CONTENTS ENVELOPE 4485.

DME 2273/61.

TENEMENT: NOT RELATED.

TENEMENT HOLDER:

2277/61

STATE PROJECT

Period Ending 27th April, 1962

RECOVERY OF POTASH FROM BITTERNS.

Project 1/1/46

Test Work using 1" Moving Bed Contactor

Three continuous runs have been done simulating the potassium recovery section by stripping potassium form resin with hydrochloric acid. The runs were done at various liquid flowrates to determine the length of column section required at different flowrates and also the stripping efficiency. The lowest flowrates represented the shortest possible column section and the highest a normal plant scale flowrate.

The analytical results on samples from the first run have just become available and these have indicated that the potassium strength obtained in the liquid was very much stronger than that obtained in the fixed bed test work. It appears to be high enough to permit the potassium concentration section to work.

The second critical section in the column is the bottom section, where the acid is regenerated from resin ex the potassium section by the sodium in the bitterns.

Runs have been planned to simulate the conditions in this section. These will be followed by runs simulating the other two sections.

Test work in ½ inch fixed bed.

Some of the test work on the potassium loading section has been repeated using Dowex 50 resin. Analytical results have not become available.

The results of the first continuous run have indicated that the potassium recovery section could be shortened if the presence of slight acidity in the liquid stream from the section is not serious. A series of runs has been planned to investigate the effect of this acidity on the operation of the lower sections.

Investigation and report by I.C. Schomburgk.

(F.R. Hartley)
Officer-in-Charge
Industrial Chemistry Section

ICS:RK

The Recovery of Potassium from Bitterns - 1/1/46

The analysis of samples from the runs done in the ½-inch bed column during January have been done and examined.

These indicate that the sodium-potassium separation can be done in reasonably short column section.

The results for the potassium loading section indicated errors in preliminary assumptions and this test work has been replanned and repeated. The analysis of samples has been completed, but the results have not been examined in detail.

The test work showed that the reflux stream from the potassium recovery section was too low and four additional runs have been done to determine the optimum and strength for stripping. The analysis of samples has been completed but the results have not been examined in detail.

Examination of the analysis and correlation of data has been started and when completed further test runs will be done in the ½-inch columns to determine data for the acid recovery section.

The valves required for the 1-inch moving bed column have been received and reassembly of the column has started. A further program of resin movement is planned which will be followed by the start test work on the potassium recovery and concentration sections.

It is planned to do test work in the column on pairs of adjacent sections initially, and this will be followed by test work with the complete system.

Investigation carried out by I.C. Schomburgk

in your reply
ADC 1/0

19th June, 1962

Your reference

The Director,
Department of Mines,
Rundle Street,
<u>ADELAIDE</u>.

Dear Sir,

Enclosed are two copies of progress reports for the period ending 25th May, 1962, on each of the State projects being investigated by our Industrial Chemistry Section.

Yours faithfully,

Dixon

for L. Wallace Coffer
Director.

PD:db
Encs 10

2273/61

STATE PROJECT

Period Ending 25th May, 1962.

RECOVERY OF POTASH FROM BITTERNS.

Project 1/1/46

Test Work Using 1 inch Bed Moving Contactor

No continuous test work has been done during this period.

The analytical results from the three continuous runs simulating the top section of the column done during April have become available. As reported previously the results of the second run, under full reflux, showed a satisfactory potassium strength in the reflux stream.

The results of the other two runs have been checked and show unsatisfactory material balances, and that closer control of the operation of the column is required, and particularly a more positive control over resin flowrate.

Extra glass sections ordered for the column have been received and installed. These have increased the column length by 2 feet 6 inches and provision has also been made for withdrawal of liquid samples from the column at intermediate points during operation for control purposes.

Test Work in ½ inch Bed Column

Analytical results of potassium stripping test runs on Dowex 50 show potassium elution characteristics very close to those of Permutit 225 and that the elution rate at a lower flowrate, viz. 1.5 gpm/sq.ft. against 6 gpm/sq.ft. is not much faster.

One test run has been done to investigate the rate of stripping acid at the bottom of the column. These results have indicated that the bottom section of the continuous column should be 6 feet long.

Test Work Planned for Period Ending 30th June, 1962.

Continuous runs simulating the bottom section of the complete column and continuous runs simulating the potassium stripping section.

Test runs in ½ inch column to determine (1) the effect of the presence of 1-8 g/l HCl in the effluent from the potassium recovery section.

(2) The length of the potassium stripping section and the effect of flowrate.

