SEPARATION AND DETERMINATION OF THE ALKALI METALS USING PERCHLORIC ACID

II. THE PRECISE ESTIMATION OF THE INSOLUBLE ALKALI METAL PERCHLORATES

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The separation of potassium rubidium and cesium from sodium and lithium by the perchloric acid method is dependent upon the extraction of the latter two perchlorates from the former, using an organic solvent. The choice of the most suitable solvent was the subject of the first paper of this series. The present paper has for its object the establishment of a correct procedure governing the separation and weighing of the insoluble perchlorates of this group. The procedures previously described are shown to have appeared exact as the result of a fortuitous compensation of errors.

THE DEHYDRATION TEMPERATURE OF POTASSIUM PERCHLORATE

Four weighed samples of potassium chloride (a foreign stock guaranteed to be 100.00%) were dissolved in hot water in weighed platinum crucibles. One cc. of pure 72.5% perchloric acid was then added, the resulting solution evaporated to dryness and heated until the large excess of acid was completely removed. The potassium perchlorate thus obtained was dissolved by the addition of hot water and again precipitated by evaporation to dryness on the hot plate and baked two hours at approximately 140°. Crucible and contents were then dried three hours at 140-150°, cooled in a desiccator and weighed.

The samples were next dried one hour at 250° in a muffle, cooled as before and weighed. They were then dried 15 minutes at 350°, cooled and reweighed. Finally the samples thus treated were dried to constant weight at 350°. The results of the experiments are listed in Table I.

TABLE I.

The Dehydration at Various Temperatures of Potassium Perchlorate Crystallized from its Solution in Water.

	$KClO_4$ Found					
KCl taken	3 hrs. 140-150°	1 hr. 250°	15 min. 350°	Constant Wt. 350°	Theoretical $KClO_4$	Error KCl
g	g	g	g	g	g	g
0.15555	0.28965	0.28945	0.28915	0.28915	0.28905	+0.00005
0.11580	0.21585	0.21555	0.21530	0.21530	0.21520	+0.00005
0.11645	0.21700	0.21685	0.21650	0.21650	0.21640	+0.00005
0.15925	0.29670	0.29660	0.29620	0.29620	0.29595	+0.00015

The potassium chloride used for the determinations of Table I had been previously ground and ignited several hours at 500°. The samples were weighed from a very small weighing bottle directly into the platinum crucibles previously cleaned and ignited. All weighings were made using a number 10 Troemner balance and weights calibrated at the Bureau of Standards. The conversion factor of potassium perchlorate to potassium chloride was taken as 0.53810. The perchloric acid used had been purified by distillation under reduced pressure from an all glass pyrex distillation apparatus and was shown to be free from nonvolatil products.

The experiments listed in Table I show that potassium perchlorate crystallized from its solution in water can be quantitatively freed from the last traces of occluded moisture at a temperature of 350°. Samples of potassium perchlorate dried at 150° may contain approximately 0.3% of their weight of occluded moisture. Half of this is removed by treatment at 250°. The potassium perchlorate prepared for the experiments of Table I after treatment at 350° was tested for chloride formed by decomposition but no trace was found. Essentially the same results were obtained using cesium chloride, the magnitude of the error in this case being considerably less.

Descriptions, in general, of procedures for the separation and determination of K by the perchlorate process call for the drying of the potassium perchlorate at 150°. One procedure requires that 200° be employed.[1] The error thus introduced in the best work, following the usual procedure, is in general very satisfactorily compensated for by the solubility of potassium perchlorate in the organic solvent used in its separation.

THE OCCLUSION OF PERCHLORIC ACID BY THE INSOLUBLE ALKALI PERCHLORATES

The conversion of potassium, rubidium and cesium chlorides to perchlorates previous to their separation from sodium and lithium requires the evaporation of their solution in water with excess of perchloric acid. This evaporation results in the concentration of the excess perchloric acid to approximately the constant boiling aqueous acid of 72.5% strength. Potassium, rubidium and cesium perchlorates are freely soluble in hot 72.5% perchloric acid. The conversion of the chlorides of these metals to perchlorates followed by the evaporation of most of the perchloric acid is therefore, to considerable extent, a crystallization process in which strong per-

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[1] Baxter and Kobayashi, J. Am. Chem. Soc., 39, 249, (1917).

chloric acid is solvent. The present section deals with the occlusion of perchloric acid during this operation.

