SECTION II

CHAPTER 5

PRECIPITATION OF POTASSIUM AS POTASSIUM DIPICRYLAMINATE FROM SEA WATER AND BITTERNS AND RECOVERY OF POTASSIUM AS NITRATE OR SULPHATE

1) Review of previous work
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1-REVIEW OF PREVIOUS WORK

A) Selective reagents for precipitation of potassium

Precipitation and separation of individual alkali cations is met with innumerable problems. These are mainly due to variable composition of precipitates, the high solubility of these precipitates in common solvents and non-selectivity of precipitants. In certain cases even the cost and time requirement for detection and estimation is also important. Ammonium carbonate precipitates lithium but not other alkalies. Sodium and lithium salts of hydrochloroplatinic acid and tartaric acid are soluble while potassium, rubidium and cesium salts are slightly less soluble. In the case of hydro-chloro-stannic acid (H_2SnCl_6) and a solution of antimony trichloride in hydrochloric acid, precipitates are obtained only from concentrated solutions of cesium, while rubidium, potassium, sodium, lithium salts are quite soluble. Sodium phosphate (Na_2HPO_4) and ammonium fluoride precipitate lithium salts. Konincks reagent (mixture of $Co(NO_3)_2$+ 10 parts $NaNO_2$ + 100 parts H_2O) is very sensitive in presence of acetic acid or nitric acid for potassium, rubidium and cesium salts. Cesium salt of silico-molybdic acid is less soluble than rubidium and potassium salts, while potassium salts of perchloric acid and Carnots reagent (Bismuth sodium thiosulphate) are less soluble. Similarly hydrofluosilicic acid and potassium pyroantimoniate ($K_2H_2Sb_2O_7$) also give less soluble potassium, rubidium and cesium salts.

Some of the more insoluble double salts of potassium are given in Table 94. Because of the high solubility of salts as seen in Table 94 and similar properties of rubidium and cesium salts, precipitation of potassium alone is considered ~~as~~ difficult.

Table 94 LESS SOLUBLE DOUBLE SALTS OF POTASSIUM
(solubility of g/100 g H_2O at 30°C)

No.	Double salt	Formula	Solubility
1	Potassium tetra fluoborate	KBF_4	0.440
2	Potassium molybdophosphate	$K_3PO_4(MoO_3)_{11}$	0.007
3	Potassium dodeca wolframophosphate	$K_3PO_4(WO_3)_{12}$	0.135
4	Potassium calcium hexacyano ferrate I	$K_2CaFe(CN)_6$	0.125
5	-do- ferrate II		0.685
6	-do- ferrate III		0.410
7	Potassium zinc vanadate	$KZnV_5$014	0.410
8	Potassium barium hexa-cynoferrate	$K_2BaFe(CN)_6$	0.330
9	Potassium -P-chloro benzene sulphonate	$KC_6H_4ClSO_3$	0.730
10	Potassium phenathevene -2-sulphonate	$KC_{14}H_{19}SO_3$	0.273
11	-do- 3-sulphonate	"	0.341
12	-do-10-sulphonate	"	0.820
13	Potassium picrate	$KC_6H_2N_3O_7$	0.500
14	Potassium-2-nitro-4 chlorobenzene sulphonate	$KC_6H_3NClSO_5$	0.860
15	Potassium hexafluosilicate	K_2SiF_6	0.005 (17.5°C)
16	Potassium hexabromoplatinate	K_2PtBr_6	2.02 (20°C)

Precipitation of potassium with a number of complex anions such as hexanitro cobaltate^{III}, perchlorate picrate, fluosilicate, hexachloroplatinate and certain tetraphenyl boron derivatives are in common use, where the solubility of these compounds are further reduced by using organic solvents. The common gravimetric methods for estimation of potassium are (1) chloro platinate method (2) perchlorate method (3) sodium cobaltinitrite method and (4) tetraphenyl boron method. Tetraphenylboron method has solved many difficulties except that the reagent is costly and rubidium, cesium salts are also insoluble. Recovery of the reagent is complicated and uneconomical to use it for the recovery of potassium salt. Recent work[60] has indicated ion exchange columns are useful for selective absorption and separation of potassium from alkali salts.

Potassium forms sparingly soluble salts with many nitro-polynitro organic compounds. The search for a selective reagent for potassium has le~~a~~d to the development of many procedures and selective reagents such as picric acid, dipicrylamine, naphthol-yellow-S, 4,6-dinitro benzo fluroxan, dilituric acid and nitro sulphonic acids. The use of 2 - chloro - 3 nitro toluene - 5 - sulphuric acid for the determination of potassium has been repeatedly tested by several workers[61,62] but so far proved unsatisfactory, owing to high solubility of potassium salt. Among the substitute radicals the nitro-group seems to be most important in rendering the reagent selective and without it, the solubilities are increased ten fold. 2 - 6 dinitrochlorobenzene - 4 - sulphonic acid gives a potassium salt twice as soluble as the salt of mono nitro derivative. Efforts have been made to decrease the solubility by using non-aqueous solvents but the results are not promi~~s~~sing.

Several investigators[62,63] report a variety of organic acids as precipitants for potassium which are chosen because of low solubility of alkali salts. The substitution of a methyl group in the 5 position on the ring in 4 chloro-3 nitro benzene sulphonic acid makes the potassium salt far less soluble but addition of more methyl groups to the ring, destroys its value as precipitant. Some bad effects of methyl or indeed any other group ~~is~~ are seen among the relatives of picric acid. Dermer[62] remarks that it is impossible therefore that substituted picryl amines will exceed or even equal the parent compound in usefulness. He also remarks that in general, little relation can be traced between the structure and solubility of salts. Dilituric acid is a selective reagent (Table 95) but addition of the phenol group to it destroys its value. The introduction of additional groups into the molecules of such potassium reagents as picryic acid, dilituric acid and 2-chloro - 3 nitro toluene - 5 sulphonic acid results in a decrease in its value as a precipitant for potassium.

b) <u>Extraction of potassium from sea</u>

Extraction of potassium from sea water and bitterns with hexyl reagent is reported by various workers. Papers (63,64,65, 66) deal with application of a continuous process not only for sea water but also for solutions containing larger concentrations of potassium salts. The final product obtained is potassium nitrate. A systematic analysis of the alkali group using hexyl reagent (dipicrylamine) is reported by Japanese workers[6]. The method consists of precipitation of potassium, rubidium and cesium together by hexyl reagent. Potassium and rubidium are extracted using a solvent containing dioxane, ammonium hydroxide and xylene. Cesium can be also extracted using 0.1 per cent ammonium sulphate solution containing ethanol.

In another method, (reported by Japanese workers) potassium is precipitated by hexanitro diphenylamine along with rubidium and cesium. The precipitates are converted to chlorides by modified Well's and Stvenson's method. Solubilities of KCl-RbCl-CsCl in 10 ml of solvent containing 4 ml hydrochloric acid saturated with alcohol are 0.075, 1.22 and 11.4 milligrams respectively at 25°C. It is reported that the solubility of potassium chloride depends on the concentration of hydrochloric acid used (which is usually 7 normal). Solvent extraction of potassium with dipicrylamine and similar compounds are reported unsatisfactory. Direct precipitation gives only 66 to 70 per cent results and processes are not economical. It is considered that magnesium can be removed by ion exchange resins but actual experiments show little separations. Perchloric acid and sodium perchlorates are used by some workers. Use of perchlorate 1.5 to 2 times over the stoichiometric ratio gives 97 per cent recoveries at 10°C. Bittern used for the purpose contain 2.72 per cent KCl, 18.78 per cent $MgCl_2$ 5.03 per cent $MgSO_4$ and 5.03 per cent NaCl. Attempts to recover perchloric acid from filtrate using sulphuric acid followed by distillation have resulted in 89 per cent recovery. The Residue is neutralysed with ammonia to explore the possibility of $NH_4 - K - SO_4$ as fertiliser but material has been found not fit for use.

Table 95 Solubility of sodium and potassium salts of nitrophenols and related acids. (soly. at 30°C g/100 g H_2O)

Compound	Na-salt	K-salt	$\frac{\text{Soly.Na-salt}}{\text{Soly.K - salt}}$
2 Chloro-3 nitro P-xylene	93.4	9.21	10.7
Methyl picrate	3.15	3.78	0.88
Chloropicrate	31.2	1.82	18.0
Styphnate	8.43	1.54	5.8
Flarianate	9.8	1.03	10.8
Picrate	5.58	0.755	7.3
Nitranilate	0.724	0.567	1.4
Picrolonate	0.285	0.338	0.89
Dipicrylamide	11.6	0.146	83
Diliturate	1.034	0.086	13

The recent work of J.B. Butt[64] and J.A. Tallamdge carried out with synthetic sea water report occlusion of calcium chloride as impurity which ranges from 0.5 to 22 per cent. Recovery of potassium from bitterns and brines is reported by Kiyoshi[68] using an aqueous solution of magnesium or calcium salt of dipicrylamine. The potassium dipicrylaminate (4 g) is mixed with butanol (80 ml) and hydrochloric acid (0.5 N 24 ml). Potassium chloride goes in solution and free amine separates out. The butanol is recovered from solution by separating funnel. Potassium chloride is recrystallised by evaporation. In another method,[69] sea water is treated with lime to recover magnesium oxide. The filtrate is treated with dipicrylamine to extract potassium salts.