Investigation and report by I.C. Schomburgk.

(F.R. Hartley)
Officer-in-Charge
Industrial Chemistry Section.

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STATE PROJECT

Period Ending 20th July, 1962

Project 1/1/46

RECOVERY OF POTASH FROM BITTERNS.

An experimental run was operated on the 1 inch equipment, simulating continuous operation of the bottom section of the contacter where resin in the hydrogen form is stripped with sodium chloride. High reflux conditions were maintained. All the analytical results have not been assessed for this run.

The officer concerned with this project has left and further experimental work will be postponed. However there has probably been sufficient work done to prepare a reasonable estimate of the costs and technical feasibility of the operation. This will be undertaken as soon as possible.

Reported by F.R. Hartley.

(F.R. Hartley)
Officer-in-Charge
Industrial Chemistry Section

FRH:RK
25th July, 1962.

Recovery of Potash from Bitterns - 1/1/46

Test work in 1 inch moving bed contactor

13/7/62

2273/61

No continuous test work has been done during this period, however all modifications to the contactor have been completed.

Test work in $\frac{1}{2}$ inch column

13/7/62

Eight complete series of runs have been done to determine the effect of free acid in the reflux from the potassium stripping section on the operation of the other sections. The analytical results from these runs have not become available yet.

Investigation and Report by I.C. Schomburgk.

(F.R. Hartley)
Officer-in-Charge
Industrial Chemistry Section

7273/61

The Australian Mineral Development Laboratories

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Telegrams: "AMDEL", Adelaide.
Address all communications
to the Director.

CONYNGHAM STREET,
PARKSIDE,
SOUTH AUSTRALIA.

Please quote this reference
in your reply
IC 1/1/46

Your reference

9th November, 1962

The Director,
Department of Mines,
Rundle Street,
ADELAIDE.

16 NOV 1962

RECOVERY OF POTASH FROM BITTERNS

PROGRESS REPORT

13th October to 9th November, 1962

Investigation and Report by: J.D. Hayton

Officer in Charge, Industrial Chemistry Section: F.R. Hartley

L. Wallace Coffer
Director.

RECOVERY OF POTASH FROM BITTERNS

1. INTRODUCTION

Previous work in the Laboratories had shown that certain procedures were technically feasible but probably economically unacceptable.(1)

The application of a continuous counter current ion exchange system was investigated in the Chemical Engineering Group of the Industrial Chemistry Section and a report is being prepared on this aspect of potash recovery. At various times the use of specific reagents for recovering potassium either by precipitation or solvent extraction has been suggested.(2)

This approach to potash recovery appears to be reasonable, and consideration has been given preparing various reagents of this nature at AMDL. However, it was decided to examine first, such reagents as were already available which might prove selective in recovering potassium salts. At AMDL much work has been done on the use of alkyl phosphate- and alkyl amine- type solvents for cation and anion extraction respectively. It was considered that an organic reagent containing sulphonic groups (such as are present in some synthetic ion exchange resins) and also incorporating some of the features of the alkyl phosphates might be useful for extracting potassium selectively.

The reagent visualised should be insoluble or only slightly soluble in water, should be soluble in organic diluents such as kerosene and should have a readily exchangeable cation. Various "Surface Active Agents" were considered for this role, and of those available, "Aerosol OT" supplied by Cyanamid Australia Pty. Ltd., appeared to be the most suitable. Most of the work referred to in this report concerns the use of this reagent.

2. MATERIALS EXAMINED

Aerosol OT

A 75 per cent solution in water as received. The Aerosol was diluted with clear lighting kerosene to give a solution of the desired concentration.

Laboratory Reagents

"A.R." grade reagents were used throughout.

Ion Exchange Resins

"Permutit" Zeocarb 225 and "Dowex" 50W cation exchange resins were used in various experiments. Both resins have an exchange capacity of about 5 milliequivalents (meq) per gram, dry weight.

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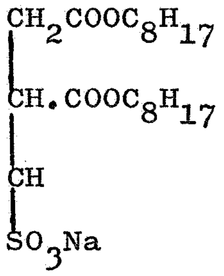
(1) Moyle, F.J. "Salt investigations: Recovery of potassium from salt bitterns" Dept. of Mines South Australia. Research and Development Branch Report RD69 parts 1-4.

(2) Skogseid, Anders: Norwegian patents Nos 72582, 72583,73344.

