

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF MICHIGAN
AND THE UNIVERSITY OF ILLINOIS]

THE SEPARATION AND DETERMINATION OF SODIUM AND LITHIUM BY PRECIPITATION FROM ALCOHOLIC PERCHLORATE SOLUTION¹

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A review of the literature on the separation of sodium and lithium shows that none of the methods so far suggested is entirely satisfactory. The solubility corrections are usually large and the separation must be repeated one or more times.

Most of the methods proposed involve the extraction of lithium chloride from the anhydrous mixed chlorides of the metals involved, using an organic solvent or mixture of solvents in which the chlorides other than lithium chloride are insoluble. Another general type of procedure consists in dissolving the mixed chlorides in the least quantity of water necessary for their solution, followed by the precipitation of the chlorides other than lithium chloride, by the addition of an organic solvent or mixture of solvents in which the chlorides precipitated are but slightly soluble, a correction being applied for this slight solubility.

A full and critical discussion of the papers relating to this subject up to the year 1912 is given by Skinner and Collins.² Of the more recent work, that of Winkler³ employs *isobutyl* alcohol in an extraction method, more than one extraction being required in each analysis. The method is tedious in operation and subject to errors because of the number of manipulations involved. In the method of Palkin⁴ a concentrated aqueous solution of the mixed chlorides is precipitated by the addition of anhydrous alcohol followed by ether. The chlorides thus precipitated are filtered, and the small amount remaining in solution is recovered by evaporating to dryness and extracting with alcohol and ether. The method is an improvement over the others since it eliminates the solubility correction, but the use of the volatile ether is a disadvantage.

The methods in which chlorides are precipitated rather than extracted most closely approximate the usual analytical processes and are theoretically more accurate. However, Palkin's process is strictly speaking not really such, as the precipitant does not carry a component which enters into the composition of the precipitate formed; moreover, the method is applied to saturated rather than dilute solutions.

¹ The work done in connection with this paper was suggested by H. H. Willard and the preliminary work was carried out at the University of Michigan. The final work was done at the University of Illinois.

² Skinner and Collins, U. S. Dept. Agr., *Bur. Chem. Bull.*, **153** (1912).

³ Winkler, *Z. anal. Chem.*, **52**, 628 (1913).

⁴ Palkin, *THIS JOURNAL*, **38**, 2326 (1916).

The object of the present paper is the development of a method for the separation and determination of lithium and sodium, based upon precipitation of the material separated, in a manner analogous to the usual analytical practice.

The Method

The process, in brief, consists in the precipitation and separation of sodium chloride from a solution of the mixed perchlorates of sodium and lithium in *n*-butyl alcohol by the addition of a butyl alcohol solution of hydrogen chloride according to the reaction, $\text{NaClO}_4 + \text{HCl} = \text{NaCl} + \text{HClO}_4$. The reagent is added to the solution of the perchlorates until a 6% acid concentration is attained. The precipitated sodium chloride is filtered on a weighed Gooch crucible, washed with a 6-7% solution of hydrogen chloride in butyl alcohol, dried at 250° and ignited for a few minutes at 600°. The lithium chloride, after removal of the organic matter by evaporation, is determined by conversion to lithium sulfate, a correction being applied for the almost negligible amount of sodium chloride remaining in the filtrate. In some cases the reagents give a slight blank. Potassium cannot be present since its perchlorate is insoluble in alcohol.

Preparation of Materials

Normal Butyl Alcohol.—This material is readily obtainable on the market at the present time at a moderate price. The alcohol used in this research had a boiling range of 112-118° and a density of 0.8065 at 25°/4°; 60% of this product boiled within a range of 1° of the true boiling point. This fraction, when dried by refluxing with a slight excess of metallic calcium, had a boiling range of 116.2-116.7° and a density of 0.8060 at 25°/4°. Half of this fraction boiled within a range of 0.05°. In most of the work the 60% fraction, obtained as described above, was used. Experiments were also carried out using alcohol of widely different constants, the data concerning which will be recorded later.

Perchloric Acid.—The method of Willard⁵ was used for the preparation of the perchloric acid. It was twice distilled under a pressure of from 5 to 15 mm. and contained about 72% HClO_4 . Ten g. of this material when evaporated in a platinum crucible gave an almost unweighable residue after ignition.

