of separation). A table of yttrium-90 decay factors is given in the report by Davis and Piper (1967).

Calculations

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

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

Y: Per cent recovery of yttrium.

Ca: Per cent Ca in ash.

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

Ash: Weight in grams of ash used.

$$\text{pCi Sr-90/g Ca} = \frac{\text{Co}}{2.22} \times \frac{100}{\text{E}} \times \frac{100}{\text{Y}} \times \frac{100}{\text{Sr}} \times \frac{100}{\text{Ca}} \times \frac{1}{\text{ash}}$$

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

5.4 Procedure for Sand

1. Dry sand sample in an air oven at 110 to 120 °C.

2. Sieve the dried sand through a 10-mesh sieve and discard material that is retained.

3. Weigh approx. 2000 g of sand and ash for 24 hours at 450 °C in a furnace. Weigh ash and record ash/dry weight.

4. Take 500 g of ash for analysis in a 1 litre beaker.

5. Add accurately approximately 25 mg Sr²⁺ carrier (5.0 ml).

6. Add accurately 5.0 ml of Sr-85 tracer.

7. Add 500 ml 5N HCl and boil on hot plate for 30 minutes with stirring; cool.

8. Filter the solution through a porosity-4 sintered glass filter under vacuum. Wash residue with demin. water and discard residue.

9. Evaporate solution to 100 ml under infra-red and dilute with 100 ml demin. water.

10. (a) If solution is completely free of iron (i.e. sand is free of soil), add 15 ml glacial acetic acid and proceed according to step (23), Section 5.3, Part A.

(b) If solution is contaminated with iron and aluminium, proceed according to Step 10, Section 5.3, Part A.

Calculation

At the A.A.E.C. Research Establishment, Sr-90 is reported for sand as pCi Sr-90/g of sand. The formula is

$$\text{pCi Sr-90/g sand} = \frac{\text{Co}}{2.22} \times \frac{100}{\text{E}} \times \frac{100}{\text{Y}} \times \frac{100}{\text{Sr}} \times \frac{1}{\text{ash}} \times \frac{\text{ash}}{\text{D.W.}}$$

where ash/D.W. is the ratio of ash/dry weight and all other factors retain their identity as in Section 5.3. Result may be reported as pCi Sr-90/g of Ca using the formula in Section 5.3. but in general, the Ca concentration in sand is too low to make this a reliable basis on which to correlate results.

6. REFERENCES

Davis, P.S. and Piper, N.R. (1967) - AAEC/TM377.

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

Lahoud, A. and Piper, N.R. (1967) - An improved method for the determination of Sr-90 in oyster flesh. AAEC/TM394.

West, T.S. and Sykes, A.S. (1960) - Analytical applications of diamino-ethane-tetra-acetic acid, 2nd Edition, British Drug Houses Limited.