Extraction of bromine and potassium from sea water is reported by Kaznokanzaki[70]. Potassium free sea water containing 0.0006 per cent bromine is treated with 100 kilograms of lime and 1.08 tonnes of hexanitrodiphenylamine and filtered at 25°C. The calcium dipicrylamine reagent is then added to 240 cubic metres of sea water containing potassium and bromine. The potassium salt is filtered and decomposed to give filtrate containing 200 kg KNO_3. The filtrate is acidified with 720 litres of 98 per cent sulphuric acid to pH 3.5 and treated with 8.8 kg chlorine; the bromine is absorbed in sodium carbonate solution and redistilled with sulphuric acid to yield 13.5 kg bromine.

c) Preparation of Dipicrylamine

Austen[71] has prepared hexanitrodiphenylamine by treatment of 2 - 4 - 6 picryl-m-nitroanaline with nitric acid and sulphuric acid mixture. Gnehm[72] during the same year has manufactured it by the action of nitric acid alone on methyl diphenylamine. Neither of these methods are of any practical value on account of high cost of intermediates involved. Merten[73] has prepared it by the action of fuming nitric acid on diphenylamine in concentrated sulphuric acid solution. In 1910 the first published report on the method for the preparation of this compound on large scale is made available. the Method consists of nitration of diphenylamine in concentrated sulphuric acid solution with fuming nitric acid, precipitation in water and purification of the compound by washing with water. By this method 100 parts of diphenylamine has yielded 170 parts of hexanitro diphenylamine.

Carter[74] has developed a method for the manufacture of hexanitrodiphenylamine from dinitrodiphenylamine formed by the combination of one molecule of 1:2:4 chloro dinitrobenzene and two molecules of aniline. The reaction begins slowly at moderate temperature followed by a more energetic one which carries the temperature to 125°C, at which point the charge is drawn in water and extracted with water and dilute hydrochloric acid to remove excess of aniline and the byproduct aniline hydrochloride. Nitration of dinitrodiphenylaniline is affected in two stages. Tetranitro diphenylamine is first prepared using 36° Be(sp.gr.1.33) nitric acid. The reactions are as follows.

1) $C_6H_5Cl + 2HNO_3 = C_6H_3(NO_2)_2Cl + 2H_2O$

chlorobenzene + nitric acid = dinitrochlorobenzene

2) $C_6H_3(NO_2)_2Cl + C_6H_5(NH_2) = C_6H_3(NO_2)_2NHC_6H_5 + HCl$

dinitrochlorobenzene + dinitrodiphenylamine

Claims for good results in laboratory experiments by this method have been made but on large scale it is difficult to control the temperature without drawing the charge before completion of the reaction, since the charge becomes viscous whereby efficient agitation is out of question and temperature shoots to a dangerous point.

3) $C_6H_3\ (NO_2)_2NH\ C_6H_5 + 2HNO_3 =$
Dinitrodiphenylamine + Nitric acid
$= C_6H_3\ (NO_2)_2 - NH - C_6H_3\ (NO_2)_2 + 2H_2O$
Tetra nitro diphenylamine

4) $C_6H_3(NO_2)_2\ NH - C_6H_3(NO_2)_2 + 2HNO_3 =$
(Tetra compound) + Nitric acid
$= C_6H_2(NO_2)_3 - NH - C_6H_2(NO_2)_3 + 2H_2O$
Hexanitro diphenylamine

Earlier method offers greater advantages and has provided basis for further development.

Manufacture of dipicrylamine is carried out by Hoffman[75] and Dame using chlorobenzene and mixed acid instead of nitric acid and have concluded that the reagent can be manufactured with remarkable ease and in good yields from chlorobenzene. They have claimed that none of the successive operations involves slightest difficulty provided nitric acid and sulphuric acid mixture is substituted by 48° Be nitric acid which has been used by Carter for conversion of tetra-nitro compound to hexanitro compound. The possibility of elimination altogether the intermediate preparation of the tetra compound and proceeding in one operation from dinitrodiphenyl amine to reduce time and cost of preparation has been also suggested by the authors.

The new method discussed in U.S.Patent[76] describes that two molecules of aniline and one molecule of chloro-dinitrobenzene are added to three times their combined weight of water and mixture is heated to 60°C and agitated to form an emulsion. Steam is introduced at this stage to raise the temperature to 80°C. The reaction begins during this heating and completes in about an hour. The dinitro compound precipitates in the form of thick cluster of red needles. Agitation at 80°C is continued for one hour to ensure complete solution of aniline hydrochloride after which charge is thrown on filter, washed with dilute hydrochloric acid and water and finally dried. 95 to 100 per cent theoretical yield is claimed and the material melts at 198 to 152°C. 40.5 kg (100 lbs) batches on a large scale has given 85 per cent recoveries. In dinitro to tetra nitro stage, Carter method involves addition of dry dinitrodiphenylamine to nitric acid (40 per cent) at temperature upto 90°C. The nitration is liable at times too serious and almost uncontrollable foaming and secondly use of excessive nitric acid and enamel ware is essential. The new modified method uses mixed acid wherein dinitrodiphenylamine is added to mixed acid containing 30 - 45 per cent HNO_3 and 50 - 40 per cent H_2SO_4 at 70°C and is raised to 80 to 90°C until evolution of NO_2 is at minimum. The charge is then cooled and filtered to recover spent acid. Product is brownish yellow containing small percentage of higher nitration products and can be directly used for final nitration. In tetra to hexanitro stage Carter method uses straight reaction of 90 per cent nitric acid tetranitrodiphenylamine at 40°C to 70°C followed by cooling and filtration. The product by this method consists of finely divided amorphous powder which consequently involves poisoning during handling. Here also it is shown that the mixed acid method is more satisfactory. As the product by this method can be controlled at will from amorphous to crystalline only by varying the proportion of nitric acid to sulphuric acid; 20% HNO_3 + 70 - 75% H_2SO_4 gives amorphous product, while 60% HNO_3 + 40% H_2SO_4 gives crystalline product.

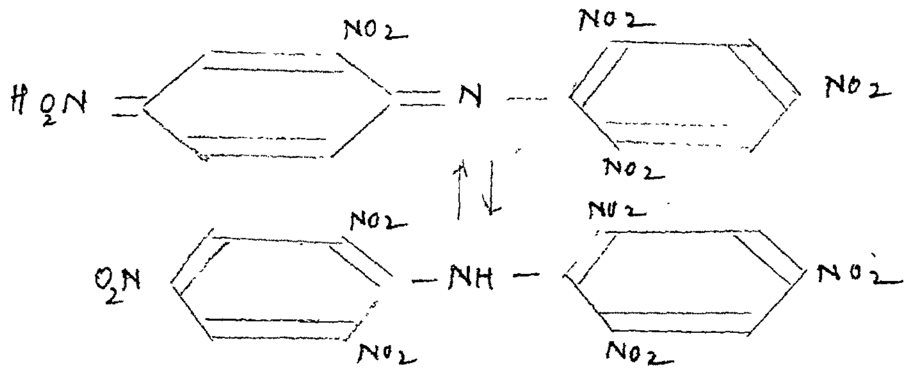
As suggested by Hoffman and Dame[75], the possibility of preparing hexanitro compound in one stage using mixed acid has been tested by the modified method; however cost estimates indicated that two stage process is more preferable.

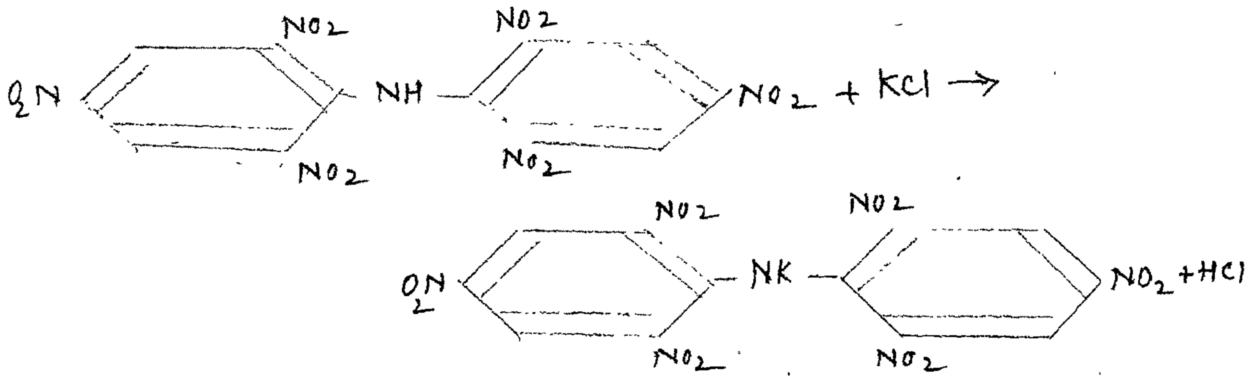
d) Explosive nature of Dipicrylamine

Very meagre information is available in literature regarding the explosive properties of this compound and its salts. Haussermanh[77] compares it with trinitrotoluene while OHO Freiherr Von Schroetter[78] has described an explosive consisting of 80 parts of hexanitro diphenylamine with 20 parts of dinitrotoluene. It is very explosive and scarcely suitable for the explosive purposes except when mixed with other substances. Hexanitrodiphenylamine is more poisonous than nitroglycerin. It causes severe blisters resembling burns when it comes in contact with skin. The fine dust effects destructively the mucuous membrane of the mouth and lungs. The three important properties of an explosive namely 1) stability 2) sensitiveness to detonation 3)explosive powers are tested by the above worker and he concluded that hexanitrodiphenylamine is more sensitive to detonation. It is less sensitive to shock than tetryl and T.N.A and also safer to handle. Hexanitrodiphemylamine as a booster material is superior to T.N.T. but somewhat inferior to tetryl and T.N.A. It is extremely stable and makes a satisfactory booster and its cost of manufacture is cheaper to that of tetryl or T.N.A.

e) Chemistry of Hexanitrodiphenylamine (Dipicrylamine)