Sodium Chloride.—An imported product of highest purity was used.

Sodium Perchlorate.—This material was prepared by treatment of the purest sodium carbonate with a slight excess of dil. perchloric acid. The anhydrous sodium perchlorate was obtained by crystallization above 50°, using centrifugal drainage. The product thus obtained was dried in a current of dry air at a temperature of 250°. To obtain samples of sodium perchlorate for the analytical separations, pure sodium chloride in weighed portions was evaporated on a hot plate with a slight excess of perchloric acid until fumes of perchloric acid were no longer evolved.

Lithium Chloride.—This material was prepared from a product which contained some sodium chloride. It was freed from the latter by solution in hot butyl alcohol under a reflux condenser. The solution was cooled and the sodium chloride filtered off. The lithium chloride in the filtrate was recovered by evaporation in a platinum dish to a pasty mass which was dried in an electric oven at 100°. It was further heated in a

⁵ Willard, THIS JOURNAL, 34, 1480 (1912).

muffle at 500° and finally fused in a current of hydrogen chloride dried with sulfuric acid. The product thus obtained was cooled, crushed, and powdered under conditions which insured no contact with atmospheric moisture. It was used only in the solubility determinations.

Lithium Perchlorate.—The method employed in the preparation of this material was that described by Richards and Willard.⁶ Lithium nitrate was purified by recrystallization and then precipitated by the addition of hydrofluoric acid. The lithium fluoride was converted to perchlorate by evaporation with pure perchloric acid. This was then recrystallized from water with centrifugal drainage, platinum vessels being used throughout. The lithium perchlorate trihydrate thus obtained was dehydrated by fusion in a current of dry air at 250°.

Samples of this anhydrous lithium perchlorate were weighed into platinum crucibles contained in glass-stoppered weighing bottles and again fused by placing the crucibles in a drying tube at 250°, through which passed a current of dry air. The crucibles and contents were then replaced in their weighing bottles, cooled, and reweighed. The original weight was usually lowered a fraction of a milligram due to the very slight hygroscopic nature of anhydrous lithium perchlorate.

The Solution of Hydrogen Chloride in Butyl Alcohol.—Butyl alcohol was treated with hydrogen chloride generated in the usual way by the action of conc. sulfuric acid on sodium chloride or conc. hydrochloric acid; 200 cc. of 20% solution could be prepared in 2 or 3 hours. For testing the strength of these solutions an hydrometer serves admirably. For use in this connection a density-concentration curve was constructed between the limits of 0 and 20% hydrogen chloride. It was found to be sufficiently close to a straight line function so that values between those given in the following table could be obtained by interpolation.

TABLE I

DENSITY OF SOLUTIONS OF HYDROGEN CHLORIDE IN DRY NORMAL BUTYL ALCOHOL

HCl %	Density	HCl %	Density	HCl %	Density	HCl %	Density
0	0.8060	6	0.8425	11	0.8685	16	0.8895
1	0.8130	7	0.8485	12	0.8730	17	0.8935
2	0.8195	8	0.8540	13	0.8770	18	0.8960
3	0.8255	9	0.8590	14	0.8810	19	0.9010
4	0.8315	10	0.8635	15	0.8855	20	0.9050
5	0.8370						

These values were obtained by using a pycnometer and thermostat and refer to 25°/4° corrected to vacuum. The hydrochloric acid was determined by titration with standard alkali.

Conditions Affecting the Precipitation of Sodium Chloride from a Solution of Sodium Perchlorate in Butyl Alcohol

Several factors, some unexpected, were found to influence the quantitative separation of sodium and lithium from solution in anhydrous butyl alcohol by the addition of the solution of hydrogen chloride in butyl alcohol. The factors in the order of their importance are: (1) temperature of precipitation; (2) concentration of hydrochloric acid, giving minimum solubility of sodium chloride; (3) conditions favoring ease of filtration; (4) prerequisites for drying and ignition of the sodium chloride obtained; (5) physical constants of butyl alcohol used in the method; (6) treatment

⁶ Richards and Willard, *THIS JOURNAL*, 32, 4 (1910).

of filtrates from sodium chloride for recovery of lithium. These factors will be taken up in the order given.

