ART. XXXVI.—*The Preparation of Perchloric Acid and its Application to the Determination of Potassium;* by D. ALBERT KREIDER.

[Contributions from the Kent Chemical Laboratory of Yale College.—XXXVIII.]

VARIOUS methods for the preparation of perchloric acid have been developed through the long felt want of a process in which the elements of time and danger would be reduced to a minimum and the product increased to quantities commensurate with the growing use of the acid in analytical chemistry. Most of these methods have been found impracticable because of the incidental formation of the dangerously explosive oxides of chlorine, or the time required in refining the product from the impurities introduced with the reagents employed.

Doubtless the best process thus far offered is that of Caspari,* which, however, is to an objectionable degree exacting of time and labor. The product has to be treated and retreated for the removal of potassium and then for the extraction of the hydro-fluo-silicic-acid and at several stages is for this purpose to be left standing for from twenty-four to forty-eight hours. Under the most favorable circumstances it could not be prepared in less than five or six days, and during a great many hours of that time it requires close attention.

The great difficulty has always been with the necessity of a perfect separation of potassium from the perchloric acid, which has been prepared by the ignition of the potassium chlorate. If, for the manufacture of the perchlorate, the chlorate of sodium—which, if not upon the shelves of every laboratory, is nevertheless in the market, almost, if not entirely free of potassium—be used instead of the potassium salt, the complete removal of the base will be unessential; since its presence in the determination of potassium will exert no influence other than that which is beneficial. It is well known that because of its deliquescence and the almost equal solubility of sodium perchlorate with that of the chloride, its separation from the latter by recrystallization from an aqueous solution, as in the case of potassium, is impossible. But the insolubility of the chloride of sodium in strong hydrochloric acid, with the aid of the acid-proof Gooch crucible, affords a means for the liberation of the perchloric acid and the removal of the greater part of the sodium in one operation. Upon this basis, therefore, the following simple method was elaborated.

A convenient quantity of sodium chlorate, from 100 to 300 grms., is melted in a glass retort or round-bottomed flask and

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* Zeitschr. für Ang. Chem., 1893, p. 68.

gradually raised to a temperature at which oxygen is freely, but not too rapidly evolved, and kept at this temperature till the fused mass thickens throughout, which indicates the complete conversion of the chlorate to the chloride and perchlorate, and requires between one and one-half to two hours: or the retort may be connected with a gasometer and the end of the reaction determined by the volume of oxygen expelled, according to the equation

$$2NaClO_3 = NaCl + NaClO_4 + O_2.$$

The product thus obtained is washed from the retort to a capacious evaporating dish where it is treated with sufficient hydrochloric acid to effect the complete reduction of the residual chlorate, which, if the ignition has been carefully conducted with well distributed heat, will be present in but small amount. It is then evaporated to dryness on the steam bath, or more quickly over a direct flame, and with but little attention until a point near to dryness has been reached, when stirring will be found of great advantage in facilitating the volatilization of the remaining liquid and in breaking up the mass of salt. Otherwise the perchlorate seems to solidify with a certain amount of water, and removal from the dish, without moistening and reheating, is impossible.

After triturating the residue, easily accomplished in a porcelain mortar, an excess of the strongest hydrochloric acid is added to the dry salt, preferably in a tall beaker where there is less surface for the escape of hydrochloric acid and from which the acid can be decanted without disturbing the precipitated chlorid. If the salt has been reduced to a very fine powder, by stirring energetically for a minute, the hydrochloric acid will set free the perchloric acid and precipitate the sodium as chloride, which in a few minutes settles, leaving a clear solution of the perchloric acid with the excess of hydrochloric acid. The clear supernatant liquid is then decanted upon a Gooch filter, through which it may be rapidly drawn with the aid of suction, and the residue retreated with the strongest hydrochloric acid, settled, and again decanted, the salt being finally brought upon the filter where it is washed with a little strong hydrochloric acid. A large platinum cone will be found more convenient than the crucible, because of its greater capacity and filtering surface. When the filter will not hold all the sodium chloride, the latter after being washed may be removed by water or by mechanical means, with precautions not to disturb the felt, which is then ready for the remainder. Of course, if water is used, the felt had better be washed with a little strong hydrochloric acid before receiving another portion of the salt. This residue will be found to contain only an inconsiderable amount of perchlorate, when tested by first heating to expel the free acid and then treating the dry and powdered residue with 97 per cent alcohol, which dissolves the perchlorate of sodium but has little soluble effect on the chloride.

