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RESEARCH AND DEVELOPMENT BRANCH

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"SALT INVESTIGATIONS .. RECOVERY OF POTASSIUM FROM SALT BITTERNS"

PART THREE

by

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ABSTRACT

The use of ion retardation as a separation procedure for the recovery of potassium from salt bitterns was investigated. The separation of potassium salts was not sufficiently great to be of practical use. It is unlikely that any variation of the procedure adopted would give an economic recovery of the potassium.

1. INTRODUCTION.

It was suggested that potassium might be recovered from bitterns by an ion retardation procedure (1).

This process involves the use of a unique type of ion exchange resin containing equivalent amounts of both an anion and a cation exchanger incorporated in each resin bead. The aqueous solution to be treated is passed through the exchanger and both cations and anions are adsorbed. When the adsorbing capacity of the resin is utilized as completely as possible the ions are eluted with water. Since the least strongly adsorbed ions are recovered in the first fractions of the effluent, it is possible to obtain a separation of certain ions. In practice a cyclic procedure involving the successive additions of feed and water rinse is used.

A sample of Retardion 11A-8 resin, which is made by polymerizing acrylic acid inside Dowex 1 resin, was obtained from the Dow Chemical Co., U.S.A. This resin was used in the following investigations which were carried out to determine the possibility of recovering potassium from salt bitterns.

2. MATERIAL EXAMINED.

A sample of salt bitterns was obtained from Solar Salt Ltd., in January, 1957. A chemical analysis of the sample, which was designated B.1, gave the following results.

Chemical Composition of Bittern B.1

Constituents		g/l.
Sodium,	Na	71.0
Potassium,	K	10.25
Magnesium,	Mg	36.5
Calcium,	Ca	nil
Chloride,	Cl	186.2
Sulphate,	SO_4	50.4
Carbonate,	CO_3	0.5
Bromine,	Br	1.76
Specific Gravity at 29°C		1.248

3. ANCILLARY MATERIALS.

3.1 "Retardion" Resin

Approximately 3 ounces of Retardion 11A-8 experimental resin was received from the Dow Chemical Company, U.S.A. This resin was used in all of the tests.

3.2 Chemical Reagents

The synthetic solutions used in the tests were prepared by dissolving "AnalaR" grade reagents in distilled water. All solutions contained both chloride and sulphate ions in a similar proportion to that of the bittern sample. The composition of each synthetic solution was determined by analysis.

4. EXPERIMENTAL PROCEDURE.

4.1 Resin Column

The resin column was prepared by suspending 70 grams of moist Retardion 11A-8 (50 to 100 mesh) resin in distilled water in a glass column 1.55 centimetres in diameter. The volume of the wet settled resin was 96.5 millilitres and the height of the resin in the column was 52 centimetres. The moisture content of a small sample of the resin was determined and the weight of resin in the column was calculated to be equivalent to 44 grams of dry "as received" resin. The total volume of water in the column was found to be 36.5 millilitres. Two burettes of 50 and 250 millilitres capacity respectively were suspended above the column and were connected to two pieces of glass tubing which passed through the rubber stopper at the top of the column. This enabled the cyclic introduction of water and feed solution without interruption to the flow of liquid through the column. The flowrate of 2 millilitres per minute was obtained by adjusting a screw clamp attached to the outlet tube at the bottom of the column.

4.2 Separation Tests

The feed solution to be tested was added to the column from the 50 millilitre burette, while at the same time water was displaced from the bottom of the column at the desired flowrate. When the required volume of feed had been added, the water rinse was run into the column from the 250 millilitre burette. All additions were made so as to minimise mixing. The addition of water was continued until the concentration of salts in the effluent was sufficiently low.

The resin was allowed to reach equilibrium prior to each test by repeating the successive additions of feed and water rinse for 4 or 5 cycles. Then the addition of feed and rinse was repeated, and small samples of the effluent were collected throughout the cycle. The fractions were analysed to determine the efficiency of the separation and to obtain a material balance. The resin was assumed to be in equilibrium when a material balance could be obtained on the feed and effluent solutions. The experimental data were plotted graphically to enable the separations obtained in each test to be observed easily. Since the composition of the effluent was not determined continuously but in separate samples, it was necessary to idealise the curves and to estimate the heights of some of the peaks.