Temperature of Precipitation.—Sodium chloride precipitated from boiling solutions of sodium perchlorate in butyl alcohol when filtered on asbestos, washed, and dried at 250° for a long time, is perfectly white, but upon ignition to 500–600° it becomes dark gray and when then dissolved in water a black deposit of carbon is obtained. This results from occlusion of solvent in the precipitated sodium chloride. The error in weight of the precipitated sodium chloride, due to this cause, is variable and too large to be neglected. Precipitation at room temperature gave a similar result but much less carbon was obtained. Wash solutions such as acetone, ether and carbon tetrachloride, are incapable of removing the occluded solvent from the precipitate. Ignition of the sodium chloride containing carbon in a stream of oxygen did not remove the impurity. The lower the temperature of the solution from which sodium chloride is precipitated, the less the tendency it shows to occlude solvent. When precipitated at –15° to –20° the dried and ignited salt contains no carbon but is pure sodium chloride.

Effect of Acid Concentration Upon the Solubility of Sodium Chloride.—Solutions of sodium perchlorate of known content were precipitated by the addition of butyl alcohol containing 20% of hydrogen chloride. A definite excess of hydrogen chloride was then added over that required for precipitation. After being heated to boiling, the precipitated samples were cooled to room temperature, filtered through asbestos, and washed with solutions of hydrogen chloride in butyl alcohol of the same strength as those from which the sodium chloride was precipitated. The precipitate was dried at 250°, ignited at 500–600° and the sodium chloride found, corrected for its carbon content, was compared with the amount present. The concentration of hydrogen chloride was gradually increased, until at 6% to 7% the solubility of sodium chloride reached a minimum of 0.6 mg. per 100 cc. This excess of hydrogen chloride can be obtained closely enough by adding to the solution of the perchlorate half as many cc. of 20% solution of hydrogen chloride in butyl alcohol, as there are grams of the solution. The wash solution is made in the same way.

The solubilities of the various salts involved are shown in the following tables.

TABLE II
SOLUBILITIES IN ANHYDROUS NORMAL BUTYL ALCOHOL AT 25°

	G. per 100 g. solution	Density 25°/4°		G. per 100 g. solution	Density 25°/4°
LiClO ₄	44.23	1.1341	LiCl.....	11.49	0.8713
NaClO ₄	1.83	0.8167	NaCl.....	0.014 ^a	0.8060

^a 0.0116 g. per 100 cc.

TABLE III
 SOLUBILITY OF SODIUM CHLORIDE PRECIPITATED FROM ANHYDROUS BUTYL ALCOHOL
 CONTAINING 6% OF HYDROGEN CHLORIDE

	NaCl taken G.	NaCl found G.	Vol. fil- trate and washings ^a Cc.	Free HClO ₄ present %	LiClO ₄ present G.	Solubility of NaCl in 100 cc. G.
1	0.3021	0.3007	102	0.0014
2	0.3004	0.2989	110	...	0.1720	0.0014
3	0.3031	0.3020	102	0.0011
4	0.3510	0.3493	87	...	0.0356	0.0019
5	0.1549	0.1546	52	0.5	0.0006
6	0.1593	0.1590	55	0.5	0.0006
7 ^b	0.1034	0.1027	43	0.5	0.0016
8	0.3505	0.3481	98	1.5	0.0024

^a Consisting of butyl alcohol containing hydrogen chloride and a little perchloric acid.

^b Alcohol as received, not dried or distilled.

It is evident from the above data that the solubility of sodium chloride is greatly reduced by the presence of hydrogen chloride. That of lithium chloride, is, however, much less affected. The addition of 4.9% of hydrogen chloride reduced it from 11.49 g. to 9.60 g. per 100 g. of solution. No lithium chloride was precipitated when a 20% solution of hydrogen chloride in butyl alcohol was added to a 40% solution of lithium perchlorate in the same solvent. The solubility of sodium chloride is reduced from 11.6 mg. per 100 cc. in pure, dry butyl alcohol to 1.4 mg. by the addition of 6% hydrogen chloride and to 0.6 mg. per 100 cc. by the further addition of 0.5% of 70% perchloric acid. The reason for this latter decrease is not evident. More than 0.5% of perchloric acid increases the solubility. In unpurified and undried 6% hydrogen chloride—alcohol containing 0.5% of perchloric acid, the solubility rises to 1.6 mg. per 100 cc.