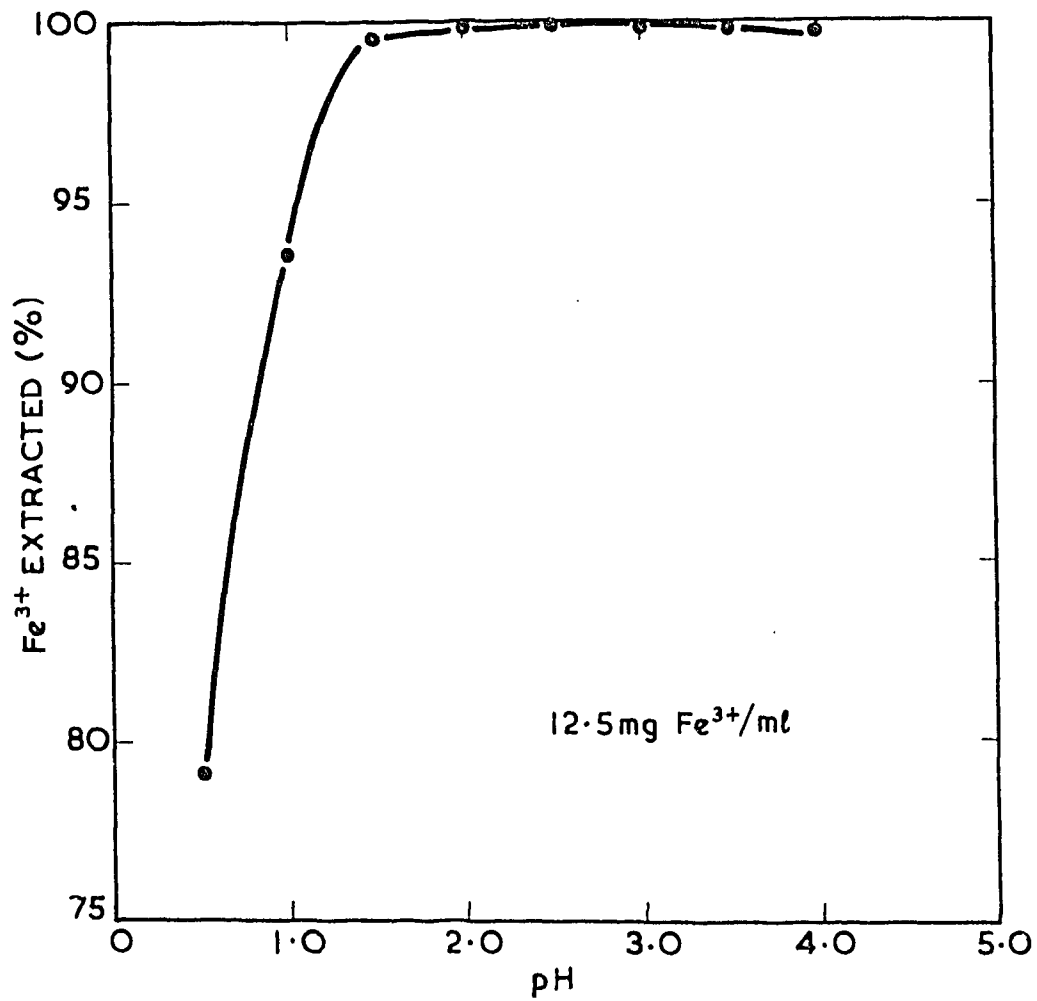


FIGURE 1. EXTRACTION OF Fe³⁺ AS A FUNCTION OF pH

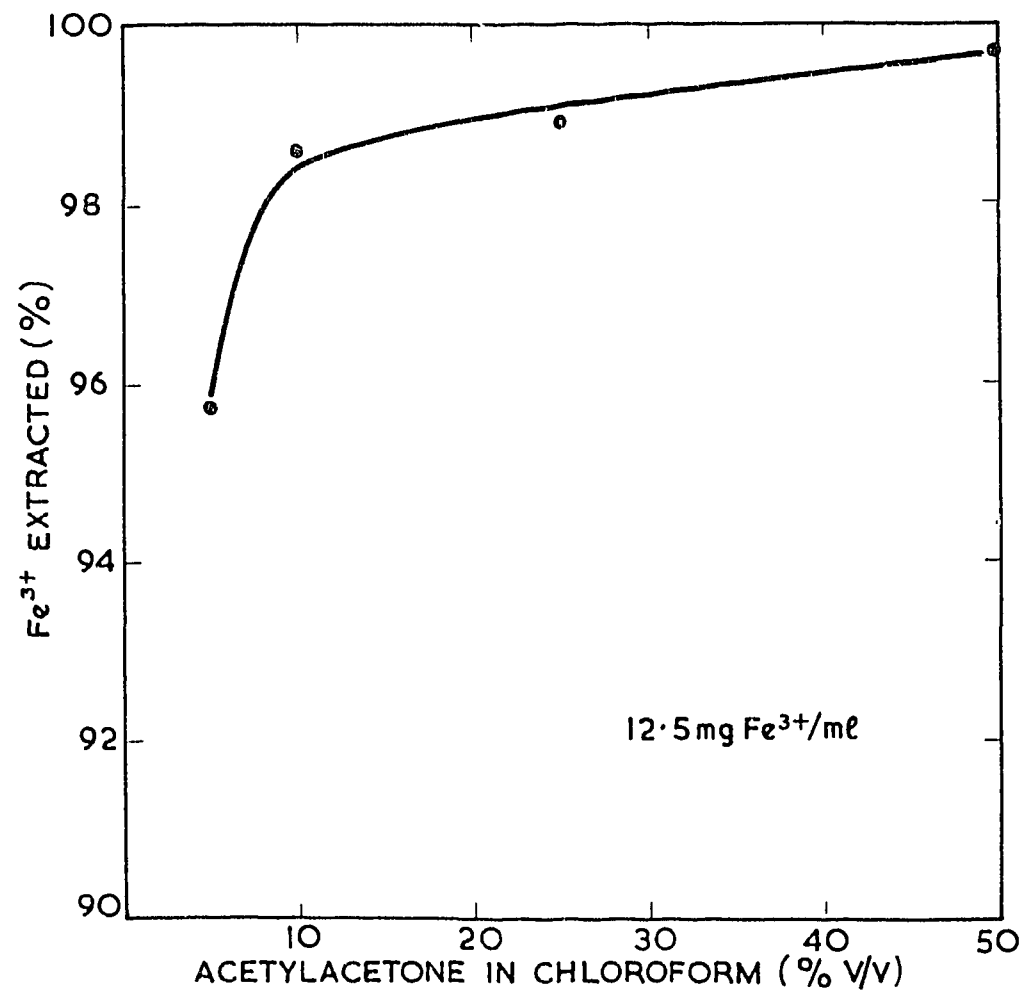


FIGURE 2. EXTRACTION OF