5. RESULTS.

5.1 Separation of Potassium from Sodium

Two tests were carried out. In the first test the concentration of both sodium and potassium in the feed solution was 1.0 normal and in the second the composition of the feed approximated to that of salt bitterns with all of the magnesium replaced by an equivalent amount of sodium. Both solutions contained chloride and sulphate ions in a similar proportion to that of the bittern. Effluent samples of 15 millilitres volume were taken throughout both tests. These were analysed for sodium, potassium, chloride and sulphate and a material balance on feed and effluent samples showed that the resin behaviour was in equilibrium for both tests. The separations obtained in the first 200 millilitres of effluent are shown graphically in Figures 1 and 2. The water rinse was continued and in both instances the chloride concentration had decreased to 0.06 grams per litre when the total effluent volume was 400 millilitres.

5.2 Separation of Potassium from Magnesium

The composition of the feed solution was similar to that of salt bitterns but with all of the sodium replaced by an equivalent amount of magnesium. The operating conditions were similar to those of the previous tests with the exception that the effluent samples were 20 millilitres in volume. The separations obtained are shown graphically in Figure 3. The elution with water was continued beyond the stage shown in the graphs and the chloride concentration decreased to 0.6 grams per litre when the total effluent volume was 500 millilitres.

5.3 Separation of Potassium from Bitterns

The feed solution for this test was a sample of bittern, B.1, which had been diluted slightly to prevent the crystallizing of salts in the resin column. The operating conditions were similar to those of the previous tests. Effluent samples 20 millilitres in volume, were collected and analysed for sodium, potassium, magnesium, chloride and sulphate. The results are shown graphically in Figure 4. Further elution with water gave an effluent containing 0.6 grams chloride per litre when the total volume of effluent was equal to 500 millilitres.

6. DISCUSSION.

In all four tests there was a reasonable separation of the sulphate and chloride ions as shown by the spacing of the effluent peaks. This introduced a complication in that two separate peaks, one in the chloride-rich and one in the sulphate-rich portions of the effluent, were obtained for each of the cations.

Magnesium was the most difficult cation to elute from the resin with water. Only about one half of the magnesium ions were removed by 200 millilitres of water in the separation of potassium from bitterns (Fig. 4). There was a slight separation of potassium from both sodium and magnesium as shown by the slight differences in the positions of the effluent peaks. The separations would not be of practical use because it would be possible to obtain only a slightly enriched solution containing a relatively small proportion of the original potassium.

Since the potassium concentration of the bittern was relatively low it would be necessary to continue the washing until the effluent contained very little salts in order that the potassium enriched fraction of the next cycle would not be excessively contaminated. For the separation of potassium from sodium a volume of 200 millilitres rinse water would be sufficient but in the other two separations where magnesium was present a much larger volume would be required. Since only 10 millilitres feed solution were used, the major part of each cycle would consist of the elution with water.

It is probable that the separations could be improved by heating the solutions and by reducing the flow rate. Neither of these possibilities should be considered from a practical point of view because of the costs involved in heating large volumes of solution and the inefficient use of the resin at low flow rates.

Precipitation of the sulphate with calcium chloride prior to ion exchange would eliminate the difficulties due to double elution peaks which were obtained for each of the cations. The separations obtained in the chloride rich fractions of the eluate were not very great, and the costs involved would be excessive. Large volumes of rinse water would still be required to ensure complete removal of the magnesium.