Hexanitrodiphenylamine is relatively weak acid. According to Alexandroff[79] hexanitrodiphenylamine is a typical example of pseudo acid. He describes a number of salts and esters of this pseudo-acid. Hautzsch and Opolski[80] describe four tautomeric forms of hexa nitro diphenylamine. It is practically insoluble in water (Table 96) and is obtained as a powder of pure yellow colour finely crystalline needle form which melts with decomposition. Its equivalent weight is 439.23 (m.p.240 to 243°C) and has a sensitivity to direct sunlight which changes its colour to brown. It forms salt like compounds with potassium ammonium, rubidium and cesium which are orange red to deep red coloured crystalline compounds and are sparingly soluble in water. Hexanitrodiphenylamine is insoluble in ether, benzene and alcohol. The best solvent is 48° Be nitric acid from which it separates after a long time as large crystals. The reagent is generally used as calcium, magnesium, sodium or even lithium salt for precipitation of potassium from its solution. The reagent solution is decomposed at 3.5 to 4 pH by addition of mineral acid. Sheintzis has found ~~out~~ that in addition to potassium, rubidium and cesium, metals like thallous thallium, beryllium zirconium, lead and mercury (ic) give coloured crystalline precipitates with the reagent while aluminium, ferric iron, chromium (ic) nickel, cobalt, copper bismuth, vanadium, titanium, thorium and mercury(ous) give colourless amorphous precipitates with the reagent. Hexanitrodiphenylamine hydrolyses with water but is insoluble in dilute acids, chloroform, carbon tetra chloride, dichloroethane and benzene. Solubility data of hexanitro diphenylamine in various solvents is given in literature (Table 96) The solubility of potassium salt and sodium salt is given by Dermer. The potassium salt is soluble in acetone, ether, ethanol, methyl amylketone but insoluble in chloroform, dichloro ethane, carbon tetra chloride and benzene. Hydrolysis of dipicrylamine and its deepening of colour is explained on the change in structure. The beso-form and aciform in which continuous chain of conjugated double bonds effect the deepening of colour. H^+ ions convert orange red aciform to bright yellow water insoluble besoform. (page 285) The formation of the complex with potassium is considered due to replacement of hydrogen atom in the amine group.





The other view is that the formation is due to the replacement of hydrogen atom of the hydroxyl group in the enol form to give a compound having the following structural arrangement. (See page 285)

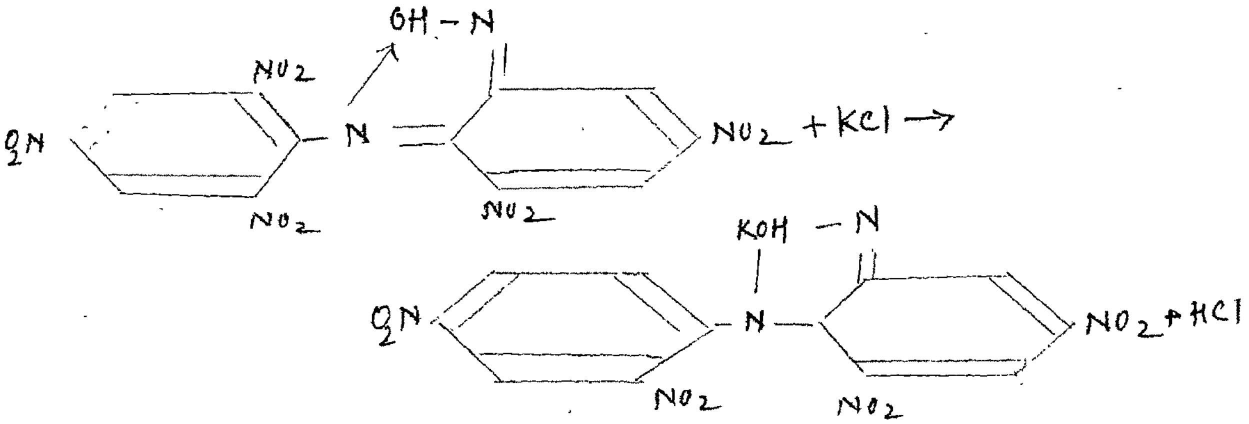


Table 96 SOLUBILITY OF HEXANITRO DIPHENYLAMINE

(g per 100 g of solvent)

Solvent	Formula	Solubility at 17°C	 50°C	 100°C
Water	H_2O	0.0060	0.0150	0.0340
Etheyl acetate	$CH_3COOC_2H_5$	0.8410	1.2510	-
Acetone	$(CH_3)_2CO$	0.5730	1.1490	-
Ethanol	C_2H_5OH(96%)	0.0730	0.104	-
Ethanol	" (100%)	0.0300	0.117	-
Benzene	C_6H_6	0.0000	0.3990	-
Chloroform	$CHCl_3$	0.0000	0.0580	-
Diethyl ether	$(C_2H_5)_2O$	trace	0.0080 at 34°C	-
Triethylamine	$(C_2H_5)_3N$	172.25	485.26 complex	
Carbon disulphide	Cs_2	0.0	0.0180 (at 35°C)	-
Carbon tetra chloride	CCl_4	0.0	0.0620	-
Toluene	$C_6H_5CH_3$	0.1310	0.2930	

F)Dipcrylamine, a reagent for potassium estimation

Poluecktoff[81] is the first to utilise a solution of sodium salt of hexa nitro diphenylamine as a reagent for potassium. Van Nicnwanburge and T.Vander Mock[82] have described the crystal habit of the above salts and recommended the reagent for microchemical detection of potassium even in presence of cesium. Feigl[83] includes the sodium salt of hexanitrodiphenylamine in his review on spot test for potassium. Winkel and Maas[84] give procedures for the quantitative determination of potassium either by weighing or by conductometric titration of a solution of the precipitate in a mixture of acetone and water. Protnov and Afansev[85] using the titration method report an accuracy of 0.5 to 1.5 per cent. Recently Killand[86] has applied the reagent to the colorimetric determination of potassium in fertilizer mixtures by using gradation photometer. Thun R and Winzel, O.[87] have reported that micro determination method using dipicrylamine is unsatisfactory and gives 3 per cent low results. Snell F.D.[88] E.D. Sandell[89] give details for colorimetric estimation of potassium using dipicrylamine as reagent. E. Andur[90] recommends a filter composed of 5.5 mm of corning glass and reports practically a linear relation between extinction and concentration over a wide range of dipicrylamine concentration. C.R. Harrigton[91] and R.H.Cotton[92] have shown applications of the method in determination of potassium in biological samples. Gravimetric and volumetric procedures are given for the determination of micro and Macro ~~Micro~~ quantities of potassium and a colorimetric procedure for determination of micro quantities (10 to 100 gamma) have been improved by I.M. Kolthoff and G.H. Bendix[93]. Their experiments conclusively show that the variation in the results is due to solubility of potassium salt which is increased ten times when the temperature is raised from 0 to 25°C and also the solubility of potassium salt is increased in excess of the reagent. The effect of co-precipitation due to sodium is negligible upto 1/10 ratio of potassium to sodium. The error is raised to 1-6 per cent when the ratio increases 1/18 while with 1/80 ratio error is only 2.5 per cent. In volumetric (acidimetric) determination, the precipitate is dissolved in acetone and water and excess of acid is added to precipitate free amine. The filtrate is back titrated with standard sodium hydroxide solution. Kolthoff and Bendix describe the specific conditions for quantitative determination of potassium and the method is considered useful for accurate estimations of potassium in microquantities . In order to determine potassium in brine and salt samples, the gravimetric estimation of potassium with dipicrylamine reagent has been tested[94] . The results show that the method is fairly accurate in presence of sodium, calcium, magnesium as long as the concentrations of these ions do not exceed the limits set (the ratios of potassium/sodium, to calcium and magnesium are 1:30 1:6 and 1:2 respectively).

