

and a pressure range from 50 to 1000 atmospheres. The volume-percentage of ammonia in the gas phase within this range of temperature and pressure is presented in graphic and tabular form. At high pressures, concentrations of ammonia in the vapor phase have been found more than six times the concentrations calculated by the usual method from the vapor pressure of pure liquid ammonia.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]
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 previously 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 is converted to perchlorates by evaporation of their solution with an excess of pure perchloric acid, the latter removed by evaporation to dryness twice with intermediate solution in water. Sodium

¹ Smith, *THIS JOURNAL*, **47**, 762 (1925).

² Willard and Smith, *ibid.*, **44**, 2816 (1922).

³ Smith and Ross, *ibid.*, **47**, 774 (1925).

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 off, 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 are separated by the addition of a butyl alcoholic solution of hydrogen chloride according to the reaction, $\text{NaClO}_4 + \text{HCl} \rightarrow \text{NaCl} + \text{HClO}_4$. The reagent is added to the solution of the perchlorates until a 6% concentration of acid 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 110–250° and finally ignited for 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).

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

***n*-Butyl Alcohol.**—This material is now readily obtainable on the market at a moderate price. The alcohol used in this research had a boiling range of 112–118°; d_4^{25} , 0.8065; 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°; d_4^{25} , 0.8060. 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. The undried 60% fraction may be used with practically identical results.

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% of 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.

Potassium Chloride.—This was 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.⁵ 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 concd. sulfuric

⁴ Willard, *THIS JOURNAL*, **34**, 1480 (1912).

⁵ Richards and Willard, *ibid.*, **32**, 4 (1910).

acid on sodium chloride or concd. hydrochloric acid; 200 cc. of 20% solution could be prepared in two or three hours.

Ethyl Acetate.—This was the same material as that tested for use in connection with the work previously described.¹ It is very easily prepared in an equal state of purity and with excellent yields from cheap technical products. "Anhydrous ethyl acetate, 99.7–100%" furnished by a well-known manufacturer was used for the work of this paper.

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 with asbestos mats have been found adequate for all filtrations involved in this work but are far less convenient than platinum sponge filtering crucibles (Monroe crucibles). The advantage of the latter is most pronounced when 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 cause them to fume. 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% acid) and the solution thus obtained is evaporated to dryness on the hot-plate in a 150cc. 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, the contents are dissolved by the addition of a minimum of hot water (2 or 3 cc. generally suffices) and the solution is again evaporated to dryness on the hot-plate.

Ten to 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 for two or three minutes. The solution is cooled to room temperature and the supernatant liquid decanted through a previously ignited and weighed Monroe crucible and washed thrice by decantation to remove most of the soluble perchlorates, 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, the liquid 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 are washed with 10 to 15 portions of 0.5 to 1 cc. from the wash bottle.

The concentration of the filtrate is started at this point on the hot-plate. Any unremoved particles of perchlorate found in the original beakers after drying on the hot-plate are brushed in with the bulk of precipitate. The crucible and precipitate are dried for a few minutes at 110° in an oven and finally for 15 minutes in a muffle at 350° , cooled and weighed. The filtrate and washings by this process should approximate 50 cc. When 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 expelled, which is accomplished by concentrating to 40% 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% solution of hydrochloric acid in butyl alcohol, the first cubic centimeter being added dropwise while the mixture is constantly stirred. After the liquid has cooled to room temperature, the sodium chloride precipitate is collected on a Monroe crucible and washed eight or ten times with a 6 to 7% solution of hydrogen chloride in butyl alcohol (made by diluting 100 cc. of alcohol with 40 cc. of a 20% solution of hydrochloric acid in butyl alcohol). The crucible and precipitate are dried for a few minutes in an oven at 110° and finally ignited for five 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 by means of a fine stream of water from the wash bottle, the crucible thoroughly washed in the same manner, and the filtrate collected in a 150cc. beaker. The precipitate of sodium chloride is gray because of occluded carbon and the dissolved sodium chloride leaves a carbonaceous residue in the crucible. If it is desired to determine sodium gravimetrically, the dried and ignited crucible should be weighed prior to the 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 by means of standard 0.1 *N* silver nitrate solution using 1 cc. of a 5% solution of potassium chromate free from chloride as indicator (Mohr's method). The silver nitrate is best standardized against pure sodium chloride; and a correction should be applied for the solution required to produce the end-point reaction. The results by both the gravimetric and volumetric procedure agree.