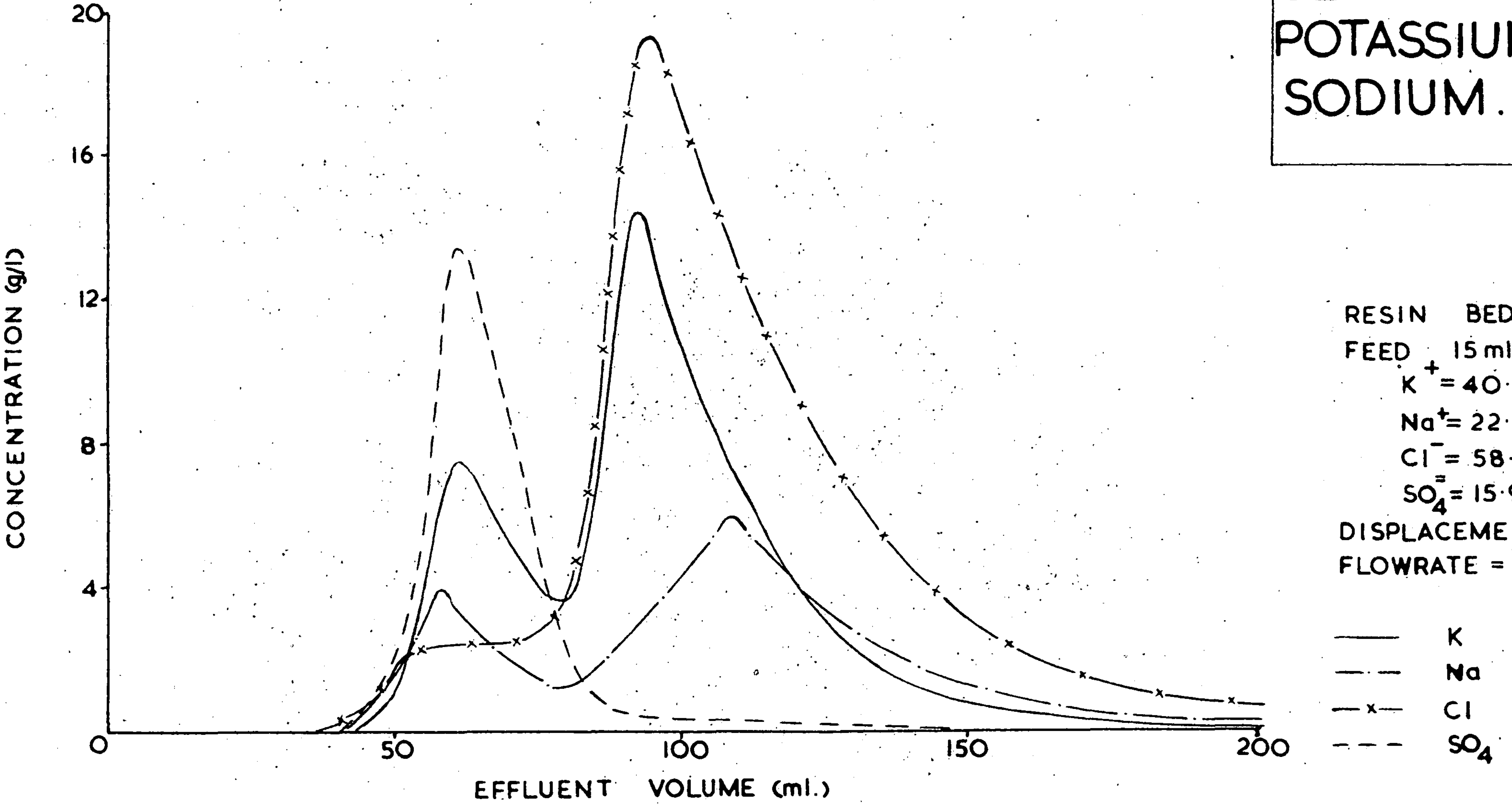
7. CONCLUSION.

The investigations have shown that effluent fractions slightly enriched in potassium can be obtained by passing feed solutions containing potassium, sodium and/or magnesium through Retardion 11A-8 ion exchange resin and rinsing with water. The separations were not sufficiently great to be of practical use in the recovery of potassium from salt bitterns. It is unlikely that any variation of the procedure would result in the economic recovery of potassium salts.