The solubilities of potassium, rubidium and cesium perchlorates in 72.5% perchloric acid at the boiling point are approximately 125 mg., 250 mg. and 1 g. in 1 cc. respectively. Their solubilities in the same acid at 25° are 3.7, 8.9 and 81.5 mg. per cc. respectively.

Potassium, rubidium and cesium perchlorates prepared as given by Willard and Smith[2] were dissolved in hot 72.5% perchloric acid and precipitated by rapid cooling to 0°. The crystals thus obtained were filtered centrifugally and washed twice with cold water using centrifugal drainage. The samples thus obtained were tested without further treatment, then after drying two hours at 120°, two hours at 250° and lastly 30 minutes at 350°, samples of approximately 0.5 gram each were dissolved in water and titrated with fiftieth normal sodium hydroxide solution, using methyl red as indicator. The results were as follows:

Treatment of Material	Per cent $HClO_4$			Chloride Test
	CsClO4	$RbClO_4$	$KClO_4$	
2 hrs.—120°	0.16	0.85	1.4	
2 hrs.—250°	0.14	0.75	1.1	Positive
½ hr. —350°	0.04	0.08	0.25	Positive

The occlusion of perchloric acid by the three perchlorates crystallized from hot 72.5% perchloric acid is thus seen to be greatest for potassium and least for cesium perchlorate. The occlusion is greatest for the perchlorate least soluble in the strong acid and least for the most soluble one. The occluded acid is not completely removed at 350° during thirty minutes heating. In all these cases the removal of perchloric acid at the higher temperatures was accompanied by a well defined decomposition with formation of chloride not obtained by heating the acid free perchlorate at the same temperature.

The nature of this occlusion of perchloric acid is easily observed upon examination of the crystals thus prepared, with the microscope, magnifying about 100 diameters. Figures 1 and 2 are micro-photographs of potassium perchlorate prepared as described, the former examined as prepared and the latter after drying at 350°.

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[2] Willard and Smith, J. Am. Chem. Soc., 45, 286 (1923).

FIG. I.

FIG. II.

From the examination of Figure I it is observed that potassium perchlorate crystallized from its solution in strong perchloric acid is obtained as long, hollow, tubular crystals in the hollow portion of which the mother liquor is frequently enclosed. Several darkened central portions of the crystals photographed indicate mother liquor enclosures. A peculiar phenomenon is the apparently convex rather than concave terminations of the liquid contained in the capillaries.

The crystals shown in Figure 2 are a separate portion of the same material dried at 350°, and are seen to have a very extensively pitted and cratered structure caused by the evolution of gaseous products accompanying the elimination of their acid impurity as well as by their own partial decomposition. Since sodium perchlorate is readily soluble in strong perchloric acid, its presence during the crystallization of potassium perchlorate would result in the occlusion of an appreciable amount of the former as a result of the occlusion of its acid solution.

The extraction process as applied to the separation of potassium and sodium, using any of the previously described organic solvents,[1] results in the separation of potassium perchlorate containing occluded perchloric acid, since the tendency towards acid occlusion is dependent upon the preliminary treatment with excess perchloric acid which is concentrated during the requisite elimination of the more volatil acids. The extent of this acid occlusion is never as pronounced in actual practice as in the analyses given since the insoluble perchlorates are not formed under the same extreme conditions.

