

THE SEPARATION AND DETERMINATION OF THE ALKALI METALS USING PERCHLORIC ACID.

III. NORMAL BUTYL ALCOHOL AND ETHYL ACETATE AS MIXED SOLVENTS IN THE SEPARATION AND DETERMINATION OF POTASSIUM, SODIUM AND LITHIUM

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N butyl alcohol and ethyl acetate as mixed solvents have been selected as one of the various combinations of organic solvents with properties best suited to the separation of the soluble from the insoluble alkali metal perchlorates by the extraction process.¹ N butyl alcohol has been used as solvent in the separation and determination of sodium and lithium by a process involving the precipitation and gravimetric determination of sodium as the chloride followed by the estimation of lithium by conversion to sulfate.² N butyl alcohol is not entirely satisfactory as extracting solvent to be used in the separation of sodium and lithium from potassium perchlorate because of the low solubility of sodium perchlorate. By the use of the mixed solvents given above this objection is eliminated. The demonstration of imperfections in pre-

¹G. Frederick Smith, J. Am. Chem. Soc., 47, 762, (1925).

²Willard and Smith, J. Am. Chem. Soc., 44, 2816, 1922.

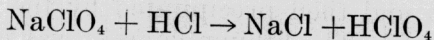
viously described methods and the development of an improved procedure for the extraction separation of the alkali metal perchlorates was the object of the second paper of this series.³ The present paper applies the principles established in references 1, 2 and 3 to the quantitative separation and determination of potassium sodium and lithium including the volumetric estimation of sodium using standard silver nitrate (Mohr's method).

THE METHOD

The process, in brief, is as follows:

The mixture of potassium, sodium and lithium chlorides are converted to perchlorates by evaporation of their solution with excess of pure perchloric acid, the latter removed by evaporation to dryness twice with intermediate solution in water. Sodium and lithium perchlorates are extracted, using a mixture of equal parts N butyl alcohol and ethyl acetate. The potassium perchlorate thus obtained after decantation, using a weighed Gooch crucible, is washed twice by decantation dissolved in water and the process repeated. The purified potassium perchlorate is filtered, using the same Gooch crucible, washed with the extracting solvents, dried at 350°, cooled and weighed.

The combined filtrate and washings totaling 50-70 cc. are evaporated on the hot plate until the ethyl acetate is removed and the sodium and lithium perchlorates in N butyl alcohol solution separated by the addition of a butyl alcohol solution of hydrogen chloride according to the reaction.



The reagent is added to the solution of the perchlorates until a 6% acid concentration is obtained. The precipitated sodium chloride is filtered, using a Gooch crucible, washed with a 6% solution of hydrogen chloride in butyl alcohol, dried at 110-125° and finally ignited a few minutes at a barely visible red heat. The sodium chloride thus obtained is dissolved in water and titrated with standard silver nitrate using potassium chromate as indicator (Mohr's method).

³G. Frederick Smith and J. F. Ross, J. Am. Chem. Soc. 47, 774, (1925).

The filtrate from the sodium determination is diluted with 10 cc. of water, evaporated to remove organic matter and the lithium salt thus obtained converted to lithium sulfate in the usual manner.

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 o/o 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 o/o fraction, obtained as described above, was used.

Perchloric Acid.—The method of Willard⁴ 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 o/o HClO₄. 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.

Potassium Chloride.—The same stock and quality of product as the sodium chloride.

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°.

The Solution of Hydrogen Chloride in Butyl Alcohol.—Butyl alcohol was treated with hydrogen chloride generated in the usual way by the action of concentrated sul-

⁴Willard, J. Am. Chem. Soc., 34, 1480, (1912).

⁶Richards and Willard, J. Am. Chem. Soc., 32, 4 (1910).

furic acid on sodium chloride or concentrated hydrochloric acid; 200 cc. of 20 o/o solution could be prepared in 2 or 3 hours.

Ethyl Acetate.—The same as that tested for use in connection with reference 1. It is very easily prepared in an equal state of purity and with excellent yields from cheap technical products.

APPARATUS AND EQUIPMENT.

Hot perchloric acid is said to have a solvent action on some types of laboratory glass and porcelain ware resulting in contaminations with silica. Pyrex glass is not thus affected and should be used for all evaporations involving perchloric acid. Gooch crucibles using asbestos have been found adequate for all filtrations involved in this work, but are far less convenient than platinum sponge crucibles. The advantage of the latter is most pronounced wherein the substances filtered are water soluble and the solutions organic in nature.