8. LITERATURE REFERENCE.

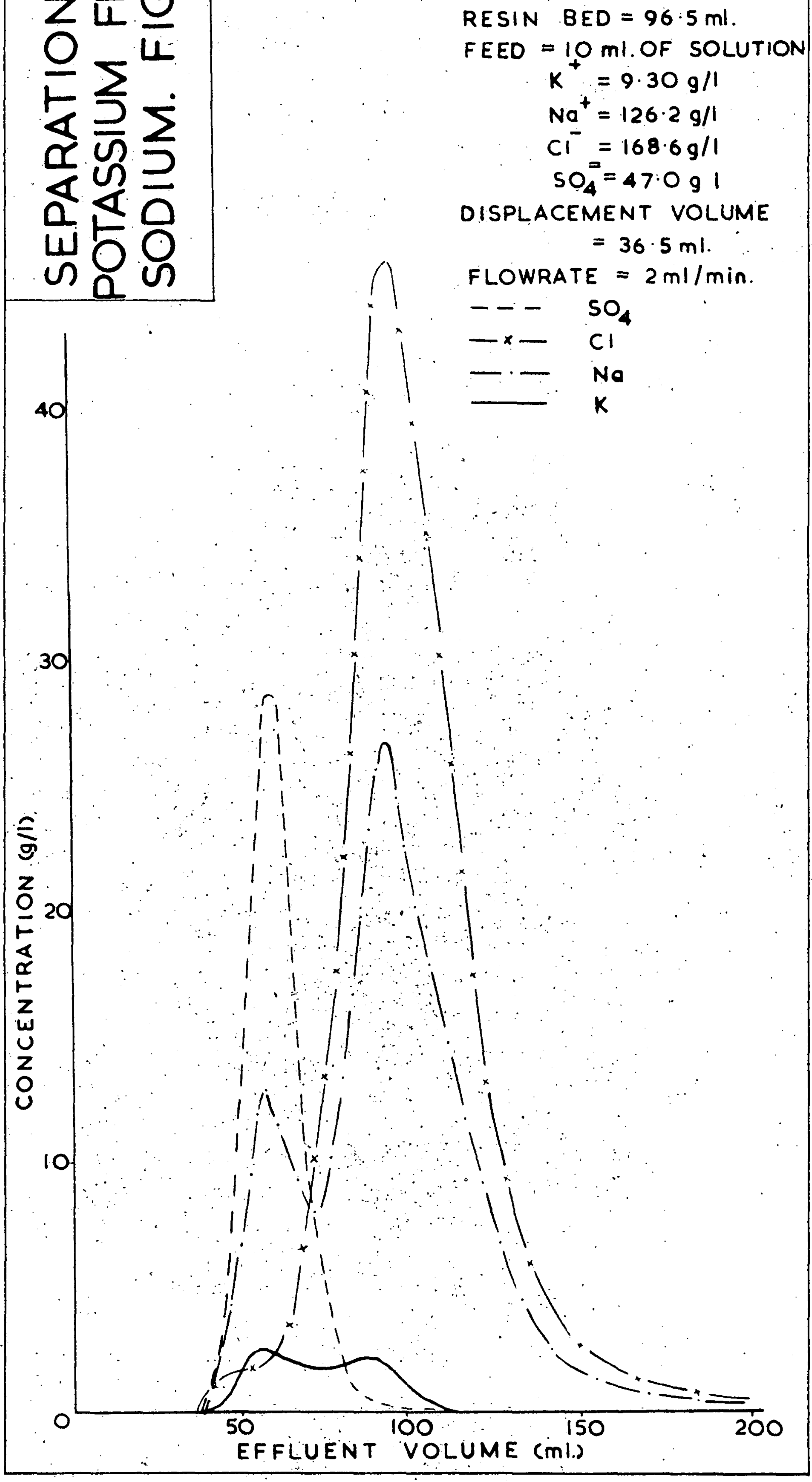
(1) "Ion Retardation" .. Dow Chemical Co.
April, 1957.

SEPARATION OF POTASSIUM FROM SODIUM. FIG. I.