3. EXPERIMENTAL PROCEDURE AND RESULTS

3.1 Composition of Reagent

Aerosol OT as supplied is said to be the sodium salt of di-octylsulphosuccinic acid with the following composition:



$$\begin{array}{l} CH_2COOC_8H_{17} \\ | \\ CH.COOC_8H_{17} \\ | \\ CH \\ | \\ SO_3Na \end{array}$$

The molecular weight of this compound is 444. Density as measured in the laboratory was 1.07 g/ml.

The "alkyl" groups ($^-C_8H_{17}$) are derived from 2-ethyl hexanol and are thus identical with those present in EHPA, (di-(2-ethylhexyl) phosphoric acid) which has been used extensively for solvent extraction studies.

From the density of the 75 per cent Aerosol solution and the supposed composition, the calculated concentration of sodium in a 10 per cent vol/vol solution in kerosene is:

$$\frac{107}{100} \times 75 \times \frac{23}{444} = 4.16 \text{ g/l}$$

The actual concentration of Na by assay was 4.08 g/l. It can be assumed therefore, that the reagent is relatively pure and of the stated concentration.

The exchange capacity of a 10 per cent vol/vol solution is:

$$\frac{4.08}{23} \quad \text{i.e.} \quad 177 \text{ meq/litre}$$

3.2 Solvent Extraction Procedure

Usually, equal volumes of aqueous and organic phases were shaken in a separating funnel for two minutes and then allowed to settle out. If the phases were slow to separate or were more than slightly cloudy they were centrifuged after preliminary separation. As long as electrolyte was present, there was no change in the volumes of the phases. Aqueous solutions of KCl and K_2SO_4 at various concentrations were used in the preliminary tests. The nature of the anion had no appreciable effect on the amount of potassium extracted.

3.2.1 Effect of Different Diluents

Solutions were made containing 10 per cent by volume of the 75 per cent Aerosol OT in various solvents. Equal volumes of the solutions and 0.25N KCl were shaken for two minutes and the phases were separated, centrifuging if necessary. The results shown in Table I are expressed as the percentage of potassium extracted into the organic phase.

Although the potassium extraction was higher for some of the diluents than for kerosene, and the effect of pH appeared to be more pronounced, there are disadvantages which would preclude their use. Benzene and toluene are toxic and are also expensive, while most of the others formed fairly stable emulsions which were difficult to break up. Methyl isobutyl ketone could be used instead of kerosene for aqueous solutions at pH 4.0 but is slightly soluble in water and would be more expensive. It was decided to continue using kerosene for the remainder of the investigation.

3.2.2 Effect of Acidity

Solutions were adjusted to pH values in the range 1.0-4.0 . There appeared to be little difference in the amount of potassium extracted. At higher acidities (pH 1.0) there was a tendency for the H^+ form of Aerosol to precipitate from the kerosene solution, thus leading to difficulties in phase separation. The phase separation was much better for only slightly acid solutions.

3.2.3 Distribution of Potassium and Sodium

The Aerosol-kerosene solution was shaken with aqueous solutions of KCl and K_2SO_4 of various concentrations, and the concentrations of Na and K in both phases were determined. By comparing the molar ratios of Na and K in the 2 phases, values were obtained for separation factors for potassium with respect to sodium. Table 2 shows some typical results.

3.2.4 Recovery of Cations from Aerosol-kerosene Solution

Stripping with acid was not practicable because the acid (H^+) form of the aerosol precipitated, forming an emulsion which was difficult to break up - in addition, removal of Na and K was inefficient. The use of ion exchange resins for recovering cations from organic solvents has been investigated(1) and shown to have promise. It was decided to apply this technique to the loaded Aerosol-kerosene solutions. 450 ml of an Aerosol-kerosene solutions containing 5.1 g K/l and 0.64 g Na/l was passed through a column containing 50 ml Dowex 50W resin in the H^+ form. The flow-rate was 1 ml/minute, equal to a retention time of 20 minutes. Samples were collected in 40-ml lots until all the organic solutions had passed through. The effluent samples separated into 2 layers because of the effect of the H^+ displaced from the resin, but no emulsion was formed..