That the occlusion of acid cannot be dependent upon the nature of the organic solvent used in the extraction was demonstrated under actual working conditions. Three 250 milligram samples of potassium chloride were dissolved in water and converted to perchlorate with excess perchloric acid and all but a small portion of the acid evaporated on the hot plate. The barely moist residue of potassium perchlorate was then partially cooled and treated with extracting solvent. Twenty-five cc. portions of absolute ethyl and N butyl alcohols and ethyl acetate were used, and the potassium perchlorate in each case filtered into platinum sponge crucibles and thoroughly washed with additional solvent. The samples thus obtained were dried one hour at 140-150°, dissolved in water and tested for acid. All contained appreciable amounts of free acid, approximately 0.5 milligram as estimated by titration with fiftieth normal sodium hydroxide.

THE RELATION TO PREVIOUS WORK OF OCCLUSION OF ACID AND MOISTURE

Willard,[3] who was the first to suggest the use of ethyl acetate in an extraction method for separating potassium and sodium, showed that potassium perchlorate obtained by the usual method of analysis occludes perchloric acid. The effect of the errors of occlusion giving high results are counterbalanced by the appreciable solubility of potassium perchlorate in the solvents usually employed in its separation. The low solubility of potassium perchlorate in ethyl acetate,[3] minimizing the latter of these two effects, appears to augment the former.

The most complete work on the perchlorate method is that of Morris,[4] which contains an extensive bibliography covering the principles and their application as well as a large number of tabulated determinations under a wide variation of conditions. This work contains the best details and procedures. Morris uses the methods described by Caspari[5] and by Gooch and Blake[6] with some slight modifications, and states that ‘‘given attention to essential details, results approach to scientific accuracy.’’ In view of the errors of occlusion already demonstrated in connection with this paper a considerable number of the determinations of Morris appeared exact only as a result of a compensation of errors.

The description of the process followed by Morris[4] is here quoted to facilitate discussion:

‘‘In nearly all cases the solution of the salt was evaporated with perchloric acid, three times in all, and the

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[3] H. H. Willard. “Advanced Quantitative Analysis.” 5th Ed. 1920. (Mimeographed by C. C. Edwards, Ypsilanti, Michigan.) Page 106, “At 24°, 100 cc. of pure ethyl acetate dissolves 1.1 mg. of potassium perchlorate; at 0°, 0.9 mg. while the solubility of sodium perchlorate is about the same as in absolute ethyl alcohol. The only difficulty attending its use is that occasionally the potassium perchlorate contains free perchloric acid or some organic compound with an acid reaction, which is not removed by drying at 150°.”

[4] Morris, Analyst, *45*, 349 (1920).

[5] Caspari, Z. angew. Chem., *6*, 68, (1893).

[6] Gooch and Blake, Am. J. Sci., *44*, 381, (1917).

final evaporation taken practically to dryness. The residue was treated with 10 cc. of wash liquid, stirred well with a flat headed glass rod, allowed to stand ten or fifteen minutes when sodium was present, occasionally stirring; the solution decanted through a weighed Gooch crucible containing asbestos. When only potassium was present, the precipitate was then rinsed out directly with the wash liquid in measured quantity by means of a wash bottle. When sodium was present the basin containing the residue from the first decantation was placed on the top of the air oven for a few minutes, till the alcohol was evaporated; then the residue was dissolved in the minimum amount of boiling water, and again evaporated to dryness. The treatment with 10 cc. of wash liquid and decantation was repeated and the residue then transferred completely by using the latter 10 cc. of the filtrate. Finally a measured volume of the wash liquid was added (by the use of a small pipet) in portions, to complete the washing on the filter. The Gooch crucible and contents were then dried for about an hour at 130° to 150° C., cooled for one hour in a desiccator and weighed. After weighing, 2 or 3 cc. more wash liquid were passed through the filter, and the drying and weighing repeated. The weight was taken as constant when, on washing with 2 or 3 cc. of liquid, the difference on successive weighings did not vary by more than one or two tenths of a mg.’’