Fe³⁺ AS A FUNCTION OF THE ACETYLACETONE CONCENTRATION IN CHLOROFORM

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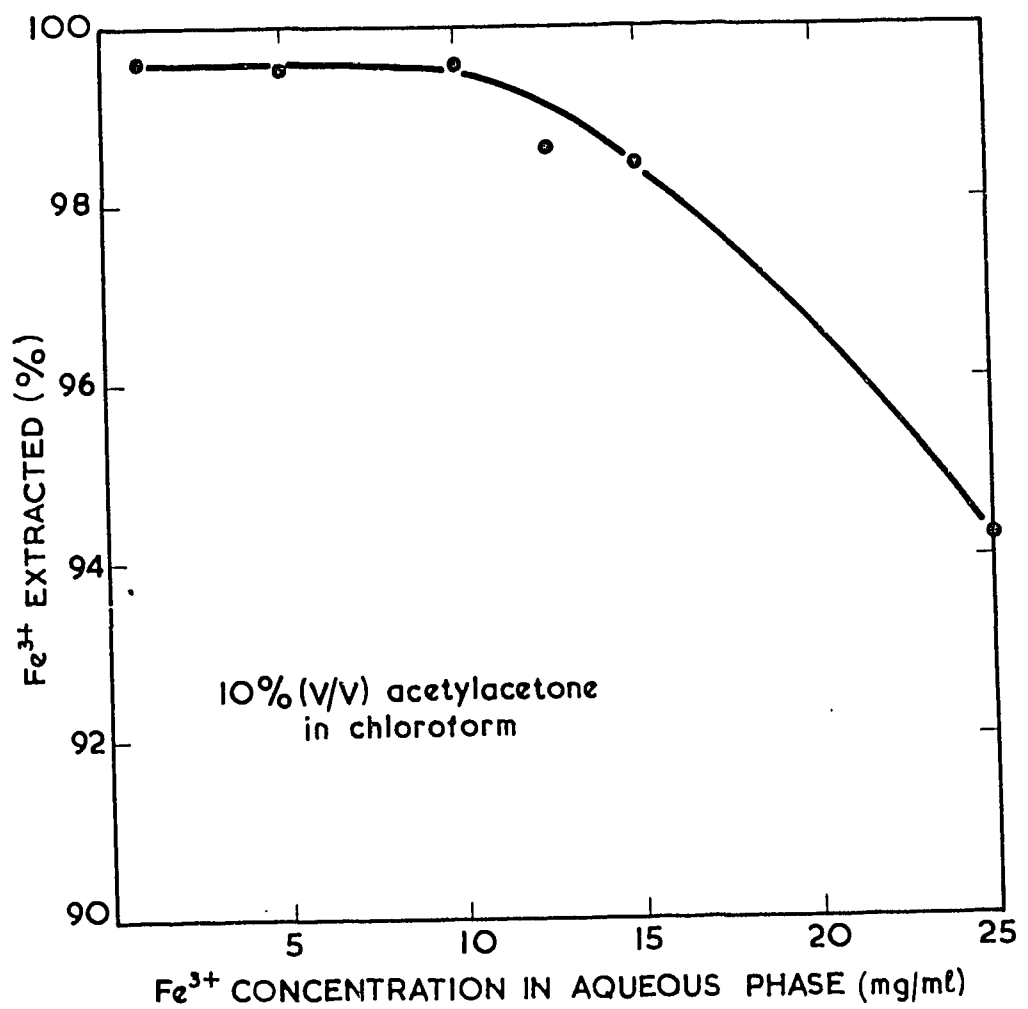