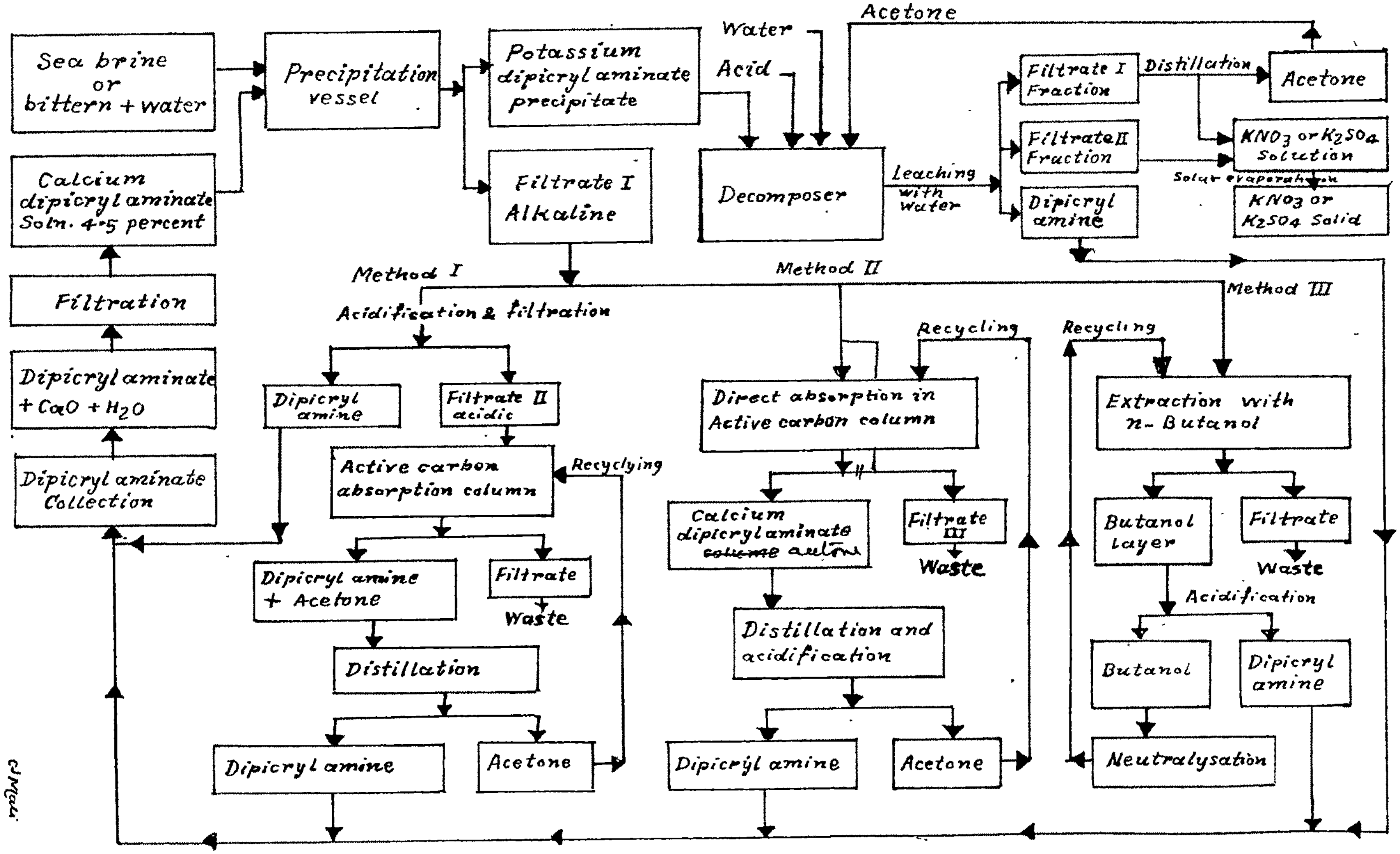
II. Description of the process

The process consists of five steps namely 1) preparation and estimation of the strength of the freshly prepared reagent solution. Hexanitrodiphenylamine (dipicrylamine) is weighed, mixed with a known quantity of calcium oxide and water (0.064 g CaO + 22 g water per gram of dipicrylamine), stirred for four hours and filtered. Fresh reagent is estimated by precipitating free amine with acid. 2) Precipitation of potassium as potassium dipicrylamine from the sea water or bitterns. A sample is first tested on flame photometer for potassium and total potassium content is estimated. Depending on the total potassium content a definite quantity of the reagent solution is added by burette with constant stirring. Sea water requires 9.43 grams of reagent (dipicrylamine) per gram of potassium chloride, while in bittern and concentrated brines 5.89 grams of reagent is sufficient. In case of bittern samples it is necessary to add equal quantity of water to the sample before addition of the reagent; this avoids co-precipitation of sodium and calcium with potassium. (3) Filtration is carried out either by filter sticks as the total precipitate obtained is small compared to the volume of the filtrate to be handled. Filtration can also be carried out in buchner or sintered glass funnels No.G3 is suitable. (4) Decomposition of the precipitate is carried out in a separate vessel where it is treated with acetone and acid after the precipitate is washed with little water. The decomposed mass (yellow) is allowed to remain in the vessel for 15 to 20 minutes with occasional stirring. Care is taken to see that all the red coloured crystals are converted to a yellow (free amine), as unreacted crystals do not decompose once the mixture is diluted with water for leaching the yellow mass to obtain potassium salt in solution. Leaching of the yellow free amine is carried out by addition of 100 ml of water each time till the filtrate is free from potassium salts. Leaching with warm water is helpful. The final washings are tested for potassium by flame photometer or by cobaltinitrite test. First two or three fractions of the filtrate contain acetone which is separately collected and distilled to recover acetone. The total filtrate is then neutralysed with potassium carbonate or hydroxide solution and evaporated by solar energy to obtain potassium salt. (5) Mother liquor obtained after the precipitation of potassium as potassium dipicrylaminate is subjected to decomposition with cheap acid to recover the free amine (unreacted reagent) which is filtered. In case of bittern the main bulk of the reagent is obtained after the decomposition of the precipitates; while in case of sea water treatment almost equal quantities of the reagent is obtained from decomposition of the precipitate and treatment of the mother liquor. Additional recovery of the reagent is carried out from the acidic end liquor solution; which contains on an average 6 to 8 milligrams of reagent per litre. Reagent is adsorbed on the active carbon. (8.4 grams of active carbon is required for per litre of the yellow coloured acidic solution). The treated solution is then filtered or passed through a glass column containing sintered disc and packed with "Hiflo" filter aid material to collect all the carbon particles for the recovery of the reagent.

(6) Elution of the reagent from active carbon bed is carried out after the active carbon is washed with water and dried. Washing of the active carbon bed with dilute sodium carbonate solution to remove all acid is helpful for quicker recovery of the reagent with acetone. Acetone solution containing reagent is distilled to recover acetone for recycling in the operation. Active carbon bed free from reagent is washed with hot water dried and used ag~~ent~~ain for the second batch. It is necessary to add 10 to 15 per cent additional active carbon for the second batch.

Two other methods shown in the flow sheet are also helpful for the recovery of the reagent (1) The end liquor (alkaline) is treated directly with active carbon. Adsorption of the reagent is better in alkaline medium. The adsorbed reagent is eluted by acetone, neutralysed and distilled to recover free amine and acetone, which are recycled in the process. The requirement of acid by this method is minimum (theoretical quantities) but the method is tedious and requires handling of large quantities of acetone. (2) The reagent from the alkaline end liquor is extracted using normal butanol. The butanol layer is separated using separating funnels. The separated butanol layer is neutralysed with acid to precipitate the free amine which is filtered and recovered. The butanol is neutralysed with alkali and recycled for second operation. The loss of butanol in the end liquor (due to solubility) is very high (8 per cent) and the method though simple is not very useful.

FIG. 33 PROCESS FLOW SHEET FOR THE RECOVERY OF POTASSIUM SALT FROM SEA (BRINE & BITTERN) BY PRECIPITATION WITH CALCIUM DIPICRYLAMINATE REAGENT



LABORATORY EXPERIMENTS

Precipitation of potassium with cobaltinitrite reagent

A Few laboratory experiments were conducted using sodium cobaltinitrite $(Na_3CO(NO_2)_6$ to find out the requirements of the reagent and to study whether potassium could be recovered at lesser cost using cobaltinitrite as a precipitating reagent. Theoretically only 2.71 grams of powdered sodium cobaltinitrite reagent was required per gram of potassium chloride; however as the concentration of potassium chloride was low, the requirement of the reagent to obtain 90 per cent recovery of potassium from sea water was roughly 39.2 g say 40 grams per gram of potassium chloride in sea water (Table 97).

Table 97 PRECIPITATION OF POTASSIUM FROM SEAWATER USING POWDERED SODIUM COBALTINITRITE REAGENT

No.	Seawater (0.071%) (KCl) ml	Powdered reagent added (g)	Wt. of precipitate obtained (g)	KCl in filtrate by flame photometer (g)	Per cent recovery
1	100	2.5	0.1980	0.0060	91.5
2	100	3.0	0.2010	0.0050	92.9
3	100	3.5	0.2027	0.0045	93.6
4	100	4.0	0.2045	0.0040	94.3

Decomposition of precipitates

30 grams of potassium cobaltinitrite precipitate was heated in porcelain dish to convert cobalt as cobalt oxide. The residue was extracted with 150 ml. of water each time till all potassium was recovered in the filtrate. The first

fraction of the filtrate analysed 8.9 per cent potassium nitrate 5.5 per cent sodium nitrate. Solar evaporation of the solution gave a mixture of salts analysing 30 per cent sodium nitrate and 70 per cent potassium nitrate. Both the nitrates can be used as a fertiliser mixture along with other plant neutriants. Comparative study of both the precipitation processes namely cobaltinitrite process and dipicrylamine process is given in Table 98. As the reagent was not recoverable in cobaltinitrite process and only 4 per cent of the cobalt was recovered directly from precipitates, it appeared that the second process was more feasible. Hence further work was carried out on the dipicrylamine process alone.

LABORATORY EXPERIMENTS

Precipitation of potassium as potassium dipicrylaminate using calcium dipicrylaminate as precipitant

Preparation of the reagent solution

30 g. of hexanitro diphenylamine and 1.93 g of calcium oxide was weighed and mixed with 600 to 650 ml of tap water. The slurry was stirred at least ~~four~~ four hours after which it was filtered on sintered glass funnel. The clear filtered solution was collected in amber coloured bottle. The adhering reagent with the insolubles on the filter bed was removed by washing with hot water till a clear solution was obtained. The washings were collected and free amine was precipitated by addition of acid. The free amine was collected for utilisation in the second cycle.

Table 98 COMPARATIVE STUDY OF TWO PRECIPITATION PROCESSES NAMELY DIPICRYLAMINE AND SODIUM COBALTINITRITE FOR POTASSIUM RECOVERY FROM SEA WATER

(Basis:- Treatment of 1725 litres seawater)
to obtain 1.356 kg KNO_3

	Dipicrylamine process	Sodium cobaltinitrite process
A)Reagents		
	1) Hexanitrodiphenylamine 14.72 kg per batch (100% recovery of reagent is considered) at Rs 2800 per kg	1) Sodium cobaltinitrite 69 kg per batch costing Rs. 5520 at Rs. 80 per kg
	2)Calcium oxide 1 kg per batch; approximate cost Rs.0.35	2) Not required
	3)Nitric acid 2.32 kg per batch Approximate cost Rs. 4.11 at Rs. 1.77 per kg	3) Nitric acid 9.75 kg (6.5 litres) Approximate cost Rs. 17.00
B)Bulk of precipitate to be handled per batch	6.4 kg	3.05 kg
C)Solution to be evaporated per batch	10 to 15 litres	10 to 15 litres
D)Recovery of the reagent(usual)	99 %	Nil
E)Recovery of potassium ion	80%	80 to 90 per cent
F)Byproducts that can be obtained	i) Bromine if acidic end liquor is treated further	i) Sodium nitrate 0.57 kg per batch ii) Cobalt oxide 0.5 kg per batch directly from precipitate which is only 4 per cent of the total cobalt oxide used iii) Recovery of cobalt oxide from end liquor can be carried out if processed further (additional cost) iv) Bromine from acidic end liquor.
G)Cost of 1 kg KNO_3 on 1% loss ~~of~~ reagent basis alone	Rs. 300 per batch	Rs. 4080 per batch (100% loss of reagent)

Strength of the reagent solution

Every time 5 ml of the clear reagent solution was taken through burette and precipitated with acid to find out the strength of the prepared reagent solution. A freshly prepared reagent was used every time as it was observed that on long standing, the strength of the reagent was slightly reduced and a brownish black precipitate appeared in the stock solution.

