Summary

A number of new methods for the preparation of selenium monochloride and selenium monobromide are given in this paper.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE SEPARATION AND DETERMINATION OF THE ALKALI METALS USING PERCHLORIC ACID. II. THE PRECISE ESTIMATION OF THE INSOLUBLE ALKALI METAL PERCHLORATES

BY G. FREDERICK SMITH AND JOHN F. ROSS

RECEIVED JANUARY 12, 1925 PUBLISHED MARCH 5, 1925

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 by means of 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 to each, the resulting solutions were evaporated to fumes 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, then baked for two hours at approximately 140°. The crucible and contents were then dried for three hours at 140–150°, cooled in a desiccator and weighed.

The samples were next dried for one hour at 250° in a muffle, cooled as before and weighed. They were then dried for 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.

The potassium chloride used for the determinations of Table I had been previously ground and ignited for 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 No. 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 non-volatile products.

Table I

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

KCl taken G.	KClO$_4$ found 3 hrs. 140–150° G.	 1 hr. 250° G.	 15 min. 350° G.	 Constant wt. 350° G.	Calcd. KClO$_4$ G.	Error KCl Mg.
0.15555	0.28965	0.28945	0.28915	0.28915	0.28905	+0.05
.11580	.21585	.21555	.21530	.21530	.21520	+ .05
.11645	.21700	.21685	.21650	.21650	.21640	+ .05
.15925	.29670	.29660	.29620	.29620	.29595	+ .15

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 potassium 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 an 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 a considerable extent, a crystallization process in which concd. perchloric acid is solvent. The present section deals with the occlusion of perchloric acid during this operation.

---

[1] Baxter and Kobayashi, This Journal, 39, 249 (1917).

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 g. each were dissolved in water and titrated with 0.02 *N* sodium hydroxide solution, using methyl red as indicator. The results were as follows:

TABLE II

OCCLUSION OF PERCHLORIC ACID

Treatment of material		Per cent. of $HClO_4$			
Time *Hours*	°C.	$CsClO_4$	$RbClO_4$	$KClO_4$	*Chloride test*
2	120	0.16	0.85	1.4	....
2	250	.14	.75	1.1	Positive
0.5	350	.04	.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 30 minutes, heating. In all these cases the removal of perchloric acid at the higher temperatures was accompanied by a well defined decomposition with the 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. Figs. 1 and 2 are microphotographs of potassium perchlorate prepared as described, the former examined as prepared and the latter after drying at 350°.

From the examination of Fig. 1 it is observed that potassium perchlorate crystallized from its solution in strong perchloric acid is obtained as long, 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.

---

[2] Willard and Smith, THIS JOURNAL, **45**, 286 (1923).

The crystals shown in Fig. 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 volatile acids. The extent of this acid occlusion is never as pronounced in actual practise as in the analyses given, since the insoluble perchlorates are not formed under the same extreme conditions.

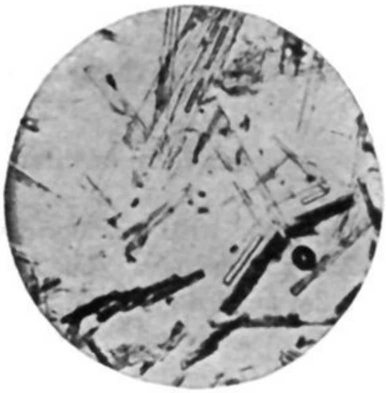

Fig. 1.

Fig. 2.

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 mg. samples of potassium chloride were dissolved in water and converted to perchlorate with an excess of perchloric acid, and all but a small portion of the acid was 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 was filtered through platinum sponge crucibles and thoroughly washed with additional solvent. The samples thus obtained were dried for one hour at 140–150°, dissolved in water and tested for acid. All contained appreciable amounts of free acid, approximately 0.5 mg. as estimated by titration with 0.02 N sodium hydroxide solution.

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 variety 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 the results approach to scientific accuracy." In view of the errors of occlusion already demonstrated in 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 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 for ten to 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°, 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

---

[3] H. H. Willard, "Advanced Quantitative Analysis," (Mimeographed by C. C. Edwards, Ypsilanti, Michigan), 5th ed., **1920**, p. 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).

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 is 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 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 re-solution 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 practise 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.

---

[7] Compare the values obtained in Table I of Ref. 4. A total of 2.3774 g. of potassium chloride taken for 21 analyses resulted in the recovery of 4.4177 g. of potassium perchlorate corresponding to 2.3773 g. 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 g. of potassium chloride was recovered from 0.6673 g. taken for analysis. It cannot be agreed (Ref. 4, p. 365) 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."

[8] Ref. 4, p. 358. Table II.

[9] Compare the values given in the first paper of this series. This Journal, **47,** 762 (1925).

[10] Baxter and Rupert, This Journal, **42,** 2046 (1920).

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.

Ten to twenty 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 for two or three minutes. The solution is cooled to room temperature and the supernatant liquid decanted through a previously ignited and weighed platinum-sponge filtering crucible (Monroe crucible) and the residue washed thrice by decantation to remove most of the soluble perchlorate extracted and 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 to 15 portions of 0.5–1 cc. each 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 found 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 volume of filtrate and washings obtained by this process should range from 35 to 45 cc. When no sodium or lithium perchlorate is present the second precipitation and extraction can be omitted.

Gooch and Blake[11] have found that perchloric acid has a decided action on glass which may result in the contamination of the perchlorates determined, by silica. The study of 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 in-

---

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

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

Gooch filtering crucibles with asbestos mats can be used wherever platinum-sponge filtering crucibles are mentioned in this paper.

Summary

1. The correct drying temperature of the insoluble alkali perchlorates has been found to be 350°.

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 are shown to be faulty and an improved method is described.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 56]

THE CRYSTAL STRUCTURES OF HEMATITE AND CORUNDUM

BY LINUS PAULING AND STERLING B. HENDRICKS

RECEIVED JANUARY 12, 1925 PUBLISHED MARCH 5, 1925

Introduction

Hematite, Fe_2O_3, and corundum, Al_2O_3, form crystals which have been assigned,[1] on the basis of observed face development, to the holohedral class of the rhombohedral system, with the rhombohedral angle α equal to 85° 42′ and 85° $42\frac{2}{3}'$, respectively. Spectrometric measurements have been made[2] of the reflection of X-rays from three faces of ruby, Al_2O_3, and two of hematite. Utilizing the hypothesis that in ruby each aluminum atom is equidistant from six oxygen atoms, and each oxygen atom equidistant from four aluminum atoms, a possible structure has been devised[3] which is not incompatible with these spectrometric observations. This structure has been used in a theoretical consideration of the influence of atomic arrangement on birefringence,[4] and in the explanation of the observed variation with temperature of the intensity of reflection of X-rays from faces of crystals of ruby and sapphire.[5] An exact knowledge of the arrangement of the constituent atoms in ruby would make the arguments of these papers much more convincing.

Powder photographic data from aluminum and ferric oxides prepared

---

[1] Groth, "Chemische Krystallographie," Engelmann, Leipzig, **1908**, Vol. 1, p. 105.

[2] W. H. and W. L. Bragg, "X-Rays and Crystal Structure," G. Bell and Sons, London, **1915**, p. 171.

[3] W. H. and W. L. Bragg, "X-Rays and Crystal Structure," 4th edition, G. Bell and Sons, London, **1924**, p. 183.

[4] W. L. Bragg, *Proc. Roy. Soc.*, **106**, 346 (1924).

[5] I. Backhurst, *ibid.*, **102**, 340 (1922).