The filtrate, containing the perchloric acid with the excess of hydrochloric acid and the small per cent of sodium chloride which is soluble in the latter, is then evaporated over the steam bath till all hydrochloric acid is expelled and the heavy white fumes of perchloric acid appear, when it is ready for use in potassium determinations. Evidently the acid will not be chemically pure because the sodium chloride is not absolutely insoluble in hydrochloric acid; but a portion tested with silver nitrate will prove that the sodium, together with any other bases which may have gone through the filter, has been completely converted into perchlorate, and unless the original chlorate contained some potassium or on evaporation the acid was exposed to the fumes of ammonia, the residue of the evaporation of a portion is easily and completely soluble in 97 per cent alcohol and its presence is therefore unobjectionable. One cubic centimeter of the acid thus obtained gave on evaporation a residue of only 0·036 grm., which was completely soluble in 97 per cent alcohol.

Caspari's acid under similar treatment gave a residue in one case of 0·024 grms. and in another 0·047 grms. If, however, a portion of pure acid be required, it may be obtained by distilling this product under diminished pressure and, as Caspari has shown, without great loss providing the heat is regulated according to the fumes in the distilling flask.

Some modification of the above treatment will be found necessary in case the sodium chlorate contains any potassium as an impurity, or if the latter has been introduced from the vessel in which the fusion was made. Under these circumstances the hydrochloric acid would not suffice for the removal of potassium, since a trace might also go over with the sodium and thus on evaporation a residue insoluble in 97 per cent alcohol be obtained. To avoid this difficulty, the mixture of sodium perchlorate and chloride, after being treated with hydrochloric acid for the reduction of the residual chlorate, being reduced to a fine powder, was well digested with 97 per cent alcohol, which dissolves the sodium perchlorate but leaves the chloride as well as any potassium salt insoluble. By giving the alcohol time to become saturated, which was facilitated by stirring, it was found on filtering and evaporating that an average of about 0·2 grm. of sodium perchlorate was obtained for every cubic centimeter of alcohol and that the product thus obtained was comparatively free of chlorides, until the perchlorate was nearly all removed, when more of the chloride seems to dissolve. This treatment with alcohol is continued until, on evaporation of a small portion of the latest filtrate, only a small residue is found. The alcoholic solution of the perchlorate is then distilled from a large flask until the perchlorate begins to crystallize, when the heat is removed and the contents quickly emptied into an evaporating dish, the same liquid being used to wash out the remaining portions of the salt. When the distillation is terminated at the point indicated, the distillate will contain most of the alcohol employed, but in a somewhat stronger solution, so that it requires only diluting to 97 per cent to fit it for use in future preparations. The salt is then evaporated to dryness on the steam bath and subsequently treated with strong hydrochloric acid for the separation of the perchloric acid.

One cubic centimeter of the acid prepared in this way, on evaporation gave a residue in one case of 0·0369 grms., and in another 0·0307 grm., completely soluble in 97 per cent alcohol, which was then ignited and the chlorine determined by silver from which the equivalent of perchloric acid in the form of salts was calculated as 0·0305 grm. By neutralizing the acid with sodium carbonate, evaporating, igniting in an atmosphere of carbon dioxide till decomposition was complete, collecting the oxygen over caustic potash, allowing it to act on hydriodic acid by intervention of nitric oxide, according to a process soon to be published, titrating the iodin liberated, with standard arsenic and calculating the equivalent of perchloric acid, after subtracting the amount of acid found in the form of salts, the amount of free acid per cubic centimeter proved to be 0·9831 grms.

The whole process, even when the separation with alcohol is necessary, can not well require more than two days and during the greater part of that time the work proceeds without attention.

