

denum trioxide which were dissolved in ammonia, then diluted to 20 cc. with water, acidified with 20 cc. of hydrochloric acid, reduced, and titrated as described above. The following results were obtained: 1 cc. of $\text{KIO}_3 = 0.00480$ g. of MoO_3 .

No.	MoO_3 taken.	Cc. KIO_3 used.	MoO_3 found.	Error.
1.....	0.0548	11.45	0.0549	+0.0001
2.....	0.0627	13.05	0.0626	-0.0001
3.....	0.0163	3.50	0.0168	+0.0005

The three sets of experiments indicate that molybdenum can be determined with accuracy by the iodate method, observing the precautions already described. It should be observed that it is of importance to maintain not less than 10 per cent. of actual hydrochloric acid in the solution in order to prevent the hydrolysis of the iodine monochloride during the titration, which would cause serious errors. Furthermore, it is important to keep the solution thoroughly cooled and in a shaded place during the titration, especially if much molybdenum is present, in order to obtain a sharp end point.

SHEFFIELD CHEMICAL LABORATORY, YALE UNIVERSITY,
NEW HAVEN, CONN.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE JR. CHEMICAL LABORATORY OF HARVARD COLLEGE.]

ON THE DETERMINATION OF POTASSIUM AS PERCHLORATE.

By GREGORY P. BAXTER AND MATSUSUKE KOBAYASHI.

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One of the chief difficulties met in determining potassium as perchlorate lies in the solubility of this substance in the washing liquid, the main component of which is alcohol. Wense¹ first proposed the addition of perchloric acid to the alcohol used in washing, in order to reduce the solubility of the precipitate, and this recommendation has been adopted by most subsequent workers upon the subject.² Even this precaution is not sufficient to prevent loss of material through solution, however, and as a remedy Davis³ has proposed previously saturating the washing liquid with potassium perchlorate, a suggestion adopted by Thin and Cumming.⁴ The reliability of the method has also been discussed by Jarrell⁵ and by Hager and Kern.⁶

We have tested further this method for determining potassium and although our experiments were unavoidably interrupted before comple-

¹ *Z. angew. Chem.*, **5**, 691 (1891).

² See Scholl, *THIS JOURNAL*, **36**, 2085 (1914).

³ *J. Agr. Sci.*, **5**, 52 (1912).

⁴ *J. Chem. Soc.*, **107**, 361 (1915).

⁵ *J. Assoc. Off. Agr. Chem.*, **1**, 29 (1915); *J. Soc. Chem. Ind.*, **34**, 1170 (1915).

⁶ *Landw. Versuchsstat.*, **87**, 365 (1915); *J. Chem. Soc.*, **110**, II, 114 (1916).

tion, it seems worth while to describe briefly some of the results. Our experience confirms in general that of previous workers.

Potassium perchlorate was purified for the experiments by two crystallizations from water. A very pure perchloric acid solution was found by determination of its specific gravity to contain 18.9% of acid. After evaporation 30 cc. left a residue of 0.0006 g., wholly soluble in a small amount of alcohol. Some of this solution was evaporated in a platinum dish until the specific gravity showed it to contain 59.6% of acid. Alcohol was dehydrated over quicklime, first at room temperature then at boiling temperature with a reverse condenser. Finally it was distilled with a Hempel column. Specific gravity determinations and qualitative tests showed it to be very nearly free from water.

We first made approximate determinations of the solubility of potassium perchlorate in alcohol containing various proportions of perchloric acid, at 0° as well as at 21°. The perchloric acid solutions were made by adding either the more dilute or the more concentrated solution of perchloric acid to the anhydrous alcohol. In the former case the percentage of water in the final liquid was six times as large as in the latter case.

In preparing the saturated solutions an excess of powdered dry perchlorate was shaken occasionally for several hours by hand in a flask with 100 (sometimes 50) cc. of alcohol. The solutions were filtered through a platinum-sponge crucible into a weighed platinum dish in which they were evaporated to dryness on an electric stove. The residue was heated to about 200°, since we found that at that temperature potassium perchlorate remains unchanged in weight.

In the columns marked A the perchloric acid was added to the alcohol in the form of the more concentrated solution; in those marked B in the form of the more dilute solution.

TABLE I.—GRAMS $KClO_4$ IN 100 CC. ALCOHOL.

% $HClO_4$.	0°.		21°.	
	A.	B.	A.	B.
0	0.0047	0.0080
0.05	0.0019	0.0040	0.0051
0.10	0.0019	0.0022	0.0030	0.0050
0.15	0.0018	0.0028	0.0042
0.20	0.0018	0.0026	0.0035
0.30	0.0019	0.0031	0.0049

The above quantities are distinctly smaller than those found for somewhat less concentrated alcohol by Thin and Cumming, although the temperature at which they worked was slightly higher, 25°. Some of their results are given in Table II.