Means should be provided for filtration under reduced pressure from beaker to beaker without transfer. Evaporations of solutions containing perchloric acid are best conducted on an electric hot plate providing a sufficient temperature to fume it. In addition to the usual laboratory oven an electric muffle is desirable for ignitions at 350° and 500-600°. A ring burner is essential for conversions of lithium perchlorate to lithium sulfate.

PROCEDURE

The mixed chlorides of potassium, sodium and lithium obtained by the J. Lawrence Smith or other method, free from ammonium salts, are dissolved in water and treated with two or three times the equivalent quantity of pure perchloric acid (not less than 1 cc. of 60-70 o/o acid) and the solution thus obtained evaporated to dryness on the hot plate in a 150 cc. pyrex beaker. The beaker and contents should be dry and any acid condensed on the side walls of the beaker should be removed by brushing with a free flame. The beaker is then cooled appreciably and the contents dissolved by the addition of a minimum of hot water (2 or 3 cc. generally suffice) and the solution again evaporated to dryness on the hot plate.

10-20 cc. of a mixture of equal parts by volume of N butyl alcohol and ethyl acetate is now added to the sufficiently cooled beaker and the solution digested near the boiling point 2 or 3 minutes. The solution is cooled to room temperature and the supernatant liquid decanted through a previously ignited and weighed platinum sponge crucible and washed three times by decantation to remove most of the soluble perchlorates extracted, the residue dissolved in the minimum of hot water and again evaporated to dryness.

The salts are extracted the second time as before, using 10 cc. of solvent, digested, cooled and filtered into the original crucible. The precipitate is transferred to the crucible, using a fine jet from a wash bottle containing the same solvents used for the extraction and the crucible contents washed with 10-15 portions of $\frac{1}{2}$ to 1 cc. from the wash bottle. The filtrate is started concentrating on the hot plate at this point. Any unremoved particles of perchlorate found in the original beaker after drying on the hot plate are brushed in with the bulk of precipitate. The crucible and precipitate are dried a few minutes at 110° in an oven and finally 15 minutes in a muffle at 350° , cooled and weighed. The filtrate and washings by this process should approximate 50 cc. If sodium is absent lithium can be completely separated from potassium by one extraction.

The filtrate from the potassium determination is evaporated on the hot plate until the ethyl acetate is dispelled, which is accomplished by concentrating to 40 o/o of the original volume and the hot solution of sodium and lithium perchlorates in N butyl alcohol 20 cc. in volume is treated with 8 cc. of 20 o/o hydrochloric acid butyl alcohol solution, adding the first cc. dropwise with constant stirring. After cooling to room temperature the sodium chloride precipitate is filtered on a platinum sponge crucible and washed 8 or 10 times with a 6-7 o/o solution of hydrogen chloride in butyl alcohol (made by diluting 100 cc. of alcohol with 40 cc. of 20 o/o hydrochloric acid-butyl alcohol solution). The crucible and precipitate are dried a few minutes in an oven at 110° and finally ignited for 5 minutes at 600° in a muffle (a free flame may be used but a very dull red must not be exceeded). The sodium

chloride precipitate is dissolved in the cooled crucible, using a fine stream of water from the wash bottle, and the crucible thoroughly washed in the same manner, receiving the filtrate in a 150 cc. beaker. The precipitate of sodium chloride will be gray because of occluded carbon, and the dissolved sodium chloride will leave a carbonaceous residue in the crucible. If it is desired to determine sodium gravimetrically the dried and ignited crucible should be weighed prior to removal of its sodium chloride content and again after the solution of sodium chloride in water and drying of the crucible and insoluble residue at 110° for one hour. The loss in weight is pure sodium chloride. By the volumetric procedure the sodium chloride solution is diluted if necessary to 50 cc. and titrated, using standard N/10 silver nitrate and 1 cc. of a 5 o/o solution of potassium chromate free from chloride as indicator (Mohr's method). The silver nitrate is best standardized using pure sodium chloride and a correction should be applied for the solution required to produce the end point reaction. The result by both the gravimetric and volumetric procedure agree.

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. 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 fumes appear. 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 concentrated 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 test analyses of various mixtures of pure potassium and sodium chlorides and lithium perchlorate are reported in Table I.