Conditions Favoring Filtration.—The higher the temperature of precipitation, the greater the ease of filtration. From a boiling sodium perchlorate solution in butyl alcohol, the sodium chloride precipitated is coarse, settles rapidly, and filters easily. From the same solution precipitated at room temperature, the precipitate is more gelatinous, settles slowly, and is difficult to filter and wash. The same solution precipitated at -15° to -20° cannot be filtered.

Since it is desirable to utilize cold precipitation to prevent occlusion of solvent by the sodium chloride, solutions precipitated at -15° to -20° were heated to boiling and allowed to cool to room temperature before filtration. The precipitate of sodium chloride should be formed by adding, drop by drop, to the cold solution, 1–1.5 cc. of the hydrogen chloride—butyl alcohol reagent, the remainder to form a 6% acid—butyl alcohol solution being added rapidly. Under these conditions the precipitated sodium chloride, after boiling, settles rapidly, and after cooling to room temper-

ature can be filtered clear, using a Gooch crucible. It is washed with a 6–7% solution of acid in butyl alcohol. If the concentration of acid is over 6%, coagulation of the sodium chloride is less effective.

Physical Constants of the Butyl Alcohol Used in the Method.—In view of the results obtained by Winkler³ in the use of *isobutyl* alcohol, a rather carefully purified *n*-butyl alcohol was employed in most of the work recorded in this paper. Winkler used *isobutyl* alcohol dehydrated over caustic potash and which had a boiling range of one degree, 106–107°. It was further specified that this fraction of the dried sample was necessary for good results. It will be shown later that drying only and no fractionation is required.

Treatment of Filtrates from Sodium Chloride for Recovery of Lithium.

—The filtrates from the sodium chloride precipitate consisted of a butyl alcohol solution of hydrogen chloride and perchloric acid, lithium and a slight amount of sodium as perchlorate or chloride, the latter resulting from the almost negligible solubility of sodium chloride. The salts were recovered by evaporation of the solvent and volatile acids, converted to lithium and sodium sulfates, ignited and weighed. From this weight, corrected for the known amount of sodium sulfate, the amount of lithium was calculated.

Although the dilute solution of anhydrous perchloric acid and lithium perchlorate could be boiled without trouble, evaporation to dryness without first adding water resulted in a violent deflagration; 30 to 50 cc. of water was added to 50–100 cc. of the cold alcoholic solution and 2 immiscible layers were obtained. The under layer of water extracted most, if not all, of the products of solution from the upper alcoholic layer. When this mixture was evaporated on a steam-bath the alcoholic layer evaporated completely, leaving the greater part of the water solution of lithium and sodium perchlorates and perchloric acid. The organic matter remaining was eventually oxidized, and after the addition of sulfuric acid the evaporation was continued to dryness. The lithium sulfate was then dissolved in a little water, washed into a weighed platinum crucible, covered and heated over a ring burner to remove excess of sulfuric acid. The conversion of lithium perchlorate to lithium sulfate is more easily carried out without loss than conversion of lithium chloride to sulfate. The lithium sulfate was ignited in a muffle at 600° for 5 to 10 minutes, or to constant weight in case of large amounts. Samples thus treated were neutral and could be fused without loss in weight.

Separation of Sodium and Lithium

When free from potassium, the mixed chlorides (free from sulfate) obtained by the J. Lawrence Smith or other method, are evaporated to dryness with excess of perchloric acid. A second evaporation is desirable if the amount is large. If potassium is present it is first separated by

the usual perchlorate method and the filtrate, *after addition of water*, to avoid explosion, is evaporated to dryness. Since a definite amount of perchloric acid should be present, it is desirable to remove first all excess of acid.