FIGURE 3. EXTRACTION OF Fe³⁺ AS A FUNCTION OF Fe³⁺ CONCENTRATION IN THE AQUEOUS PHASE

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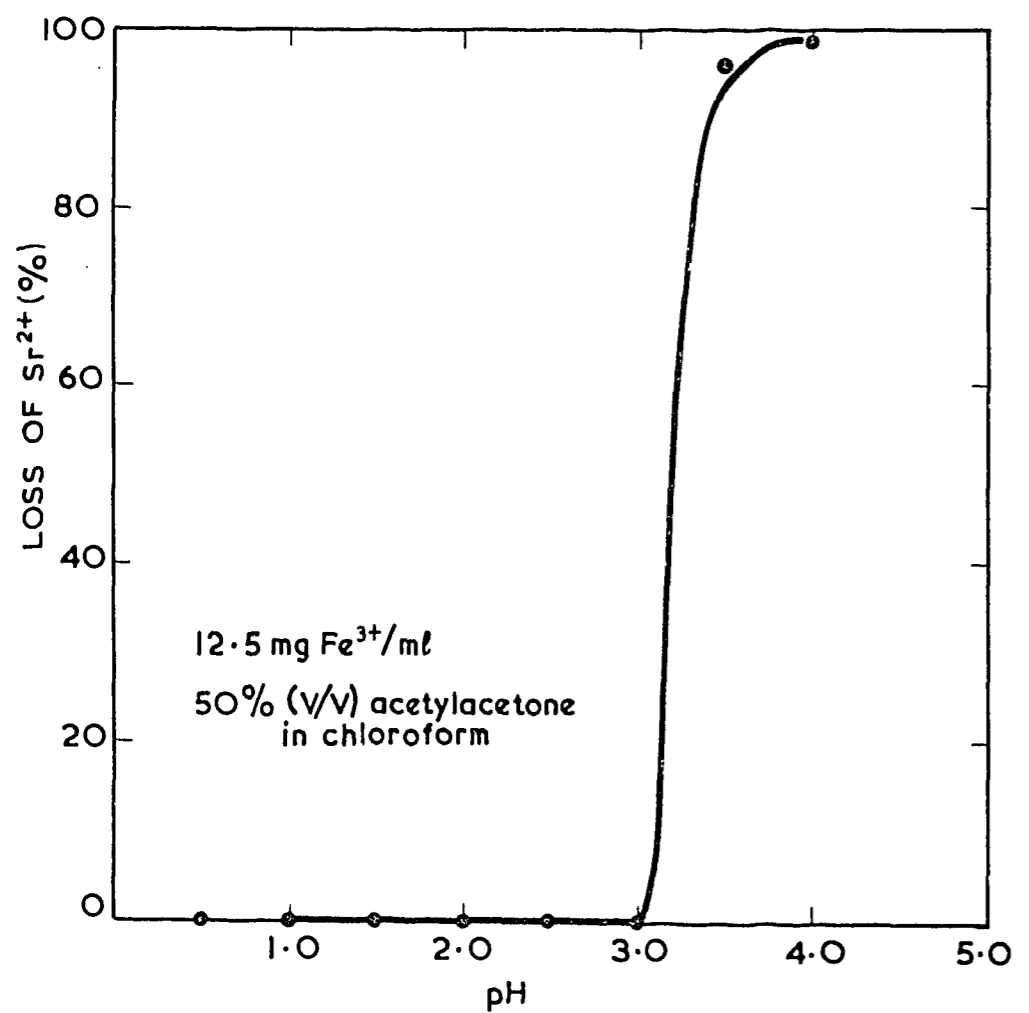