Procedure for precipitation

Laboratory experiments were performed in glass beakers and the exact quantity of the reagent solution was added slowly (dropwise) with burette, depending on the potassium content in the solution. The solution was constantly stirred and the precipitated solutions were kept aside for an hour or so with occasional stirring. The precipitates were filtered in sintered glass crucibles dried below 100°C and then weighed. Details of the potassium recoveries in laboratory experiments are given in Table 99.

Co-precipitation of impurities

Testing of impurities co-precipitating along with potassium hexanitrodiphenylamine precipitates was carried out by dissolving the precipitates in hot water. Free amine was estimated by neutralysing the solution with nitric acid or by gravimetric method. The filtrate was tested for chloride by Mohr's method and total calcium and magnesium was estimated by flamephotometry. Contamination of sodium and calcium increased with the concentration of salts in the solution. The contamination of impurities in case of bittern samples decreased appreciably when the bittern samples were diluted

Table 99 PRECIPITATION OF POTASSIUM FROM SEAWATER, BRINE AND BITTERN SAMPLES AS POTASSIUM DIPICRYLAMINATE

Density Description Sp.gr.	4°Be' Sea water 1.029	14°Be' Brine 1.108	24°Be' Brine 1.199	29° Be' Bittern 1.25
	Composition weight by volume			
KCl	0.074	0.36	0.57	2.15
NaCl	3.109	12.38	24.51	14.32
$MgCl_2$	0.465	1.48	2.90	11.26
$MgSO_4$	0.183	0.87	1.63	7.80
$CaSO_4$	0.150	0.40	0.18	0.20
Total KCl in solution(g)	i)0.3700 ii)0.3700 iii)0.0740 iv)0.0740	i) 0.3600 ii) 0.1800	i) 0.5700 ii) 0.2850	i) 0.5375 ii) 0.5375
Reagent Added (g)	i)2.1840 ii)3.4860 iii)0.7140 iv)0.7140	i) 2.1840 ii) 1.0920	i) 3.6960 ii) 1.8980	i) 3.1080 ii) 3.1080
Wt.of ppt. obtained (g)	i)1.4016 ii)0.8515 iii)0.3718 iv)0.3698	i) 1.8662 ii) 0.9336	i) 3.2102 ii) 1.6054	i) 3.1648 ii) 3.1650
Concentration of reagent in filtrate (g)	i)0.2347 ii)0.285 iii)0.3031 iv)0.3015	i) 0.4754 ii) 0.4743	i) 0.3144 ii) 0.4638	i)0.2260 ii)0.2267
Average recoveries of potassium ion(per cent)	78	81	88	92

with equal amounts of water before precipitation. Contamination was also found to decrease when the bittern or diluted solution was added to the reagent solution rather than addition of reagent to the solution. In case of sea water precipitation washing of precipitates with cold water or wash liquid solution previously saturated with potassium dipicrylamine at room temperature removed most of the impurities. Details are given in Tables 100,101 and 102.

Table 100 PRECIPITATION OF POTASSIUM AS POTASSIUM DIPICRYLAMINATE FROM SEA WATER(Laboratory data)

No.	Seawater litres	Reagent added in (g)	Ratio of addition KCl/Reagent	Potassium dipicrylamine ppt. (g)	Composition of the precipitate per cent K	Na	Ca	Mg	Per cent recovery potassium
1	1	6.95	1:1.6	3.719	8.02	0.440	0.020	-	78.4
2	"	6.95	1:1.6	3.703	8.05	0.442	0.020	-	78.3
3	"	6.96	1:1.6	3.722	8.03	0.450	0.020	-	78.5
4	"	4.28	1:1	2.820	8.10	0.401	0.014	-	60.0
5	"	3.45	1:0.8	2.568	8.18	0.380	0.013	-	55.2
6	"	2.99	1:0.7	2.129	8.19	0.201	0.003	-	45.8

Table 101 PRECIPITATION OF POTASSIUM AS POTASSIUM DIPICRYLAMINATE FROM 29° Be BITTERN (2.15 per cent KCl)

No.	29°Be' Bittern (ml)	Reagent added g	Ratio of addition	Potassium dipicrylamine g	Composition of precipitate per cent K	Na	Ca	Mg	Per cent recovery of potassium
1	25	3.17	1:1	3.471	7.47	0.83	0.62	0.02	92
2	25 + 25H_2O	3.17	1:1	3.201	8.10	0.52	0.46	0.01	92

<u>Solubility studies</u> Solubility study was carried out to find out how best recoveries of potassium could be improved, how the recoveries of the reagent could be obtained quantitatively and

Table 102 WASHING OF POTASSIUM DIPICRYLAMINE PRECIPITATES WITH WATER ON BUCHNER FUNNEL TO REMOVE ADHERING IMPURITIES

40.2 g potassium dipicrylaminate precipitated from sea water was washed with water (29°C) on the buchner funnel with 100 ml of water each time and the washings were analysed. The results show that two to three washings are required to remove adhering impurities.

Composition	Wash solutions Sol. 1	 Soln. 2	 Soln. 3
$Na^{\cdot}$	0.15	0.12	<0.01
$K^{\cdot}$	0.22	0.23	0.23
$Ca^{\cdot\cdot}$	0.054	0.011	nil
NO_3'	0.746	0.683	0.386
Cl'	1.450	0.296	-

—how to obtain simultaneously a concentrated solution of potassium. Solubility of potassium dipicrylaminate at various temperatures was determined mainly to obtain a concentrated potassium solution in filtrate. Pure potassium dipicrylaminate was prepared by adding reagent solution to pure potassium chloride solution. The precipitated potassium dipicrylaminate was washed with cold water and dried below 100°C. The pure potassium dipicrylaminate was used for determining the solubility of the salt at various temperatures. Excess of potassium dipicrylaminate and water were stirred for a long time in thermostat and clear solutions were drawn using sintered glass filter sticks kept at same temperature. The solutions were immediately cooled and weighed. The solution with the precipitated potassium dipicrylamine was dissolved in excess of water and de-

decomposed with acid. The free amine was filtered and dried below 100°C. From the weight of the free amine, weight of potassium salt in solution was calculated. The solubility of potassium dipicrylaminate even though increased with temperature, the solubility even at 90°C was only 2.133 g per 100 grams of solution. The details are given in Table 103.

Table 103 SOLUBILITY OF POTASSIUM DIPICRYLAMINATE IN WATER (g/100 g. soln.)

	Temperature °C	Wt. of free amine (g)	Wt. of potassium dipicrylaminate (g)	Concentration of KNO_3 in solution % (w/v)
1	25	0.1011	0.1110	-
2	27	0.1043	0.1145	-
3	30	-	0.145	-
4	50	0.4381	0.4811	-
5	70	0.8273	0.9085	-
6	80	1.5660	1.7200	-
7	90	1.9430	2.1330	0.4519

Sea water contains 0.07 % KCl(0.095 % KNO_3)
The concentration of KNO_3 obtained is only 5 times the original

Solubility of potassium dipicrylaminate in sea water and brines

Pure potassium dipicrylaminate was prepared and added in excess to different solutions. The solutions were stirred at room temperature (28°C) for 3 to 4 hours and filtered using sintered glass filter sticks. First few ml. was rejected while the remaining solution was collected, weighed in weighing bottles and diluted to 250 ml. Standard solutions containing 0.1 to 1 g potassium dipicrylaminate per litre was prepared by dissolving known quantities of potassium dipicrylaminate in water. The test solutions were compared with the standard solutions using Duboscq - colorimeter. The results are tabulated in Table 104. It was seen that potassium dipicrylaminate was more soluble in sea water than in brine and bittern samples.

Table 104 SOLUBILITY OF POTASSIUM DIPICRYLAMINATE AT 28°C IN DIFFERENT SOLUTIONS

Description	Solubility milligrams per 100 grams of solution
1) Distilled water	86.50
2) Sea water	14.69
3) 14° Be sea brine	2.12
4) 24° Be sea brine	1.30
5) 28° Be seabittern	0.92
6) 36° Be sea bittern	0.39

Solubility of hexanitrodiphenylamine

It was necessary to find out solubility of hexanitrodiphenylamine in acid solutions as the colour of the filtrate was differing every time. Pure hexanitrodiphenylamine was recrystallised from acetone and used for determining the solubility. The hexanitrodiphenylamine or free amine was added in excess to nitric acid solutions and stirred at room temperature (28°C) for 3 to 4 hours. The solutions were then filtered using dry sintered glass filter sticks and the solutions obtained were weighed in weighing bottles. The solutions were than diluted to a known volume after neutralising it with sodium hydroxide solution. The red coloured solutions thus obtained were then compared with standard solutions similarly prepared by weighing exactly 1 g of hexanitro-diphenylamine dissolving in alkali and making the volume to one litre. Further dilutions were made from standard stock solution as required. The results obtained by comparing test solutions with standard solutions using Dubseq -colorimeter are given in Table 105.

Table 105 SOLUBILITY OF FREE AMINE (DIPICRYLAMINE) IN NITRIC ACID AT 28°C

	Strength of acid	Solubility mg/litre	Remarks
1	N/100	0.10	1) Dipicrylamine is less soluble in dilute acid
2	N/10	0.16	
3	N	0.60	2) Addition of excess of acid in decomposition of end liquor causes more loss of reagent and acid.
4	2N	2.00	
5	4N	3.00	
6	6N	6.00	
8	8N	15.00	

Recovery of the reagent

Reagent was to be recovered from precipitates of potassium hexanitrodiphenylamine which contained 91.81 per cent reagent and also from the filtrate which contained on an average about 0.3 grams reagent per 100 ml of the solution.