In applying perchloric acid, thus prepared, to the determination of potassium according to the treatment suggested by Caspari* very satisfactory results were obtained. Briefly, the method is as follows: The substance, free from sulphuric acid, is evaporated to the expulsion of free hydrochloric acid, the residue stirred with 20 cm^3 of hot water and then treated with perchloric acid in quantity not less than one and one-half times that required by the bases present, when it is evaporated with frequent stirring to a thick, syrup-like consistency, again dissolved in hot water and evaporated with continued stirring till all hydrochloric acid has been expelled and the fumes of per-

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* loc. cit.

chloric acid appear. Further loss of perchloric acid is to be compensated for by addition of more. The cold mass is then well stirred with about 20 cm^3 of wash alcohol—97 per cent alcohol containing 0·2 per cent by weight of pure perchloric acid—with precautions against reducing the potassium perchlorate crystals to too fine a powder. After settling, the alcohol is decanted on the asbestos filter and the residue similarly treated with about the same amount of wash alcohol, settling and again decanting. The residual salt is then deprived of alcohol by gently heating, dissolved in 10 cm^3 of hot water and a little perchloric acid, when it is evaporated once more with stirring, until fumes of perchloric acid rise. It is then washed with 1 cm^3 of wash alcohol, transferred to the asbestos, preferably by a policeman to avoid excessive use of alcohol, and covered finally with pure alcohol: the whole wash process requiring about 50 to 70 cm^3 of alcohol. It is then dried at about 130° C. and weighed.

The substitution of a Gooch crucible for the truncated pipette employed by Caspari will be found advantageous; and asbestos capable of forming a close, compact felt should be selected, inasmuch as the perchlorate is in part unavoidably reduced, during the necessary stirring, to so fine a condition that it tends to run through the filter when under pressure. A special felt of an excellent quality of asbestos was prepared for the determinations given below and seemed to hold the finer particles of the perchlorate very satisfactorily.

A number of determinations made of potassium unmixed with other bases or non-volatile acids are recorded in the following table:

KCl taken. grms.	Volume of filtrate. cm^3.	$KClO_4$ found. grms.	Error on $KClO_4$. grms.	Error on KCl. grms.	Error on K_2O. grms.
0·1000	54	0·1851	0·0008 —	0·0004 —	0·0003 —
0·1000	58	0·1854	0·0005 —	0·0002 —	0·0002 —
0·1000	51	0·1859	0·0000	0·0000	0·0000
0·1000	50	0·1854	0·0005 —	0·0002 —	0·0002 —
0·1000	48	0·1859	0·0000	0·0000	0·0000
0·1000	52	0·1854	0·0005 —	0·0002 —	0·0002 —

Considerable difficulty, however, was experienced in obtaining equally satisfactory determinations of potassium associated with sulphuric and phosphoric acids. As Caspari has pointed out, the sulphuric acid must be removed by precipitation as barium sulphate before the treatment with perchloric acid is attempted, and unless the precipitation is made in a strongly acid solution, some potassium is carried down with the barium. Phosphoric acid need not be previously removed; but to secure a nearly complete separation of this acid from the potassium, a considerable excess of perchloric acid should be left upon the potassium perchlorate before it is treated with the alcohol. When these conditions are carefully complied with, fairly good results may justly be expected. Below are given a number of the results obtained.

Compounds taken. grms.	Vol. of filtrate. cm³.	$KClO_4$ found. grms.	Error on $KClO_4$. grms.	Error on KCl. grms.	Error on K_2O. grms.
KCl = 0·1000					
$CaCO_3$ = 0·13	50	0·1887	0·0028+	0·0014+	0·0009+*
$MgSO_4$ = 0·13	82	0·1875	0·0016+	0·0008+	0·0005+*
Fe_2Cl_6 = 0·05	80	0·1861	0·0002+	0·0001+	0·0001+†
$Al_2(SO_4)_3$ = 0·05	80	0·1843	0·0016−	0·0008−	0·0005−†
MnO_2 = 0·05	92	0·1839	0·0020−	0·0010−	0·0006−†
$HNa_2PO_4 \cdot 12H_2O$ = 0·40	60	0·1854	0·0005−	0·0002−	0·0002−†

In the last three experiments of the above table the amount of perchloric acid was about three times that required to unite with the bases present and the phosphoric acid subsequently found with the potassium was hardly enough to appreciably affect the weight, although its absolute removal was found impossible.

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* The residue showed phosphoric acid plainly when tested.

† Only traces of phosphoric acid found in the residue.