FIGURE 4. LOSS OF Sr²⁺ DURING Fe³⁺ EXTRACTION AS A FUNCTION OF pH

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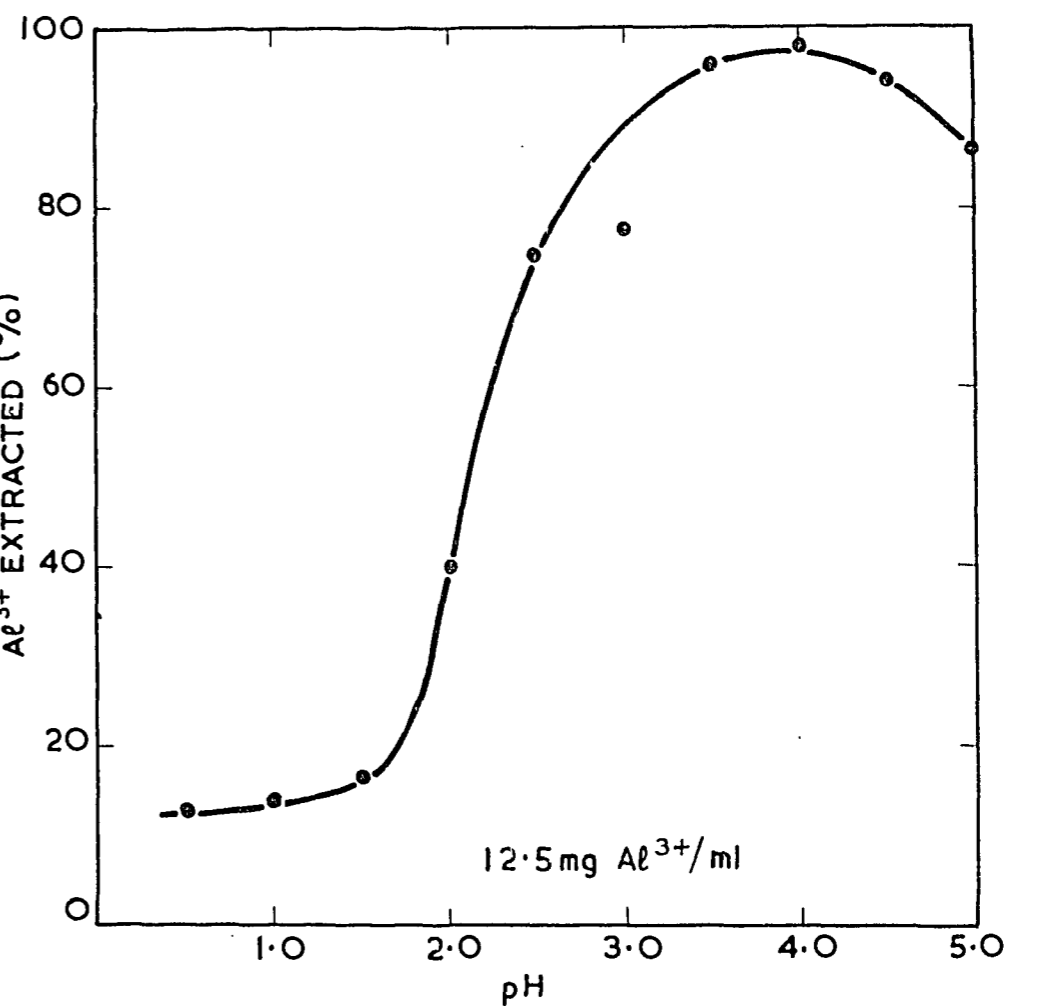