Recovery of the reagent by decomposing the potassium dipicrylaminate precipitates was carried out by three different methods namely 1) dissolving the precipitates in hot water and decomposing the solution with dilute acid. (2) decomposing the precipitates with concentrated acids (3). decomposing the precipitates with acetone and acid mixture. The details of these methods are as follows:-

1) Dissolving the precipitates in hot water and decomposing the solution with dilute acid

Potassium hexanitro diphenylamine precipitates were dissolved in hot water at 90°C and the hot concentrated solution was decomposed with the addition of dilute acid. It was observed that any strength of the acid could be used. The requirement of acid was only theoretical quantities. Concentration of potassium nitrate or sulphate obtained in filtrate by this method was below 0.5 g per 100 ml of solution. Considering the concentration of potassium chloride in sea water as 0.07 g per 100 ml roughly five times concentration was only obtained. If precipitation was carried out from bittern, a dilute solution was obtained as the solubility of potassium dipicrylaminate at 90°C is only 2.133 g per 100 g solution. Thus the method is unsuitable for getting a concentrated potassium salt in solution.

2) Decomposing the precipitates with concentrated acid

It was observed that any mineral acid or even acetic acid could be used for this purpose. It was also observed that time ~~ed~~ for decomposition depended on concentration of the acid used and temperature. The time required for decomposition could be appreciably reduced by using higher temperature for decomposition. e.g. time required for decomposition was half that of the time reported in the Table 106; if the temperature was maintained at 60°C instead of room temperature. The minimum concentration of acid required was 7 normal if decomposition was carried out ~~at~~ only at room temperature.

If decomposition was carried out at higher temperature such as 80 to 100°C even lower strength of acid (4 normal) could be utilised.

Table 106 DECOMPOSITION OF POTASSIUM HEXANITRODIPHENYLAMINE PRECIPITATES WITH NITRIC ACID OF DIFFERENT CONCENTRATIONS AT 30 °C

No.	Sp.gr.	Approx. normality	Precipitate taken (g)	ml.of acid added	Remarks
1	1.0256	0.6	10.0	25	No decomposition
2	1.0620	1.8	10.2	25	No decomposition
3	1.1134	3.0	10.2	25	No decomposition even after 8 days
4	1.1774	5.5	10.3	25	Partial decomposition after 72 hrs.
5	1.2255	7.0	10.1	25	Decomposes after 6 hrs.
6	1.2792	9.0	10.2	25	Complete decomposition after 2 hrs.
7	1.3283	11.0	10.1	25	Complete decomposition in 10 to 12 minutes
8	1.4100	11.0	10.1	25	Complete decomposition within 5 minutes

As potassium dipicrylaminate was sensitive for explosion in presence of heavy metals such as zinc, and as detail information was not available, decomposition at higher temperature was not studied. Decomposition of precipitates was carriedout only in glass vessels. Acid requirement for decomposition was very high as 1 g precipitate required almost 1 g of concentrated nitric acid. If nitric acid of lower normality was used such as seven normal, decomposition required a very long time. On washing the precipitates with hot water, 70 to

80 per cent of potassium nitrate was obtained as 8 to 10 per cent concentrated solution. The filtrate (Con.KNO_3 solution) was highly acidic and would require neutralisation with potassium carbonate before it could be evaporated to obtain potassium nitrate. Neutralisation with sodium carbonate or lime would require further purification of the obtained potassium salt. The advantage of this method was that a concentrated solution of potassium salt was obtained over the previous method. The requirement of high acid however would make it impracticable as the cost of the acid directly effected the cost of production (Table 107).

Table 107 DECOMPOSITION OF POTASSIUM DIPICRYLAMINATE
WITH CONCENTRATED NITRIC ACID (at room temperature)

No.	Precipitate taken (g)	Conc. acid (HNO_3) Normality	Amount (ml)	Free amine (g)	Theoretically required 100% acid (g)	KNO_3 removed in wash solutions 25 ml I	25ml II	25 ml III	50 ml IV
1)	10.53	11	11	9.67	1.39	6.0	2.9	*	-
2)	20.25	11	20	18.59	2.67	8.4	6.0	2.8	*
3)	25.26	11	25	23.19	3.33	10.1	8.0	3.3	-
4)	21.30	11	21	19.56	2.81	8.8	8.4	0.9	-

* = Traces, - = nil

3) Decomposition of precipitates using acetone and acid

Potassium dipicrylamine precipitate was mixed with acetone in the ratio of 1 g precipitate to ½ ml of acetone, stirred and decomposed with 3 to 4 normal nitric acid solution.

Decomposition with 1 to 2 normal nitric acid was not complete. The decomposed precipitate was washed with water to remove acetone and potassium nitrate in solution. Acetone was removed from the filtrate by distillation. Washing the free amine with hot water gave potassium salt in solution as high as 10 per cent. The method was easy to operate and required only theoretical quantities of acid. The filtrate contained 8 to 10 per cent potassium nitrate in solution and did not require neutralisation with alkali as required in earlier method 2 (Tables 108 and 109).

Recovery of reagent from filtrate

The end liquor or filtrate contained (table 3) roughly 0.3 g reagent per 100 ml. The reagent (hexanitrodiphenylamine)could be recovered from the large volume of the end liquor by various ways namely (1) by acid treatment (2) by adsorption of the reagent on active carbon and eluting it with organic solvent such as acetone (3) extraction of the reagent in organic solvent. All the three methods are examined.

(1) Acid treatment

The end liquor after the separation of potassium as potassium dipicrylaminate contained roughly 0.3 g reagent per 100 ml. The pH of the solution was 8 and was red in colour. The requirement of acid to bring down the pH to 4 was roughly 1 ml of concentrated nitric acid per litre of the end liquor solution. This was roughly double the theoretical requirement. Addition of little less acid and adjusting the pH little higher such as 4.5 the decomposition required a longer time and the precipitate

Table (108) STUDIES ON REQUIREMENT OF ACETONE AND THE STRENGTH OF ACID FOR THE DECOMPOSITION OF POTASSIUM DIPICRYLAMINATE

ppt. taken (g)	Acetone added (ml)	HNO_3 added Strength	(ml)	Requirement per g of ppt. (Acetone) ml	+(HNO_3) ml	Remarks
10.036	20	11 N	2.0	2	+ 0.2	Decomposition complete
2.785	2.5	11 N	0.4	1	+ 0.14	-do-
3.429	2.0	11 N	0.5	1	+ 0.12	-do-
6.359	3.0	11 N	0.6	0.5	+ 0.1	-do-
7.580	4.0	11 N	0.8	0.5	+ 0.11	-do-
3.144	3.0	1 N	10	0.5	+ 10	Decomposition not complete even after addition of 10 ml of excess of acid
4.455	4.0	4 N	3	1	+ 3	Decomposition complete
5.260	5.0	2 N	10	1	+ 10	Decomposition not complete even with addition of excess of acid

Table 109 DECOMPOSITION OF POTASSIUM DIPICRYLAMINATE WITH ACETONE AND ACID TO OBTAIN A CONCENTRATED SOLUTION OF POTASSIUM NITRATE IN FILTRATE

ppt. taken (g)	Acetone added (ml)	HNO_3 added Sp.gr. 1.42 (ml)	KNO_3 in wash solution fractions per cent (w/v) I 25 ml	II 25 ml	III 25 ml	IV 50 ml
25.86	13	4.6	9.04	8.00	4.80	0.035
32.15	16	5.7	9.20	8.60	8.00	0.730

remained floating and required minimum 12 hours to settle. The very fine precipitate was difficult to filter sticked to vessels and there was creeping action on the sides of the beaker. If the pH was adjusted to 3.5 to 4, the reagent separated out as a flocculent curd type yellow precipitate which settled very fast and was easy to filter. The acidic filtrate obtained at the end of the operation contained 6 to 10 milligrams of reagent per 1000 ml which corresponds to the solubility of the reagent in the acidic solutions. The solubility had increased with the concentration of the acid (Table 105).

2) Recovery by active carbon

'Hycol 3x' was used to adsorb reagent from both alkaline as well as acid treated end liquor which contained 6 to 10 milligrams of reagent per 100 ml of the solution. It was found out that roughly 1.3 g of 'Hycol 3 x' (active carbon) per gram of the reagent was required to adsorb all the reagent from alkaline solution. In the case of acidic solution containing lesser concentration of the reagent required 8 g Hycol 3 x per 1 g of the reagent. Addition of alkali to neutralize the acidic solution and make it slightly alkaline reduces the requirement of Hycol 3 x to 2.3 g instead of eight grams as in case of acidic medium. This would indicate that adsorption was better in alkaline medium. The clear solution containing active carbon on which the reagent was adsorbed passed through a glass column containing sintered disc and 'Hiflo' filter aid material. It was observed that use of filter aid was necessary to keep the sintered disc clean which otherwise would choke with active carbon which was difficult to remove. The clear solution containing no reagent was allowed to go waste. The active carbon was once washed with little water and acetone was passed through the column. The reagent on the ~~re~~active carbon was eluted completely. Nearly 80 per cent of the reagent was recovered with 500 ml acetone per 1 g of reagent,~~ratio,~~ while the remaining 20 per cent reagent on the active carbon required more acetone treatment. On an average, 1 litre of acetone per 0.1 g of reagent (hexanitrodiphenylamine) was required. The requirement of acetone for eluting the reagent by the column technique was very high. The requirement of acetone could be reduced by using soxhlet type apparatus (Table 110)

Table 110 RECOVERY OF REAGENT (DIPICRYLAMINE) FROM ACTIVE CARBON BY ACETONE

End liquor used litres	Reagent (g)	Acetone used (L)	Reagent recovered (g)	Active carbon used	Per cent recovery of reagent
1	3.13	30	3.10	4.10	99
1	3.24	31	3.25	4.06	100
1	3.21	29.5	3.13	4.15	98
10 Acidic	0.70	10	0.69	5.60	98
10 Acidic	0.78	10	0.70	6.00	91
10 (alkaline	0.73	10	0.71	1.73	97
10 alkaline	0.78	10	0.72	1.84	92
0.65	2.00	20	1.98	2.60	99
0.90	2.60	30	2.58	3.50	99
1.3	3.80	40	3.80	5.20	100

3) Recovery of reagent with n-Butanol

In order to reduce the requirement of acid for the recovery of reagent from the large volume of the end liquor some organic solvents were tried. Out of the various solvents tried such as kerosene, petrol, carbon tetra-chloride, alcohol, benzene,xylene, ISO-amyl alcohol and n-butanol; only n-butanol was useful. N-butanol extracts the reagent in alkaline medium. In the extracted reagent in the butanol layer was treated with acid to recover the reagent and the n-butanol. It was found out that 250 ml of n-butanol was sufficient to extract almost all the reagent~~s~~ from one litre of end liquor solution. The experiments (Table 111) showed that it was possible to extract the reagent from the alkaline solution (end liquor). The reagent could be precipitated from the butanol layer by acid treatment or by distilling n-butanol. However n-butanol was not completely immiscible with water. Thus out of 200 ml, 120 ml was only obtained in other words 80 ml of butanol was lost with one litre of the end liquor solution.