According to this procedure if potassium perchlorate alone is present its determination is accompanied by an acid as well as moisture occlusion neither of which are eliminated at 150°. These errors are satisfactorily counterbalanced by the solvent action of the alcohol.[7] If sodium is present the procedure calls for a double extraction with intermediate evaporation of the potassium perchlorate. This eliminates the acid occlusion error but not that of the occlusion of moisture. The contamination

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[7] Compare the values obtained in Table I of reference 4. A total of 2.3774 grams of potassium chloride taken for 21 analyses resulted in the recovery of 4.4177 grams of potassium perchlorate corresponding to 2.3773 grams of potassium chloride. 664 cc. of filtrate and washings were accumulated in the 21 analyses. Analysis 7 is illustrative of the failure of the solvent action to compensate for the errors of occlusion in the large sample used. 0.6685 grams of potassium chloride were recovered from 0.6673 grams taken for analysis. It cannot be agreed (page 365, reference 4) that "it is obvious that the mere stirring up of pure potassium perchlorate with the wash liquid and decantation (twice with 10 cc. each time) causes no appreciable loss, so that the loss by continued washing of the precipitate on the asbestos is the chief cause of low results."

of potassium perchlorate by the sodium salt, even after double extraction, more than equals the acid occlusion error which has been eliminated.[8] This condition is unavoidable using ethyl alcohol as extracting solvent. By the use of mixed solvents,[9] which have much greater solvent action on sodium perchlorate, the sodium occlusion error can be appreciably diminished. The washing of a dried and weighed sample of potassium perchlorate with additional solvent, followed by a second drying and weighing to test the complete removal of sodium which might have remained from previous washing as a result of a restricted use of wash alcohol, is a very unsatisfactory portion of the procedure.

Some procedures[10] for the separation of potassium and sodium provide for the resolution in a dilute solution of perchloric acid of the potassium perchlorate, following its original formation in the same acid and first extraction. The potassium perchlorate is then precipitated by evaporation nearly to dryness. Obviously this practice does not eliminate acid occlusion.

IMPROVED PROCESS FOR THE SEPARATION BY EXTRACTION OF THE ALKALI PERCHLORATES

As a result of the experiments of the first two papers of this series the following procedure for the separation of the alkali perchlorates by extraction is proposed:

The mixed chlorides 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 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 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.

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[8] Table II. Reference 4, page 358.

[9] Compare the values given in the first paper of this series. J. Am. Chem. Soc., 47, 762, (1925).

[10] Baxter and Rupert, J. Am. Chem. Soc., 42, 2046, (1920).

10-20 cc. of the mixed organic solvent selected for the extraction 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 weighted platinum sponge crucible and washed three times by decantation to remove most of the soluble perchlorate extracted, and 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 solvent, and the crucible contents washed with 10-15 portions of ½-1 cc. from the wash bottle. The filtrate is concentrated on the hot plate to the proper volume preparatory to its subsequent analysis. The precipitating beaker is returned to the hot plate until dry and any unremoved particles of perchlorate thus formed brushed in with the bulk of precipitates.

The crucible and precipitate are dried a few minutes at 100° in an oven and finally 15 minutes in a muffle at 350°, cooled and weighed. The filtrate and washings by this process should range from 35 to 45 cc. If no sodium or lithium perchlorate is present the second precipitation and extraction can be omitted.

Gooch and Blake[11] have found that perchlorate acid has a decided action on glass which may result in the contamination of the perchlorates determined by silica. The study in connection with the perchloric acid process reported in this series of papers has shown no appreciable action on pyrex beakers. Platinum sponge filtering crucibles have in most cases been weighed subsequent to their use in filtering potassium perchlorate obtained by evaporation of perchloric acid in excess, and no increase in weight due to silica has been found. Any silicic acid resulting from the action of the acid on the beakers would have been dehydrated during the evaporation process.

It will be noted that the improved procedure given above does not involve the use of any organic solutions

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[11] Gooch and Blake, Am. J. Sci., *44*, 381, (1917).

containing perchloric acid. Any remote danger of violent reaction resulting from the use of such solutions is eliminated.

SUMMARY.

1. The correct drying temperature of the insoluble alkali perchlorates has been determined.
2. The occlusion of perchloric acid by these salts has been studied.
3. Previous procedures for the perchloric acid separation of the alkali metals by extraction were shown to be faulty and an improved method is described.

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