TABLE I.
SEPARATION OF POTASSIUM, SODIUM AND LITHIUM WITH DETERMINATION OF POTASSIUM AND SODIUM

	KCl taken G.	NaCl taken G.	LiClO ₄ taken G.	KCl found G.		NaCl found G.		Error* NaCl Mg.	Error† KCl Mg.	Determination of	
				1 extr.	2 extr.	Grav.	Vol.			K	N
1	0.12925	0.1306	0.1305	0.1292	0.1306	0.1307	+0.1	-0.05	60	41
2	.14625	.13491472	.1462	.1344	.1345	— .4	— .05	50	52
3	.16105	.135851624	.1608	— .25	55	..
4	.1416	.1354514265	.1416	.13495	.1352	— .25	± .0	50	38
5	.1310	.13521323	.1311	.13465	.1343	— .9	± .1	56	51
6	.2346	.0817523360316	— .15	— 1.0	75	62
7	.05275	.194405281934	— 1.0	+ .05	75	65
8	.10555	.088910520886	— .3	+ .05	60	49
9	.0851	.1198508471194	— .45	— .4	61	54
10	.103851036	— .25	45	..
11	.133151329	— .25	45	..
12	.10385	0.2045	.1039	— .05	63	..
13	.180220135	.1801	— .1	50	..
14	.1101524665	.1103	+ .15	51	..
15	.210856045	.2108	± .0	59	..
16	.120451984	.1205	± .05	58	..

*Based on two extractions if made.

†Based on volumetric sodium determination.

‡Sodium determination lost by "running through" and was discarded.

DISCUSSION OF RESULTS

It will be seen upon examination of the results of Table I that two extractions are necessary for the satisfactory separation of potassium and sodium (analyses 1-5 inclusive). The results obtained are considerably better for both a single and double extraction using the mixture of equal parts N butyl alcohol and ethyl acetate than are obtained by the use of absolute ethyl alcohol.⁶

⁶Compare with the results obtained by Baxter and Kobayashi, J. Am. Chem. Soc., 39, 249, (1917).

A single extraction gives excellent results for the separation of potassium and lithium (analyses 12-16 inclusive) even though samples larger than ordinarily separated are taken (analysis 15). In all the separations, although results for potassium are very close to the truth, this can result only from a very slight occlusion of the material extracted partially substituting for the potassium perchlorate dissolved.

The solubility of potassium perchlorate in the mixture of equal parts of *N* butyl alcohol and ethyl acetate under actual working conditions at room temperature is seen to be 1.0 mg. in 100 cc. corresponding to 0.6 mg. of potassium chloride or 0.34 mg. of potassium oxide. (Analyses 10 and 11.)

The results for the sodium determination are somewhat low, 0.9677 grams of sodium chloride being recovered from 0.9710 grams taken for eight analyses, an average loss of 0.4 mgs. per determination. Volumetric and gravimetric sodium chloride determinations agree satisfactorily, and by either method are much more rapid than the usual sodium sulfate estimation. The sodium chloride precipitation can be made more complete than that of Table I by using ethyl acetate alone as wash liquid during filtration of potassium perchlorate, which results in the presence of less butyl alcohol during precipitation with hydrogen chloride.

The average filtrate and washings for the potassium determinations of Table I was 58 cc., and 51 cc. for the sodium determination. No attempt was made to restrict the use of solvent either in the extraction or filtration and washing of the precipitates dealt with in Table I beyond amounts needed in ordinary manipulation. The use of a solubility correction for the sodium determinations of Table I was not applied as was justified by the work of reference 2. The latter reference should be consulted for a more thorough discussion of all the points involved in the separation and determination of sodium and lithium and for test analyses in the same separation. For this reason the determinations of lithium in Table I were omitted.

The analyses of Table I were consecutive results with no omissions. The reliability of the process is thus

demonstrated. No violent reactions were encountered throughout this work.

SUMMARY

The use of a mixture of equal parts N butyl alcohol and ethyl acetate has been shown by test analyses to be satisfactory for:

1. The extraction separation of potassium and sodium perchlorates, two extractions with intermediate solution of potassium perchlorate being required.
2. The extraction separation of potassium and lithium perchlorates, one extraction only being required.
3. The separation of sodium and lithium subsequent to their extraction from potassium following the procedure of Willard and Smith in which sodium chloride is precipitated from solution in N butyl alcohol, by a hydrogen chloride solution in the same solvent. The sodium was determined volumetrically by Mohr's method.

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