Table 111 RECOVERY OF DIPICRYLAMINE FROM END LIQUOR USING N-BUTANOL

End liquor ml	Butanol ml	Dipicrylamine present	Dipicrylamine obtained	Per cent recovery
200	100	0.6545	0.6544	100
200	100	0.6575	0.6574	100
200	50	0.7073	0.6871	97.10
200	50	0.6603	0.6412	97.10
Above extracted solution	50	0.0194	0.0171	2.60
		Overall recovery for 4 & 5 was 99.7%		
1000	250	3.2700	3.1720	97.00
1000	200	3.6941	3.4221	92.64
Above end liquor acidified with HNO_3	-	0.2720	0.2028	5.49
	Over all recovery for 7 & 8 was 100 %			

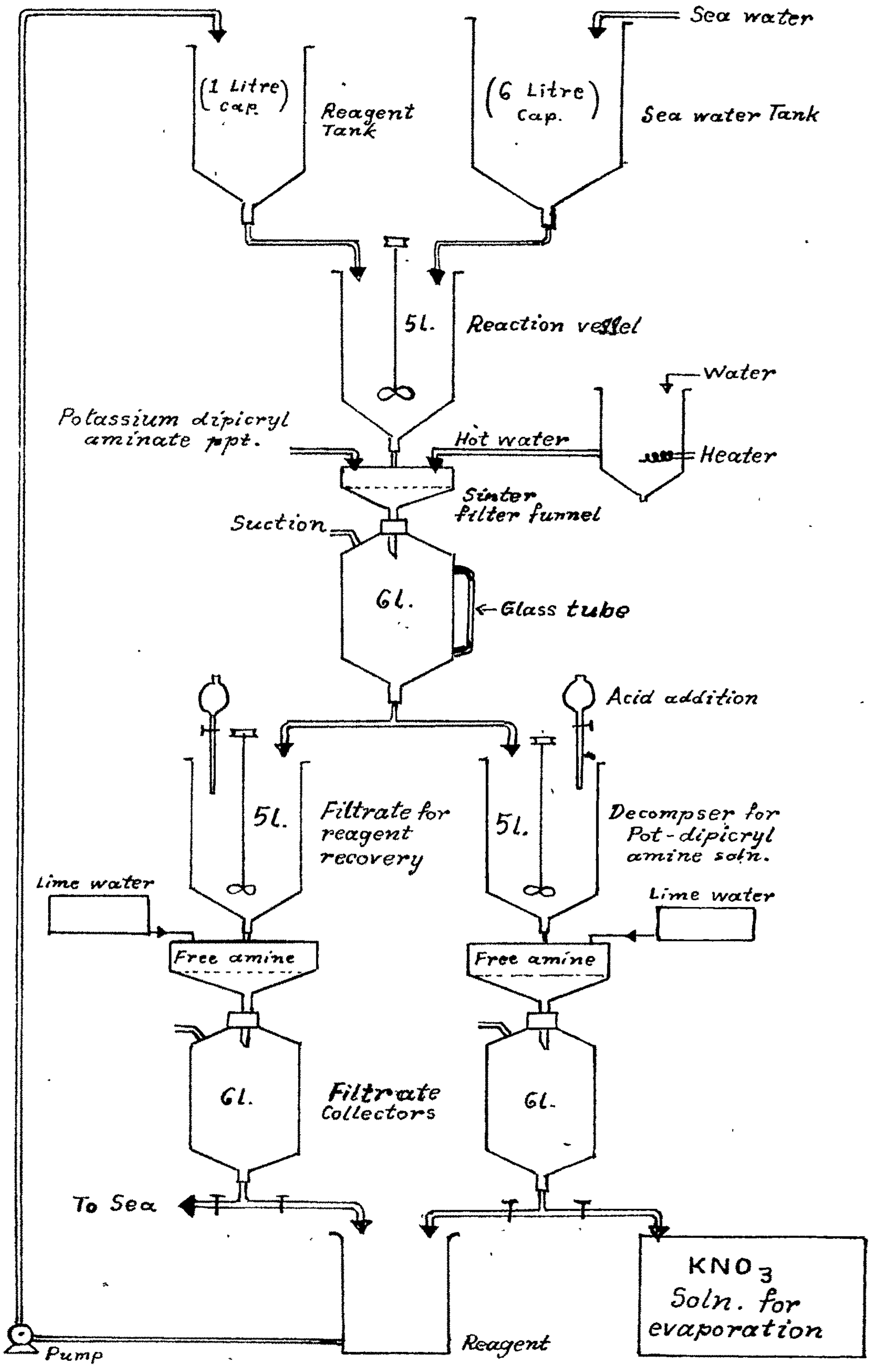
Bench scale experiments

Bench scale experiments were performed with sea water to find out handling difficulties and the reagent losses on the large scale. A small unit with a capacity to treat five litres of seawater per batch was designed and prepared out of 1.5 mm.(1/16") thick G.I. sheets for this purpose (Fig. 34).

Operation

5 litres of sea water was pumped in reservoir vessel each time from which sea water was taken in reaction vessel by gravity. The known quantity of the prepared reagent was added drop by drop with constant stirring. The slow addition lasting over a period of half an hour was necessary to obtain large size crystalline precipitates which were easy to filter and less adhering to the sides of the stirrer and vessel. The mixture was stirred at room temperature for an hour after the reagent was completely added. The red coloured crystalline precipitates were filtered on 15 cms. diameter glass funnels with G 3 sinter bed. Recovery of potassium was estimated by knowing the volume of the end liquor and the concentration of the potassium in the solution by flame photometer. The end liquor was taken by gravity to another reaction vessel with stirring arrangement where it was treated with nitric or sulphuric acid. The pH of the solution was brought down to 4 (tested with pH papers) and the free amine was separated by filtration on sintered glass crucible using little 'Hiflo' filter aid on the sintered bed. The end liquor slightly yellow coloured solution containing 6 to 8 milligrams of reagent per 100 ml was stored separately for further treatments.

Fig. 34 FLOW SHEET SHOWING ARRANGEMENT OF VESSELS IN BENCH SCALE EXPERIMENTS



Recovery of the reagent was difficult to calculate as lot of precipitates adhere to the sides of the vessel and stirrer blade. However, same quantity of the reagent was used over again and again after treatment with lime. Loss in the end liquor was 300 to 350 milligrams per cycle (1.03 per cent). The free amine was washed with water (slightly acidic) on the sintered glass funnel itself and collected in a separate vessel for preparing fresh reagent solution. The potassium dipicrylaminate precipitates were separately treated to recover the reagent and the filtrate containing potassium salt. Results are reported in Table 112.

Table 112 RECOVERY OF POTASSIUM AS POTASSIUM DIPICRYLAMINATE FROM SEA WATER, BENCH SCALE EXPERIMENTS

Reagent used			Potassium in filtrate		
Per cent reagent	Total added (ml)	Total reagent present (g)	Per cent potassium	Total potassium (g)	Per cent recovery
4.20	810	34.02	0.0155	0.90	75.0
4.30	790	33.97	0.0147	0.85	76.4
4.15	820	34.03	0.0163	0.95	73.6
4.51	750	33.82	0.0156	0.90	75.0
3.96	858	33.98	0.0155	0.91	74.7
4.25	800	34.00	0.0150	0.87	75.8
4.10	830	34.03	0.0151	0.88	75.6

5 litres of sea water containing 0.072 per cent potassium was used for the above experiments. Total potassium in filtrate was estimated by flame photometer and recovery is reported on that basis as total precipitate in each case was not recoverable for quantitative estimation.

Table 113 A COMPARATIVE STUDY OF RAW MATERIAL REQUIREMENTS

<u>Basis</u> :- Treatment of 1430 kilolitres of sea water (0.07% KCl) and 50 kilolitres of 29° Be bitterns (2.0% KCl) containing approximately 1 tonne of potassium chloride

	Description	Sea water	Bitterns
1	Potassium chloride in solution, tonnes	1	1
2	Precipitates obtained per batch, tonnes	5.124	5.758
3	Volume of solution to be handled per batch, kilolitres	1639	1809
4	Free amine in filtrate per batch, tonnes	4.73	0.61
5	Potassium nitrate obtained, tonnes	1.091 (0.92 K_2SO_4)	1.220 (1.05 K_2SO_4)
6	Loss of reagent if unrecovered from the acidic end liquors, in kg	$\frac{48.64}{9436}$	$\frac{7.524}{5891}$
7	Loss of reagent, per cent	0.52	0.13
	RAW MATERIALS		
1	Reagent (free amine) required per batch, tonnes	9.436	5.891
2	Water required to prepare reagent solution kilolitres	209.7	130.9
3	Lime required per batch, tonnes	0.6	0.4
4	Acid required for decomposing precipitate and recovering reagent from filtrate, tonnes of 96% H_2SO_4	1.65	0.76
5	Acetone required for decomposition of precipitates, litres	5124	5728
6	Replenishment of the reagent (free amine) due to loss in end liquor, kg	49	7.6

DISCUSSION

Potassium salts either as sulphate, chloride, nitrate or phosphate are essential as plant nutrients. The availability of potassium salts from sea bittern or mixed salt source is limited. Seawater or saline brines from desalination plants is the only unexhaustible source of potassium. India has no potassium deposits and the large quantity of potassium fertilisers can be supplied if potassium recoveries are made possible from sea water or saline brines from desalination plants.