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(1) Small, H: "Gel-liquid extraction"
J. Inorg. Nucl. Chem 19
1/2 September, 1961

TABLE 1: EFFECT OF VARIOUS DILUENTS FOR AEROSOL OT

Diluent	Aqueous Phase		Organic Phase		Condition of organic phase
	Init. pH	Final pH	K g/l	K extd %	
Petroleum ether	1.0	1.2	3.5	36	Clear
	4.0	3.8	4.1	43	"
Benzene	1.0	1.3	3.2	33	"
	4.0	3.7	4.0	41	"
Toluene	1.0	1.3	3.9	41	"
	4.0	3.7	4.7	49	"
Cyclohexane	1.0	1.3	3.2	33	Emulsified
	4.0	3.8	3.1	32	"
Carbon-tetrachloride	1.0	1.1	2.6	27	"
	4.0	3.8	3.2	34	"
Chloroform	1.0	1.2	3.2	33	"
	4.0	3.8	4.6	48	"
Methyl-isobutyl ketone	1.0	1.3	1.5	16	Clear
	4.0	3.7	4.1	43	"
Trichlorethylene	1.0	1.0	3.5	37	Emulsified
	4.0	1.4	4.0	42	"
Perchlorethylene	1.0	1.0	3.3	35	"
	4.0	2.1	3.9	41	"
Kerosene	1.0	1.2	3.52	35	Clear

TABLE 2: DISTRIBUTION OF Na,K IN AEROSOL OT-KEROSENE SOLUTION

K Solution	Init. pH	Aqueous Phase Na/K	Organic Phase Na/K	Separation factor for K o/a
0.125N KCl	3	1.78	1.04	1.71
0.25 N KCl	1	0.85	0.49	1.74
0.25N KCl	2	1.04	0.61	1.70
0.50N KCl	2	0.39	0.25	1.56
0.50N KCl	4	0.39	0.25	1.56
0.50N K_2SO_4	4	0.45	0.28	1.60

The separated layers of a bulk sample of the organic solution were assayed to determine the distribution of Na and K. The results were:

	Na ppm	K ppm
Top layer, colourless, (kerosene)	3	0.5
Bottom layer, viscous, pale yellow (probably a "Sol" of H+ form Aerosol)	119	770

Thus virtually all of the Aerosol was displaced from the kerosene solution when converted to the H^+ form. However, it was found later that the 2 layers recombined when the organic solution was shaken with neutral salt solutions.

There were only very small amounts of Na and K in the effluent fractions, the final samples containing 0.082 g Na/1 and 0.42 g K/1. The column was thus not fully loaded; in fact, it was calculated that only 75 per cent of the exchange capacity had been used.

The remaining Aerosol was displaced from the column by kerosene and the column was then drained and expanded by back washing with water. The Na and K were recovered from the resin by eluting with 10 per cent HCl at a flow-rate of 1 ml/min. Samples were collected in 20 ml lots. The total amounts of K and Na collected were determined from the assay results for individual samples. The amounts adsorbed and eluted were:

	K g	Na g
Adsorbed on resin	2.22	0.27
Eluted from resin	2.05	0.27

These results are considered satisfactory in view of the probably variations in assays.

Elution curves for K, Na are shown in Figure 1.

The adsorption of cations from the Aerosol-kerosene solution and their subsequent elution with acid appears to be feasible, although the rate of adsorption from the organic solution is somewhat slow.

4. DISCUSSION

A solution of Aerosol OT in kerosene extracted potassium from aqueous solutions, exchanging it for sodium or hydrogen. The separation factor for potassium with respect to sodium was about 1.6 compared with a value of about 1.2 with cation exchange resins. The loaded Aerosol solution could be stripped of cations and converted to the hydrogen form by passing through a column of hydrogen-form cation exchange resin. The cations could then be recovered by conventional elution with either hydrochloric or sulphuric acids.

It is not considered that Aerosol OT would be particularly suitable for recovery of potash from bitterns, but the results are sufficiently encouraging to warrant further investigation of reagents of similar type. There are several aspects in which the Aerosol is unsuitable, the main ones being:

> The reagent is precipitated by acid and displaced from the kerosene solution.
>
> It forms insoluble precipitates with calcium and magnesium, both of which are present in sea water.
>
> It is slightly soluble in water, so that some losses could occur during extraction.
>
> The exchange capacity is fairly low.
>
> The separation factor for K/Na although higher than for ion exchange resins is still not high enough to compensate for other disadvantages.

It is considered that further investigation should be aimed at obtaining reagents which act in a similar manner to the Aerosol but which do not have the disadvantages referred to above. It is unlikely that many of such reagents would be readily available, so the more likely approach would be to prepare materials having certain specified properties. There are several types of reagent which might be successful. One type incorporates the sulphonic acid group as in Aerosol OT and another contains nitro-groups. An example of the latter type which has been used for recovery of potassium is hexanitro-diphenyl amine (dipicrylamine). (1,2). However, attempts which were made in the South Australian Laboratories to recover potash from bitterns using this reagent were not highly successful. Nevertheless further investigation along these lines is considered to be warranted and it is proposed that work should be continued with the objective of developing suitable reagents.