FIGURE 5. EXTRACTION OF Al³⁺ AS A FUNCTION OF pH

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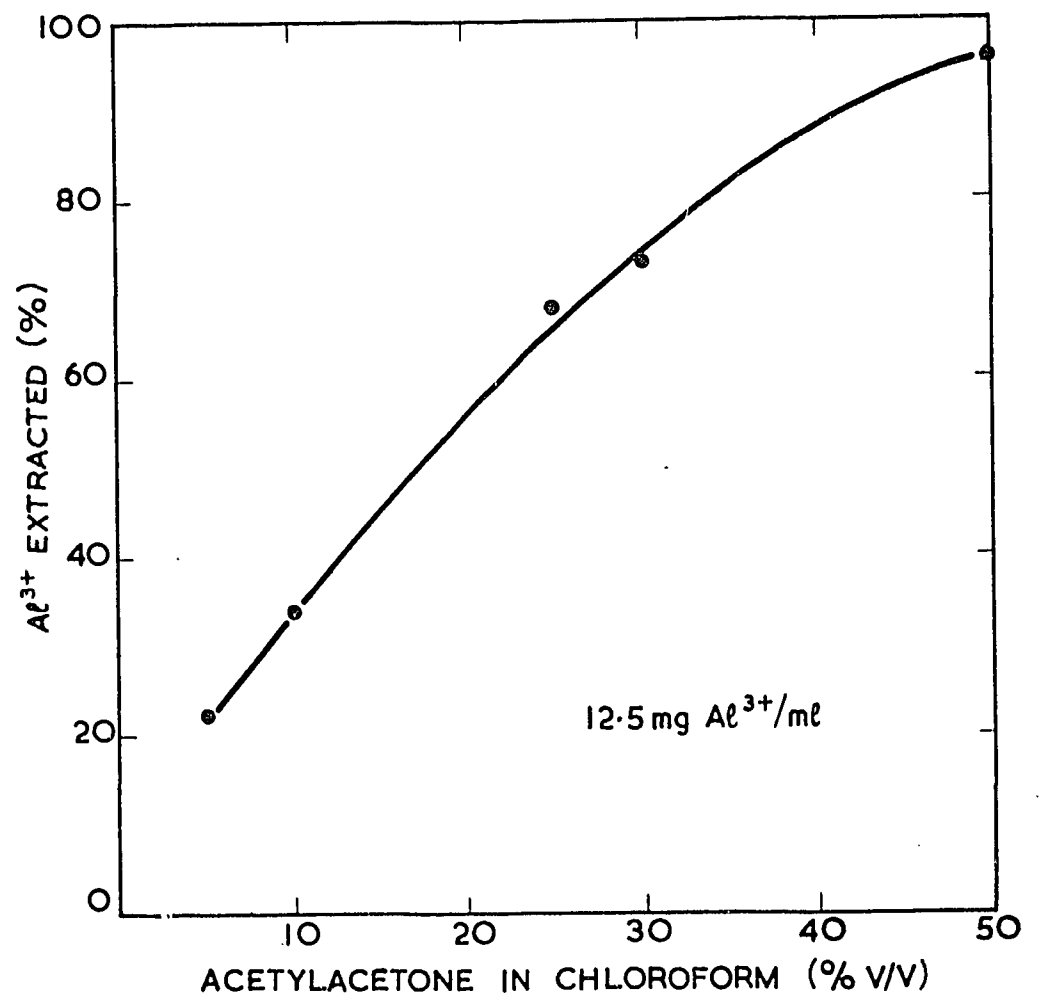


