ART. XXX.—*Contributions from the Sheffield Laboratory of Yale College.* No. VII.—*On the Indirect Determination of Potash and Soda;* by PETER COLLIER, B.A., Assistant in the Sheffield Laboratory.

THE method customarily employed in estimating potash and soda, viz: by the precipitation of the former as platinchlorid of potassium and reckoning soda from the loss, though sufficiently accurate in patient and skillful hands, is yet open to many sources of error and at the best is exceedingly tedious and troublesome.

The indirect method does not yet appear to possess the confidence of chemists, at least, it is rarely mentioned in published investigations. I have therefore, at the suggestion of Prof. Johnson, made a number of experiments to ascertain the limits of error in this process.

The volumetric estimation of chlorine as perfected by Mohr offers by far the best basis for an indirect determination of the alkalies. It is in fact requisite in employing the usual direct method, to procure the alkalies in the condition of pure chlorids before precipitation.

When the alkali chlorids are obtained free from all foreign matters, it is but the work of a few moments to ascertain their content of chlorine.

The silver solution used for this purpose is best prepared by weighing off in a porcelain crucible about 4·8 grm. of clean crystallized nitrate of silver, fusing it at the lowest possible heat, and then ascertaining its weight accurately. After fusion it should weigh *a little more* than 4·7933 grm., the quantity, that, contained in a liter of water, gives a solution of which 1 c. c. =

·001 grm. of chlorine. The fused salt is dissolved in a little warm water, the solution brought into a liter flask and filled to the mark, observing the usual precautions as to temperature, &c. When thus adjusted, add to the contents of the flask, from a burette, enough water to bring the excess of nitrate of silver above 4·7933 grms. to the requisite dilution. In this way it is easy with a burette and liter flask to make a perfectly accurate standard solution, while this would be hardly possible should the operator weigh off *less* than 4·7933 grm. of nitrate of silver.

This solution, which may be preserved in a well corked bottle indefinitely, without change, is next tested by means of a solution of pure chlorid of sodium or chlorid of ammonium, a quantity, say about 2 grams, of one of these salts being dissolved in a liter of water and 20 c. c. of the liquid taken for the comparison. The solution being ready, the estimation of chlorine is conducted as described by Mohr, Fresenius, Sutton and others, chromate of potash being employed to indicate the completion of the reaction. The use of Erdmann's float in a burette (which may hold 70 c. c.) graduated to fifths ensures the needful accuracy of reading. In my determinations $\frac{2}{10}$th c. c. of silver solution were deducted as the excess needed to produce a visible quantity of chromate of silver.

The appended table gives the results I obtained in the analyses of the chlorids of potassium and sodium. The salts were perfectly pure and the quantities were weighed out in each case. In order to test the method thoroughly I have varied the proportions of the mixtures from one extreme to the other.

Summary of Volumetric Chlorine Determinations.

	K Cl taken.	NaCl taken.	Cl found.	K Cl calculated.	NaCl calculated.	Cl calculated.
1st analysis.	·0582	----	·02780	·05725	·00095	·02768
2nd "	·1668	----	·07940	·16617	·00063	·07932
3rd "	·1507	----	·07168	·15056	·00014	·07167
4th "		·0590	·03600		·06062	·03579
5th "	·0782	·0317	·05640	·07831	·03159	·05642
6th "	·0305	·0379	·03750	·03044	·03796	·03750
7th "	·0455	·0169	·03200	·04464	·01776	·03189
8th "	·0166	·0480	·03720	·01514	·04946	·03701
9th "	·0530	·0429	·05120	·05319	·04271	·05123
10th "	·0431	·0820	·07027	·04282	·08228	·07024
11th "	·0992	·0182	·05820	·09929	·01811	·05821
12th "	·0967	·0102	·05217	·09669	·01021	·05217
13th "	·0101	·1029	·06718	·01039	·10260	·06722
14th "	·1284	·0067	·06512	·12841	·00669	·06512
15th "	·0065	·1100	·06990	·00584	·11066	·06982

It may be seen from the above list of analyses, which includes all the determinations I have made, from first to last, for the purposes of this paper, that in no case does the difference between the quantities taken and found of either alkali chlorid exceed two milligrams, and in most instances it is less than one milligram. The correspondence between the amounts of chlorine

as taken and found is of course still more near. The errors that appear in the estimation of the chlorids would be considerably reduced, if, as usually happens, they were calculated as oxyds.

Here follow the formulæ which I have employed for calculating the quantities of NaCl and KCl, or of NaO and KO, contained in or corresponding to any mixture of alkali-chlorids whose total weight and amount of chlorine are known.

W = weight of mixed chlorids.
C = weight of chlorine.
NaCl = C × 7·6311 − W × 3·6288.
KCl = W × 4·6288 − C × 7·6311.
NaO = C × 4·0466 − W × 1·9243.
KO = W × 2·9243 − C × 4·8210.

The results I have obtained thus demonstrate that the indirect method is in all cases equal in accuracy to the ordinary separation, while in the matter of convenience and economy of time there is no comparison between them.