Concentration of alkali metals in sea water is as follows:-

Sodium 10600 mg Na per litre = 27 g NaCl per litre

Potassium 380 mg K per litre = 0.726 g KCl per litre

Considering 0.726 g potassium chloride per litre and 80 per cent recovery of potassium (say 0.58 g KCl per litre), we have to treat 1725 litres of sea water per kilogram of potassium chloride. In other words, 580 grams of potassium chloride or 786 grams of potassium nitrate, or 677 grams of potassium sulphate are obtained by treatment of one cubic metre or 1000 litres of sea water. Concentration ratio of potassium to sodium in sea water evaporation changes from 1:40 in sea water to 1:6 in 29° Be bittern. Solar evaporation of bittern further changes the ratio to 1:1 at 34° Be/36°Be density and 1:2 at 36/38°Be bittern respectively.

The object of the present work is to find out suitable precipitation method to obtain potassium salts directly from sea water, bitterns or concentrated brines from water conversion plants where 8 to 10° Be brines are obtained as waste liquors. Preliminary work is concerned to find out whether precipitation by sodium cobaltinitrite is cheaper than precipitation by dipicrylamine. Preliminary studies show that the cobaltinitrite process is costlier than dipicrylamine process. Further work is carried out on dipicrylamine process.

Studies on precipitation of potassium with calcium salt of dipicrylamine is concentrated on four aspects namely (1) Recovery of potassium (2) Decomposition of potassium dipicrylamine precipitates to obtain a concentrated solution of potassium salt in solution in a single step from 0.07 per cent of potassium chloride in sea water; and to use theoretical quantities of acid. (3) Recovery of the reagent from the end liquors left after the precipitation of potassium and from potassium dipicrylamine precipitate for recycling. (4) Requirement of acid for decomposition of precipitates and recovery of reagent from end liquors.

Recoveries of potassium from sea water, 14° Be, 24° Be brines, 29° Be bitterns and saturated mixed salt solutions are 78, 81, 88, 92, 98 per cent respectively. Solubility of potassium dipicrylaminate in sea water, distilled water, 14° Be brine, 24° Be brine, 28.5° Be and 35° Be bitterns varies appreciably with the result that recoveries of potassium are better from concentrated solutions. In order to obtain 78 per cent recovery from sea water at room temperature (28°C) it is essential to add the reagent in excess such as 1:1.6 over the stoichiometric ratio. As recovery of potassium from bittern (29° Be) is 92 per cent and the volume of the filtrate is small, the requirement of reagent is only in stoichiometric ratio. It is advantageous to treat bittern from the point of recovery of potassium and requirement of acid for treatment of filtrate to recover the reagent. The reagent is precipitated out from the end liquor (filtrate) as free amine at 3.8 to 4 pH by addition of a cheap acid. It is necessary to wash the potassium dipicrylamine precipitates on the buchner funnel with cold water to remove most of the adhering impurities. In precipitation from bittern it is better to dilute the bittern with water in 1:1 ratio before potassium is precipitated.Solar evaporation of the filtrate obtained by decomposing the precipitates to dryness gives a crystalline mass which analyses potassium nitrate 97.50 per cent sodium nitrate 4.92 per cent, calcium nitrate 3.33 per cent. Evaporation of filtrate from decomposition of precipitates obtained by treatment of 29° Be bittern analysis potassium nitrate 78.05 per cent,sodium nitrate 2.55 per cent, calcium nitrate 9.40 per cent. The impurities are due to contamination of precipitates with other salts. Various methods are tried to minimise the requirements of acid in decomposing the precipitate. Results are summarised in describing the methods adopted and the advantages obtained are reported in Table 114.

Table 114 DECOMPOSITION OF POTASSIUM DIPICRYLAMINATE PRECIPITATES

Method	Advantage	Disadvantage
1) Dissolving the precipitates in hot water (90°C) and decomposing the hot clear solution with addition of dilute mineral acid	i) Theoretical amounts of acid are required ii) Any concentration of acid is suitable	Solubility of precipitates is less even at 90°C. Hence only 0.5 per cent solution of potassium salt is obtained Volume of the solution to be evaporated to recover salts is large
2) Decomposing the precipitat~~ion~~s with concentrated mineral acid	Concentrated solution of potassium salt is obtained (upto 10 per cent)	Lot of heat is evolved. Acid addition should be slow. Decomposition cannot be carried out in columns where ~~after~~ evolution of heat NO_2 gas was observed. Concentration of acid that can be used with reasonable time for the reaction is 7 normal. Consumption of acid is enormous. Filtrate obtained contains diluted acid which is difficult to recycle without previous concentration.
3) Decomposition of the precipitate with acetone and acid mixture	i) Requirement of acetone is negligible which is easily covered and reused. ii) Requirement of acid is theoretical quantities iii) Acid of 1 normal strength can be used iv) Concentrated solution of potassium salt upto 10 per cent is obtained.	Distillation of acetone from the first two washings of the precipitate is necessary

Method (3) using acetone and acid mixture offers definite advantages over the other two methods in utilising minimum acid of low concentration and producing a filtrate containing as high as 10 per cent potassium nitrate which can be easily evaporated to obtain pure potassium nitrate.

The economics of the process is based on consumption of the mineral acid and handling losses of the reagent. Most of the earlier work reports quantitative recoveries of the reagent. In laboratory experiments, recovery of reagent is quantitative but in large scale experiments one per cent loss of reagent is noticed in the filtrate. Recovery of the reagent from the end liquor (pH 8) containing 0.3 per cent reagent is a serious problem which is not successfully, solved. Solubility of free amine in nitric acid varies with strength of the acid such as with N/100 the solubility is only 0.1 milligram per litre which increases to 15 milligrams per litre when the acid strength is 8 normal. Concentrated nitric acid is actually a good solvent for free amine (hexanitrodiphenylamine); while in dilute acid solutions, amine is practically insoluble. Absorption of the reagent (hexanitrodiphenylamine) on mellamine resin shows that it is absorbed both in alkaline and in acidic medium. In the first experiment mellamine is packed in glass column and the end liquor is passed as such, through the mellamine bed. All the reagent is absorbed on the mellamine bed and requirement is 70 grams mellamine per gram of the hexanitrodiphemylamine. In the other experiment end liquor is treated with acid the free amine is filtered and the yellow coloured liquid containing 6 to 8 mg reagent per litre is passed through a mellamine bed. Reagent is absorbed on the bed. In both the cases, recovery of reagent is not complete and most of the reagent is absorbed on the bed in such a way that it is not possible to elute it even with acetone and such other solvents. Elution with strong sodium hydroxide solution meets other difficulties namely it gives brown coloured precipitate which is soluble in acid, and reagent is not recovered. Eluting with strong acid affects the resin itself.

Reagent from the filtrate or end liquor can be recovered by using active carbon (Hycol 3 x). Reagent is absorbed both from alkaline and acid solutions. The operations involved are i) absorption of the reagent on active carbon ii) filtration iii) washing of the active carbon with water iv) extraction of reagent using organic solvent (acetone) v) recovery of the organic solvent (acetone) by distillation. It has been assessed that requirements of 'Hycol 3 x' per gram of the reagent (hexanitrodiphenylamine) in alkaline and in acid solutions are 1.3 and 8 grams respectively. While the requirement of acetone per gram of the absorbed reagent on the active carbon bed is one litre. The loss of acetone is estimated as 2 per cent which is due to handling losses.

Absorption of the reagent from alkaline filtrate in n-butanol solution and separation of n-butanol with separating funnel is tried. The n-butanol solution on treatment with acid precipitates the absorbed reagent. The difficulties experienced in this case are due to partial solubility of n-butanol in water (8 per cent). Butanol forms several constant boiling mixtures and losses of butanol can not be avoided.

Consumption of mineral acid is for two purposes

(1) to decompose the potassium hexanitrodiphenylamine precipitate to obtain potassium salt in solution and to recover the reagent as free amine. Here in this case it has been found out that if precipitate is decomposed using acetone and acid mixture the requirement of acid is only theoretical and the concentration of potassium salt obtained in the filtrate is upto 10 per cent. Thus in one stage it is possible to obtain from 0.07 per cent potassium chloride in sea water, a solution containing 10 per cent potassium nitrate, chloride, sulphate or acetate depending on the acid used.

(2) Acid is also required to decompose the filtrate or the end liquor left after the precipitation of potassium from sea water or bitterns. Here it has been found out that the precipitation of free amine takes place only at 3.8 to 4 pH. Addition of little less acid requires a long time (overnight settling) to separate the free amine which is obtained as fine dust and it is difficult to filter and it flies with wind. Requirement of acid for recovering the reagent as free amine from the end liquor obtained by treatment of sea water is as high as five times while in case of bittern requirement of acid is 1½ to 2 times over the theoretical requirements.

It appears that if cheap dipicrylamine is made available by preparing indigenously from chlorobenzene and mixed acid by Hoffman and Dame process and also cheap acid is made available by installing a plant along with the sea water treatment plant, it may be possible to produce potassium salts directly from sea water. The capital investment is high; and care is necessary to avoid the losses of the reagent in its handling and storage. It is explosive in dry state and affects skin, mucuous membrane and lungs if inhaled.

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