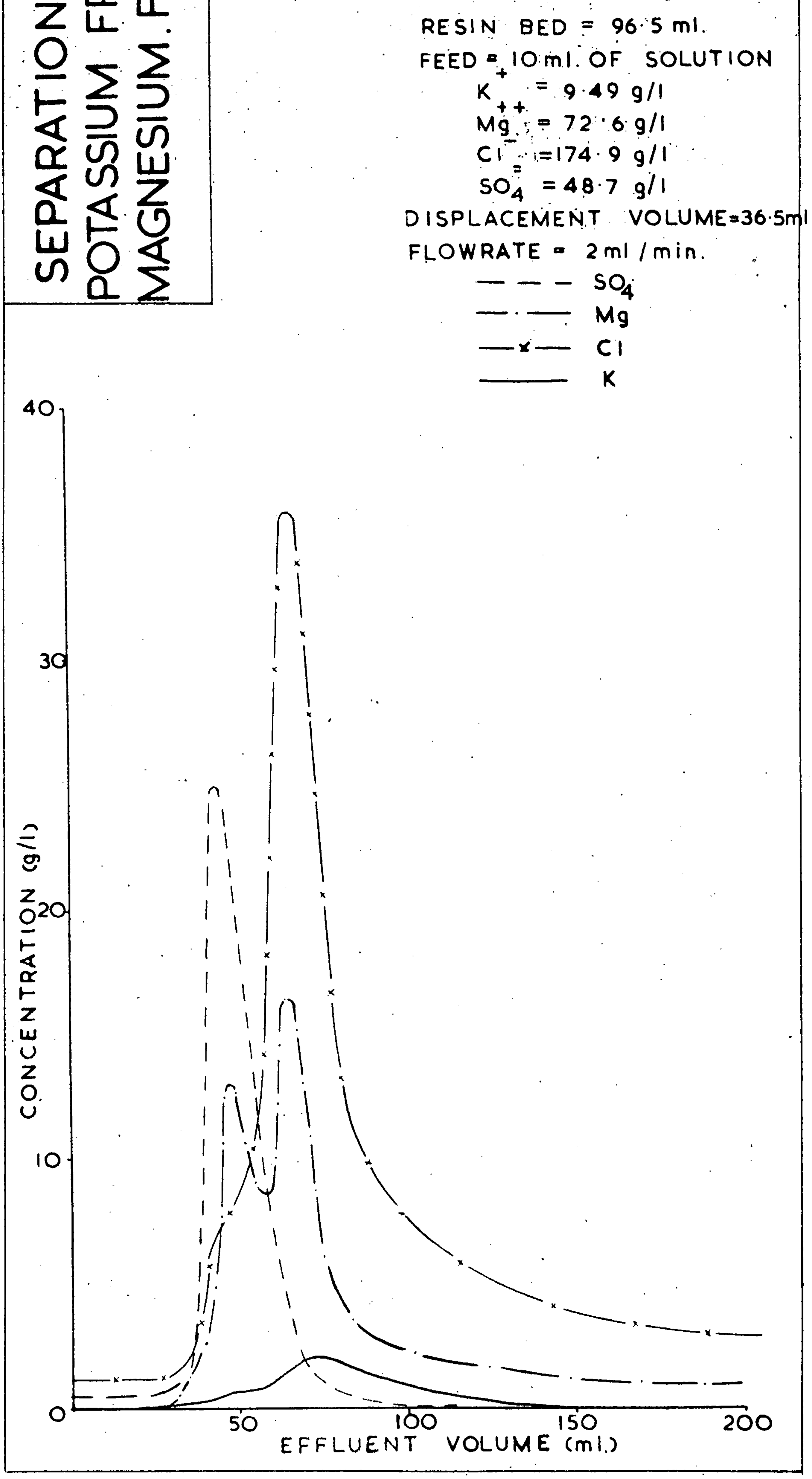


RESIN BED = 96·5 ml.
FEED 15 ml. OF SOLUTION
$K^+ = 40{\cdot}1$ g/l
$Na^+ = 22{\cdot}3$ g/l
$Cl^- = 58{\cdot}7$ g/l
$SO_4^= = 15{\cdot}9$ g/l
DISPLACEMENT VOL = 36·5 ml.
FLOWRATE = 2 ml / min.