It is obvious that alcohol containing about 0.1% of perchloric acid at 0° dissolves as little potassium perchlorate as any practicable mixture, although the salt is appreciably soluble even in such a liquid. It

is also noticeable from a comparison of Columns A and B that the solubility is fairly sensitive to the presence of small proportions of water in the alcohol. The recommendation of Davis, of washing with a liquid already saturated with the salt, is therefore substantiated. With a solution saturated at 0° there is no danger of deposition of salt owing to changing temperature. Furthermore, this solution when treated at 0° with a large amount of sodium perchlorate, gives no precipitate.

TABLE II.

% alcohol.	25° % HClO ₄ .	Gram KClO ₄ in 100 g. solution.
93.5	0.0	0.051
93.5	0.2	0.018
98.8	0.0	0.019
98.8	0.2	0.010
98.8	2.0	0.028

We next performed experiments for the recovery of potassium as perchlorate, in which the salt was washed with alcohol containing 0.1% of perchloric acid and saturated with the salt at 0° . All the operations of washing and transferring the salt were carried on so far as possible at 0° . About 0.3 g. of potassium perchlorate was dissolved in water in a platinum dish, together with a varying amount of sodium chloride. A considerable excess of perchloric acid was added and the solution was evaporated to dryness. In all experiments where sodium chloride was used, the residue was dissolved and again evaporated with an excess of perchloric acid. The dish was chilled and after about 20 cc. of the above washing liquid were added, the mixture was allowed to stand for 5-10 minutes, while the lumps were crushed finely with a flattened stirring rod. The salt was then washed by decantation with the above washing liquid, transferred to a weighed platinum-sponge crucible,¹ dried at about 200° on an electric stove, and weighed. The total volume of washing liquid was not far from 125 cc. in each case.

TABLE III.

Gram of KClO ₄ taken.	Gram of NaCl taken.	Gram of KClO ₄ found.	Difference, G.
0.3021	...	0.3021	0.0000
0.3045	...	0.3044	-0.0001
0.3149	...	0.3150	+0.0001
0.3037	0.05	0.3048	+0.0011
0.3021	0.1	0.3044	+0.0023
0.3018	0.3	0.3062	+0.0044
0.3006	0.5	0.3092	+0.0086

From the results it appears that no potassium is lost by the method under examination, but that apparently sodium salt is retained by the

¹ A platinum-sponge crucible is particularly well adapted for the purpose because there is practically no possibility of finely divided precipitate passing through the mat, and because of ease of cleansing.

potassium perchlorate. To remedy this difficulty Caspari¹ has already suggested solution of the precipitate after preliminary washing, and re- evaporation, with subsequent washing as above. This was done in the following experiments in which the total volume of washing liquid used was 135-140 cc. The salt was dissolved after once washing by decantation.

TABLE IV.

Weight of KClO ₄ taken.	Weight of NaCl taken.	Weight of KClO ₄ found.	Difference. G.
0.3006	0.05	0.3010	+0.0004
0.3024	0.1	0.3028	+0.0004
0.3053	0.3	0.3062	+0.0009
0.3047	0.5	0.3063	+0.0016

The results suggest that a second solution of the precipitate with evaporation is desirable to avoid inclusion of sodium salt. Possibly if the preliminary washing is more thorough and if the quantity of sodium is not large one solution is sufficient.

The recommendations which we have to offer for the determination of potassium as perchlorate in the presence of sodium are as follows:

1. The use of absolute alcohol.
2. The use of a low temperature in washing (0°).
3. The use of a platinum-sponge crucible.

We support the suggestion of Davis, of using a washing liquid already saturated with potassium perchlorate. This may be prepared most easily by dissolving a suitable proportion of salt in the alcohol at a high temperature before adding the perchloric acid; also that of Caspari of dissolving the precipitate, after preliminary washing, and again evaporating to dryness before the final washing.

CAMBRIDGE, MASS.

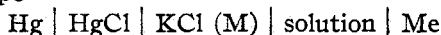
[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA.]

THE TITRATION OF SOME BIVALENT METAL SULFATES BY THE CONDUCTANCE METHOD.

BY HERBERT S. HARNED.

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In recent years, two important physical chemical methods have been employed in determining the end point in volumetric analysis. The first of these depends on measuring the change in electromotive force of a cell of the type



on adding a standardized titrating solution to the solution containing the substance to be determined. Behrend² used a silver concentration cell

¹ *Z. angew. Chem.*, 7, 71 (1893).

² *Z. physik. Chem.*, 11, 466 (1893).