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(1) The extraction of potassium from sea water" Chemical Trade Journal and Chemical Engineer (April 1940)

(2) Japanese Patent No. 174,663 July, 1947

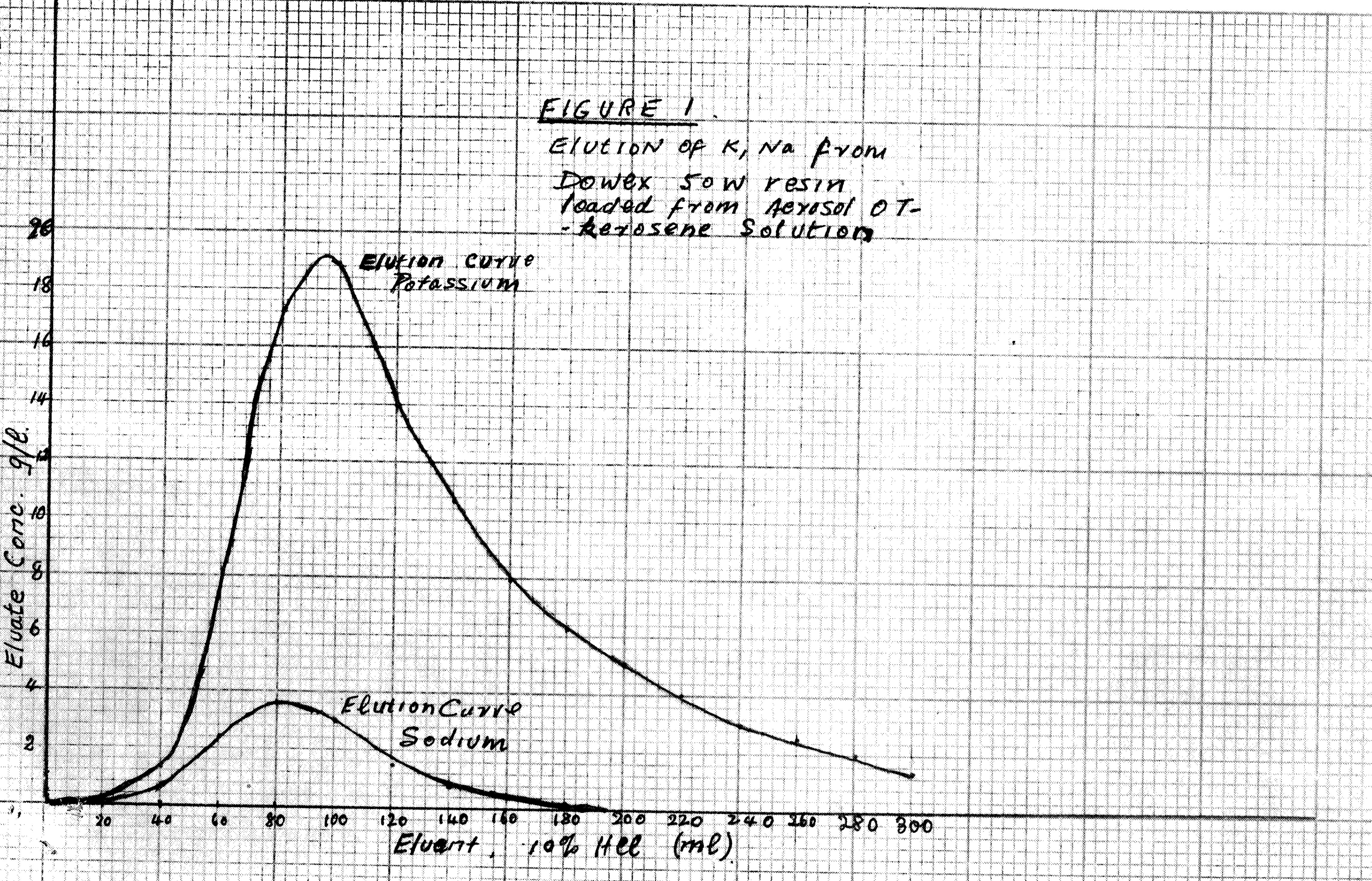

FIGURE 1

Elution of K, Na from Dowex 50W resin loaded from Aerosol OT-kerosene Solution