FIGURE 6. EXTRACTION OF Al³⁺ AS A FUNCTION OF ACETYLACETONE CONCENTRATION IN CHLOROFORM

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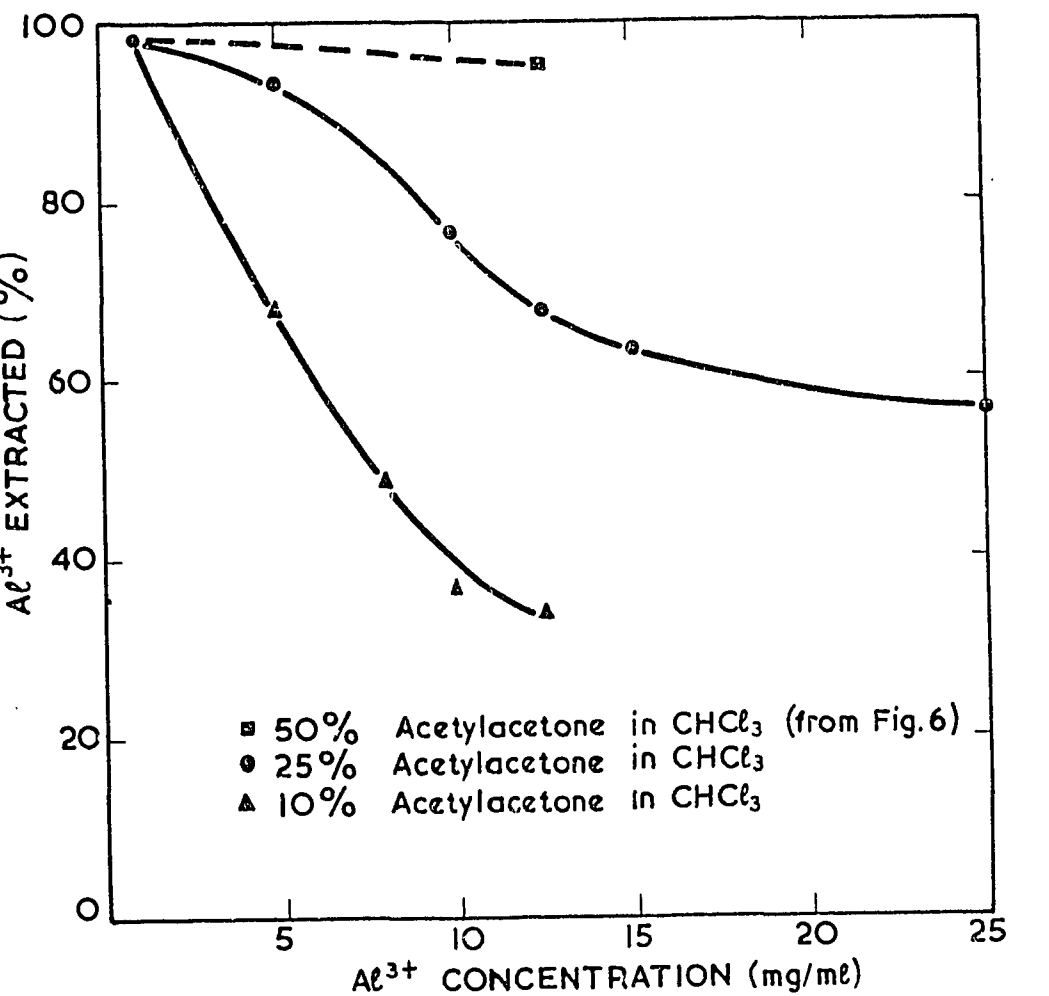