The mixed perchlorates of sodium and lithium free from perchloric acid are dissolved in anhydrous *n*-butyl alcohol using at least 15 g. or 18.5 cc. for each 100 mg. of sodium chloride present. The containing beakers may be conveniently weighed upon a small platform balance. The mixture dissolves readily if the alcohol is heated to boiling, which can be done with a burner over a wire gauze; 0.1 cc. of 70% perchloric acid is added and the solution is cooled to -15° by means of a freezing mixture. The sodium chloride is precipitated by adding from a buret, drop by drop, with constant stirring, 1–1.5 cc. of a 20% solution of hydrogen chloride in anhydrous butyl alcohol after which the amount necessary to form a 6% solution is rapidly added (half as many cubic centimeters as there are grams in the solution to be precipitated). The precipitate of sodium chloride is then coagulated by heating the solution to boiling on a wire gauze with a free flame. After cooling to room temperature the sodium chloride is filtered on a weighed Gooch crucible and washed 8 or 10 times with a 6–7% solution of hydrogen chloride in butyl alcohol. (A rubber-tipped rod can be used in transferring the precipitate from beaker to crucible. It is well to preserve it by washing with a little acetone after use.) The sodium chloride is dried for one hour at 250° and ignited for 5 to 8 minutes at 600° in a muffle furnace (a free flame may be used but a very dull red must not be exceeded). A correction of 0.6 mg. for the sodium chloride remaining in each 100 cc. of filtrate and washings is added to the weight of sodium chloride found, to obtain the total sodium chloride present.

The filtrate and washings from the sodium chloride are diluted with $\frac{1}{3}$ their volume of water, (to avoid subsequent deflagration) forming 2 layers, and the whole is evaporated on the steam-bath in such a way as to avoid any condensation on the upper part of the beaker, which causes loss by "creeping." It is well to add 5 to 10 cc. of water at the end to make the removal of organic matter more complete before the perchloric acid takes effect. By such treatment a colorless residue of lithium perchlorate and perchloric acid can be obtained. If a slight brown coloration is present, remove the watch glass supports from the beaker and heat the covered beaker on a wire gauze to fumes of perchloric acid. If any brown color remains adhering to the beaker walls after this treatment, it can be removed by brushing the walls of the beaker with the flame. If not enough perchloric acid is present to oxidize the last traces of organic matter, a few drops are to be added. When the brown coloration is removed, 0.5 cc. of conc. sulfuric acid is added, the watch glass replaced and the acid fumed off, using either a hot plate or low flame and wire gauze. The beaker is then cooled, 5 to 10 cc. of water is added, and the cover glass and beaker walls washed. The lithium sulfate is then transferred to a platinum crucible previously ignited and weighed with its lid. The solution is cautiously evaporated to dryness and the covered crucible is heated, preferably by a ring burner, until every trace of acid is removed, after which it is heated to 600° in a muffle for 5 to 10 minutes. When the same treatment is carried out using a free flame and a very dull red heat, some reduction to sulfide often takes place, due to diffusion of the flame gases through the platinum. Fusing with a free flame to check the weight obtained by the above treatment is possible if the temperature is not too high or the treatment too long.

The weight of lithium sulfate is to be corrected for its sodium sulfate content by subtracting the weight of the solubility correction calculated as sodium sulfate, or 0.7 mg. per 100 cc. of filtrate and washings. A further correction to be applied is a blank for the reagents employed. This correction is found by precipitating a weighed sample

of sodium chloride in the manner above described. One cc. of perchloric acid is ample for any ordinary quantity of salts to be converted and the subsequent additions of 0.5 cc. each of sulfuric acid and perchloric acid are enough to provide excess. The weight of material obtained at the end of this process should be less than 1 mg. when corrected for the sodium chloride solubility.

Gooch crucibles with 0.5mm. holes are much better than those with large holes. Platinum Gooch crucibles with their much smaller perforations are still better. A heavy mat of asbestos is essential and a perforated porcelain disk should be placed on it to prevent disturbance of the mat. If platinum-sponge filtering crucibles are used, weighing of the empty crucible should be made after the sodium chloride has been washed out with water, since spongy platinum is slightly attacked. Asbestos for use in filtrations with solutions of hydrogen chloride in butyl alcohol should be refluxed with some of this material in preparation for its use. The same crucible should be used many times over, and in such a case previous treatment of the asbestos with the acid-alcohol solution is not necessary. To show the effect of the solvent upon asbestos, the same crucible was used repeatedly, starting with untreated asbestos. The sodium chloride was washed out each time. The following successive weights were obtained: 26.6413, 26.6405, 26.6401, 26.6401, 26.6401. In order to avoid an additional operation the filtration with suction can be made directly from the crucible to a beaker by using a vacuum desiccator of the usual form but with a hole provided in the cover for the passage of a filtering tube and rubber stopper. In this way the beaker to receive the filtrate can be placed in the bottom of the desiccator. The filtering tube should have a small perforation in its side about an inch from the bottom to prevent spattering.