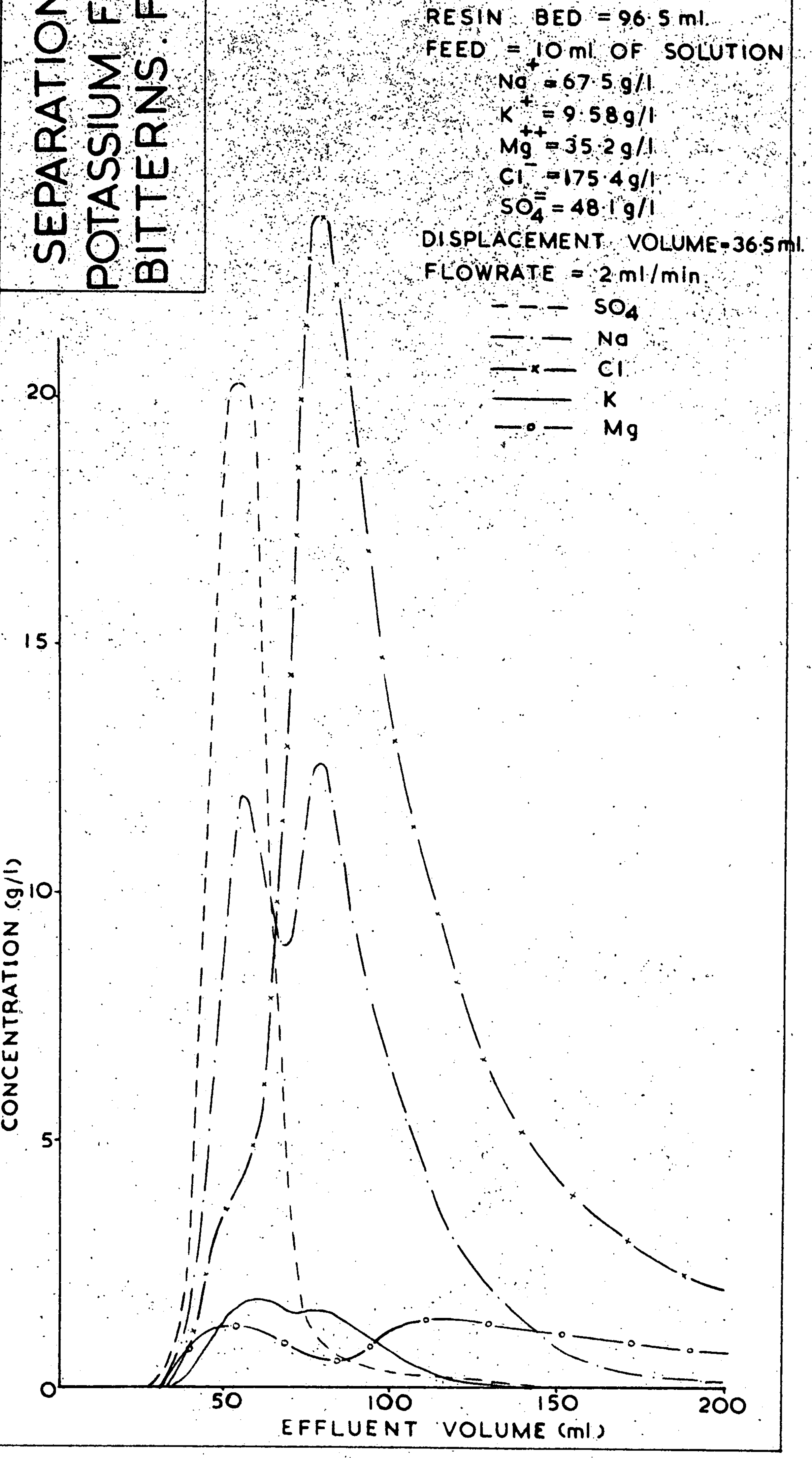
SEPARATION OF POTASSIUM FROM SODIUM. FIG. 2.



SEPARATION OF POTASSIUM FROM MAGNESIUM. FIG. 3.



SEPARATION OF POTASSIUM FROM BITTERNS. FIG. 4.



RESIN BED = 96·5 ml.
FEED = 10 ml. OF SOLUTION
Na^+ = 67·5 g/l
K^+ = 9·58 g/l
Mg^{++} = 35·2 g/l
Cl^- = 175·4 g/l
$SO_4^=$ = 48·1 g/l
DISPLACEMENT VOLUME = 36·5 ml.
FLOWRATE = 2 ml/min