

ART. VII.—*The Detection of Alkaline Perchlorates associated with Chlorides, Chlorates, and Nitrates*; by F. A. GOOCH and D. ALBERT KREIDER.

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THOUGH perchloric acid in the free state is an exceedingly active body, its combinations with alkaline metals are, as is well known, so characterized by inertness toward ordinary reagents that in order to effect its detection it has been customary to place dependance either upon the insolubility of the potassium salt in alcohol, or upon tests for the corresponding chloride derived by ignition.

In experimenting at high temperatures upon mixtures of potassium perchlorate with salts of the halogens we have found it possible to effect the liberation of the halogen to a greater or less degree by the oxygen of the perchlorate, but the amount thus evolved has never been sufficiently complete or regular to warrant the application of the reaction to the quantitative determination of the perchlorate. In two parallel experiments, for example, a mixture of the double chloride of aluminum and sodium with 0.05 gram. of potassium perchlorate evolved in fusion in a tubulated flask (which was fitted by a ground joint to an inlet tube carrying a constant current of carbon dioxide and connected with Will and Varrentrapp absorption bulbs filled with a solution of potassium iodide), an amount of chlorine corresponding to 0.0482 gram. and 0.0460 gram. of the perchlorate. A similar experiment conducted in an atmosphere of hydrochloric acid gas and carbon dioxide in mixture yielded chlorine amounting to 0.0477 gram. of the perchlorate. Fusion of the perchlorate with cadmium iodide resulted in the liberation of much oxygen accompanying the iodine, and a mixture of zinc chloride with potassium iodide (melting at about 200° C.), yielded a large evolution of oxygen which was somewhat diminished but not wholly prevented when manganese chloride was included in the mixture. A series of 14 experiments in which mixtures of the perchlorate with potassium iodide were treated with meta-phosphoric acid (made by heating the syrupy ortho-acid to 360° C.) in an atmosphere of carbon dioxide showed deficits in the amounts of iodine evolved amounting to 1.7 per cent on the average between extremes of 3.6 per cent in excess and 7.7 per cent in deficiency, and these particular experiments doubtless point to a more complete utilization of the oxygen of the perchlorate than was actually attained owing to the inevitable partial de-

composition of hydriodic acid at the temperature necessary to effect the decomposition of the perchlorate.

We have, however, succeeded in developing a simple and delicate method of detecting perchlorates, and one which may be applied without great sacrifice in delicacy to mixtures of the perchlorates with chlorides, chlorates and nitrates. It is evident that for a rapid qualitative test conditions should be so chosen that the effect of atmospheric air shall not interfere with the certainty of the indication. Of the various salts which we have employed we choose by preference fused zinc chloride, chiefly because, while sufficiently energetic in its action upon the perchlorate, it does not, like manganese chloride or the double chloride of aluminum and sodium, evolve chlorine under the influence of ordinary air at the high temperature of the reaction.

In the experiments recorded in Table I varying portions of a solution of potassium perchlorate were evaporated to dryness in a test tube and fused with anhydrous zinc chloride. A trap made by cutting off an ordinary two-bulbed straight drying tube was hung with the larger end downward in the test tube, after moistening the interior of the bulbs with a solution of potassium iodide. The chlorine evolved during the heating was registered by the iodine set free from the iodide and subsequently washed with a little water from the trap and tested with starch emulsion.

TABLE I.

| KClO ₄ taken. | Indication by the starch test. |
|--------------------------|--------------------------------|
| 0.00100 gm. | Strong. |
| 0.00050 " | " |
| 0.00020 " | " |
| 0.00010 " | " |
| 0.00010 " | " |
| 0.00005 " | Distinct. |
| 0.00005 " | " |
| 0.00003 " | Trace. |
| 0.00003 " | None. |
| 0.00001 " | " |
| 0.00000 " | " |

The test for 0.00005 gm. of potassium perchlorate is sure and distinct; and it is, of course, evident that the presence of a chloride in the original test can in no way interfere with the certainty of the indication. All substances, however, which yield chlorine by decomposition or by the action of the air must be removed or destroyed before the application of the test. We find by experiment that 0.1 gm. of potassium chlorate is completely broken up by treatment with 5 cm³ of

the strongest hydrochloric acid and evaporation to dryness. Nitric acid does not yield so readily to the decomposing action of hydrochloric acid and may be detected in the residue after four similar treatments. To destroy nitrates, therefore, we followed the general plan of decomposition employed in a quantitative method for the determination of nitrates previously elaborated in this laboratory* and treated the dry substance to be tested with 2 cm³ of a saturated solution of manganous chloride in the strongest hydrochloric acid. The liquid was evaporated to dryness, and the residue was again treated similarly with one or two cubic centimeters of strong hydrochloric acid. This method of decomposing the nitrate is peculiarly advantageous since the decomposing agent is itself an excellent indicator of the completeness of the work of removal. Two or three treatments serve to remove the nitrate entirely; but before proceeding with the test it is necessary to remove the manganese which has been introduced, inasmuch as manganese chloride will of itself evolve chlorine, by exchange for oxygen, when heated in air. Sodium carbonate in solution answers the purpose of removing the manganese (together with other interfering substances) and the filtrate from the precipitated manganous carbonate leaves on evaporation a residue, which, when treated with the anhydrous zinc chloride, gives indications for the perchlorate if it is present in appreciable amount. The results of a series of tests for potassium perchlorate associated with the chlorate and nitrate of the same element and recorded in the following table.

TABLE II.

| KClO ₄ taken. gram. | KClO ₃ taken. gram. | KNO ₃ taken. gram. | Treatment for the removal of chlorate and nitrate. | Indication of the perchlorate. |
|-----------------------------------|-----------------------------------|----------------------------------|--|--------------------------------------|
| 0.0005 | ---- | ---- | By HCl | Strong. |
| 0.0003 | ---- | ---- | “ | “ |
| 0.0002 | ---- | ---- | “ | Good. |
| 0.0001 | ---- | ---- | “ | “ |
| 0.0001 | ---- | ---- | “ | Trace. |
| 0.0005 | 0.1 | 0.1 | By HCl + MnCl ₂ | Strong. |
| 0.0003 | 0.1 | 0.1 | “ “ | Good. |
| 0.0003 | 0.1 | 0.1 | “ “ | Good. |
| 0.0002 | 0.1 | 0.1 | “ “ | Trace. |
| 0.0001 | 0.1 | 0.1 | “ “ | Trace. |
| 0.0000 | 0.1 | 0.1 | “ “ | None. |

It is plain that 0.0001 gram. of potassium perchlorate may be found with certainty when associated with 0.1 gram. of the nitrate or chlorate or both.

* Gooch and Gruener, this Journal, xlv, 117.