FIGURE 7. EXTRACTION OF Al³⁺ AS A FUNCTION OF Al³⁺ CONCENTRATION

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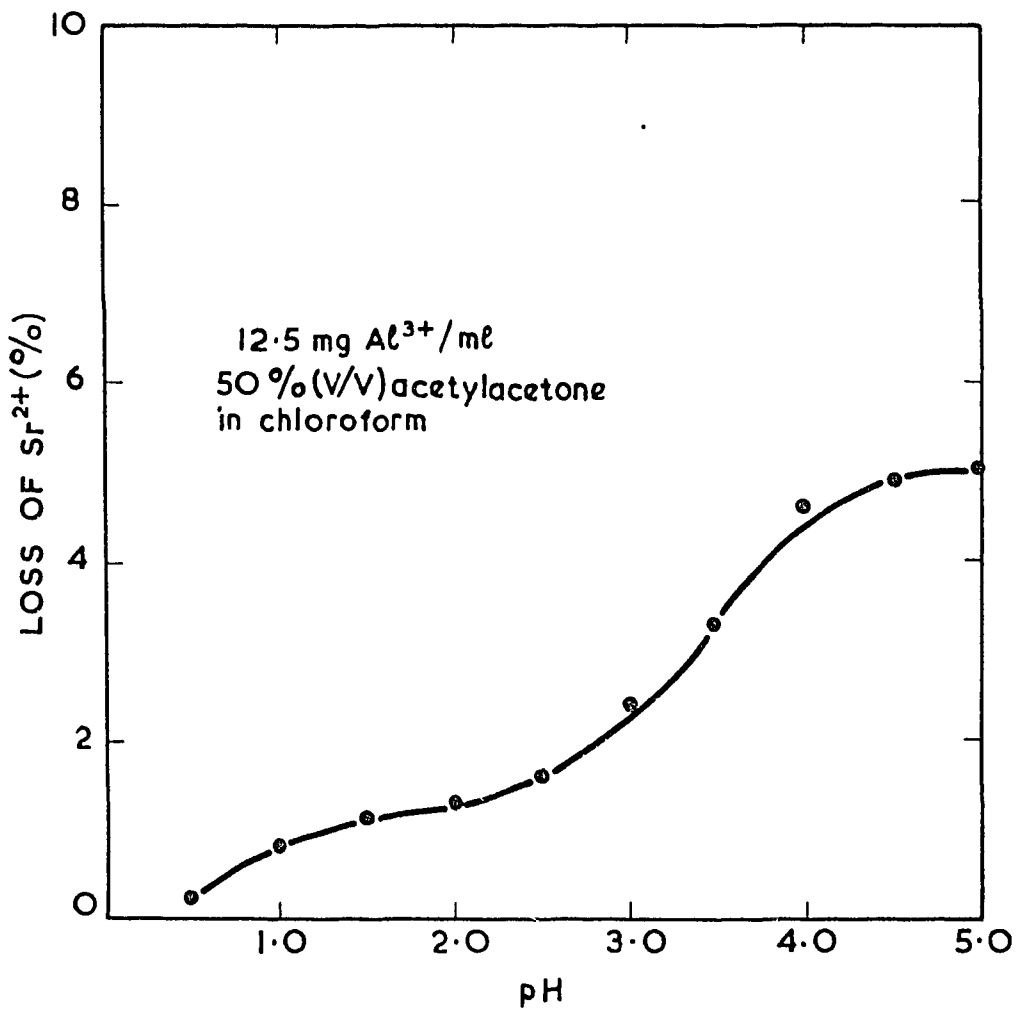


FIGURE 8. LOSS OF Sr^{2+} DURING EXTRACTION OF Al^{3+} AS A FUNCTION OF pH