The filtrate and washings from the sodium chloride are diluted with one-third their volume of water (to avoid subsequent deflagration), forming then two 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 nearly complete before the perchloric acid fumes appear. When a slight brown coloration is present, the watch glass supports are removed from the beaker and the covered beaker is heated on a wire gauze until fumes of perchloric acid appear. 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. When not enough perchloric acid is present to oxidize the last traces of organic matter, a few drops more should be added. When the brown coloration is removed, 0.5 cc. of concd. 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 are 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 five or ten 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 treatment described above is possible if the temperature is not too high or the treatment too long.

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 ^a NaCl Mg.	Error ^b KCl Mg.	Filtrate, cc.	
				1 extr.	2 extr.	Grav.	Vol.			Determi- nation of K	Na
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 ^c	-.25	55	..
4	.1416	.1354514265	.1416	.13495	.1352	-.25	± .0	50	38
5	.1310	.13521323	.1311	.13465	.1348	-.9	+ .1	56	51
6	.2346	.0317523360316	-.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	..

^a Based on two extractions if made.^b Based on volumetric sodium determination.^c Sodium determination lost by "running through" and was discarded.

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

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 a double extraction with the mixture of equal parts of *n*-butyl alcohol and ethyl acetate than are those obtained by the use of absolute ethyl alcohol.⁶ 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 g. of sodium chloride being recovered from 0.9710 g. taken for eight analyses, an average loss of 0.4 mg. 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 nearly complete than that of Table I by using ethyl acetate alone as wash liquid during the 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. A solubility correction for the sodium determinations of Table I was not applied although this was justified by previous work.² That work 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

⁶ Compare with the results obtained by Baxter and Kobayashi, *THIS JOURNAL*, 39, 249 (1917).

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; and (3) the separation of sodium and lithium subsequent to their extraction from potassium, following the procedure of Willard and Smith² 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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THE CRYSTAL STRUCTURE OF BARITE

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Introduction

Barite, BaSO_4 , a member of a large class of isomorphous crystals, is described by Groth¹ as orthorhombic bipyramidal, with axial ratios $a:b:c = 0.8152:1:1.3136$. This crystal has been recently investigated by Allison² by means of X-rays. The axial ratios were redetermined by goniometric measurements, using X-rays instead of visible light, and the values $0.8148:1:1.3131$ were obtained. Spectrometric measurements were made from thirteen planes, using a tungsten tube operated at 90,000 volts; and values of d/n were then calculated from the angles of reflection of the tungsten lines and the barium K absorption edge. The conclusions drawn from the data as to the structure of the crystal seem, however, to be clearly erroneous. For the author bases the determination of the unit of structure upon the assumption that the unit must have the crystallographic axial ratios, which in fact result from an arbitrary choice of a parametral plane from among the many permitted by the crystallographic data. Moreover, his derived unit of structure is inconsistent with his data, in that he gives in Table IV for plane (102) $d_{\text{calcd.}} = 2.792$ and $d_{\text{obs.}} = 5.562$; yet his observation shows that $d/n = 5.562$; and this obviously requires that $d = 5.562n$, where n is an integer, and hence does not permit that $d = \frac{1}{2} \times 5.562$ as calculated (approximately) from his unit of structure.³ The

¹ Groth, "Chemische Krystallographie," Engelmann, Leipzig, 1908, Vol. II, p. 388.

² S. K. Allison, *Am. J. Sci.*, [5] 8, 261 (1924).

³ The author is aware that there is a difficulty here, for he states that this result from (102) may be due to some "accidental" arrangement of atoms; however, it is not possible with any arrangement of atoms in his unit to explain the observed reflection. The analogy suggested to (100) of succinic acid and (010) of succinic anhydride [Yardley, *Proc. Roy. Soc.*, 105A, 451 (1924)] is not pertinent, for in these cases $d_{\text{calcd.}}$ is twice $d/n_{\text{obs.}}$, not one-half of it.