The filtrates were rapidly evaporated on the steam-bath by immersing the beaker in a copper capsule flanged at the top and fitted to the rings of the steam-bath so that condensation did not take place on the walls of the beaker or cover glass. This is very important because the alcoholic solution shows a strong tendency to "creep."

The value of the method was tested by a series of analyses of known mixtures, with the results recorded in the following table.

TABLE IV
SEPARATION AND ESTIMATION OF SODIUM AND LITHIUM

Expt.	NaCl	NaCl	Error	LiClO ₄	LiCl	Li ₂ SO ₄	LiCl	Error
	taken	found		taken	calc.	found	found	
	G.	G.	G.	G.	G.	G.	G.	G.
1	0.1521	0.1519	-0.0002	0.4819	0.1920	0.2488	0.1919	-0.0001
2	0.1481	0.1478	-0.0003
3	0.1017	0.1017	0.0000	0.5534	0.2205	0.2860	0.2206	+0.0001
4	0.2027	0.2024	-0.0003	0.5295	0.2110	0.2736	0.2110	0.0000
5	0.1016	0.1016	0.0000	0.3004	0.1197	0.1558	0.1202	+0.0005
6	0.0217	0.0218	+0.0001	0.4455	0.1775	0.2315	0.1785	+0.0010
7	0.0502	0.0503	+0.0001	1.5354	0.6118	0.7929	0.6116	-0.0002
8 ^a	0.1017	0.1019	+0.0002

^a Alcohol dried but not fractionated; boiling range 112-118°.

The separation of sodium from very large amounts of lithium is accomplished by one precipitation (Expt. 7).

In case it is desired to avoid a cold precipitation, (a step which requires but one short additional operation), the method can be applied exactly as described, omitting cooling to -15° before precipitation, and adding the precipitant to the mixed perchlorate solution at nearly its boiling

temperature. In this case the solubility of sodium chloride was found to be 1.6 mg. in 100 cc. of solvent. The carbon occluded by a precipitate of about 0.5 g. of sodium chloride is approximately 1.5–1.0 mg. under these conditions. The weight of sodium chloride in the precipitate can be determined by dissolving it in water, drying the crucible with its carbon impurity, and weighing after filtration rather than before.

Summary

1. A method is described for the separation of sodium and lithium based upon the precipitation of sodium chloride from a solution of the perchlorates in anhydrous *n*-butyl alcohol by the addition of an alcoholic solution of hydrogen chloride.
2. Conditions affecting the accuracy of the process were studied and the accompanying errors eliminated.
3. The solubilities of the anhydrous perchlorates and chlorides of lithium and sodium in anhydrous *n*-butyl alcohol at 25° are given.
4. A table is given showing the density and composition of solutions of hydrogen chloride in butyl alcohol.
5. Test analyses show that one separation gives accurate results even in the presence of large amounts of lithium.

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THE DEGREE OF IONIZATION OF ETHYL ALCOHOL. I. FROM MEASUREMENTS OF CONDUCTIVITY¹

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Introduction

Ethyl alcohol may be assumed to ionize in either or both of the following ways $C_2H_5OH = C_2H_5^+ + OH^-$, and $C_2H_5OH = C_2H_5O^- + H^+$. The slow formation of ethyl chloride from alcohol and hydrochloric acid is an example of the reactions which indicate some ionization of the first type, while the rather rapid formation of alkali ethylates indicates the second type of ionization. That alcohol is in reality amphoteric, ionizing in both ways, is indicated by the formation of ether. The greater part of the evidence, however, points to the predominance of the second kind of ionization. The formation and decomposition of ethyl esters are slow, whereas there are a large number of smooth and rapid neutralization reactions between acids and alkali ethylates. In the present investiga-

¹ The material here given is taken from a thesis presented by the first-named author in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of California.