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

The Separation and Determination of the Alkali Metals Using Perchloric Acid. V. Perchloric Acid and Chloroplatinic Acid in the Determination of Small Amounts of Potassium in the Presence of Large Amounts of Sodium

BY G. FREDERICK SMITH AND J. L. GRING

Introduction.—In a previous paper[1] the combined use of perchloric acid and chloroplatinic acid in the quantitative separation and determination of mixtures of sodium and potassium was shown to be superior to the customary use of either acid alone. We have now studied the conditions under which this method can be applied to the determination of 0.02 to 0.2% of potassium in sodium chloride.

Very small amounts of potassium in the presence of large amounts of sodium are usually determined by precipitation as potassium-sodium cobaltinitrite and the determination of potassium in the precipitate by the perchloric acid process. The present method involves but a single precipitation and is, therefore, much simpler and more rapid.

Solubility Relationships Governing the Process.—As has been shown previously,[1] the rate of decrease in solubility of potassium perchlorate in alcohol-water solutions with increasing proportions of alcohol is slight by comparison with the decrease in solubility of potassium chloroplatinate under the same conditions. Potassium perchlorate is quantitatively insoluble only in practically absolute alcohol. On the contrary, potassium chloroplatinate is quantitatively insoluble in 85% alcohol and an excess of the chloroplatinate ion. Sodium perchlorate is satisfactorily soluble in either absolute alcohol or any mixture of water and alcohol suitable for the quantitative separation of potassium as perchlorate or chloroplatinate.

For the separation of very small amounts of potassium from large amounts of sodium, conversion of the potassium to chloroplatinate is preferable to the formation of potassium perchlorate for numerous reasons, the most important consisting in the fact that the ratio $K_2PtCl_6/2KCl$ is larger than the ratio $KClO_4/KCl$. This is true notwithstanding the fact that potassium perchlorate can be shown to be less soluble in 97–100% alcohol-water mixtures when a sufficient excess of perchlorate ion is present for its common ion effect than is potassium chloroplatinate with excess of the chloroplatinate ion. In the method under discussion, the perchlorate ion is present in large excess as a result of the high concentrations (0.25–0.30 molal) of sodium perchlorate necessarily present. On the other hand, the process as a whole becomes practicable only in case a small excess of chloroplatinic acid is required as compared to the unmodified Fresenius method.

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[1] Smith and Shead, THIS JOURNAL, **54**, 1722 (1932).

The reaction upon which the method is based is $2KClO_4$ (small amounts) + $NaClO_4$ (large amounts) + $H_2PtCl_6 \rightleftharpoons K_2PtCl_6 + NaClO_4 + 2HClO_4$. The present study consists in the determination of the maximum concentration of sodium perchlorate which may be present to complete the reaction in the sense from left to right. Partial reversal of this reaction would result in the formation of a mixed precipitate of $K_2PtCl_6 + KClO_4$, whereas only potassium chloroplatinate is desired. The reaction is affected by two remaining variables, first, the water concentration in the solvent alcohol, and second, the excess of chloroplatinic acid used as precipitant.

Materials for the Study of the Method.—The reagents used are from the same stock previously described in connection with earlier papers of this series and require therefore no further description. Sodium chloride was used in such quantities that a separate stock perhaps somewhat less pure than that previously described was used. This was prepared by the recrystallization of c. p. sodium chloride from water by the use of gaseous hydrogen chloride. A trace of potassium chloride was a possible contamination but by the application of the method the amount was shown to be barely perceptible.

Determination of Maximum Permissible Perchlorate Ion Concentration and the Influence of Alcohol Strength.—The method employed consisted in preparing solutions of anhydrous sodium perchlorate in 80–100% ethyl alcohol of variable concentrations. Potassium was added to these various solutions in small amount either by the suspension of 100–200 mg. of potassium chloroplatinate or by the addition of potassium perchlorate and a slight excess of chloroplatinic acid. The solutions and precipitates thus formed were sealed in glass tubes and rotated in a thermostat at 25° until an equilibrium was established. The tubes were then opened and the precipitates filtered, dried, and examined for any potassium perchlorate partially precipitated together with potassium chloroplatinate. The study of the precipitates was carried out in a number of ways as follows: (a) microscopic examination. Suitable for extensive contamination of potassium chloroplatinate by potassium perchlorate. (b) Determination of platinum in the potassium chloroplatinate to prove the presence or absence of potassium perchlorate. (c) By the color of the solutions produced by the addition of potassium chloroplatinate to the alcoholic sodium perchlorate after equilibrium. Precipitation of potassium perchlorate resulted in the formation of chloroplatinic acid in solution, identified by its color. (d) By adding weighed amounts of potassium chloroplatinate and testing for quantitative recovery.

The data thus obtained defined the maximum concentration of sodium perchlorate which may be present without the formation of potassium perchlorate. The data are presented graphically in the accompanying Fig. 1. But a slight excess of chloroplatinic acid was employed in these experiments since in actual practice larger excesses would make the results more selective in the proper sense due to the decreased solubilities of potassium chloroplatinate.

Analytical Interpretation of the Experimental Results.—The study of the data of Fig. 1 leads to the following conclusions. (1) The maximum concentration of sodium perchlorate which may be present is 0.28 molal using 95% alcohol. (2) 80–90% alcohol permits the presence of a constant concentration of sodium perchlorate, 0.20 molal. (3) Using 95–100% alcohol, the precipitation of potassium perchlorate takes place to the exclusion of potassium chloroplatinate with rapidly decreasing concentrations of sodium perchlorate. (4) For each 100 cc. of 95% alcohol, 1.63 g. of sodium chloride can be used as sample for analysis. (5) Since potassium perchlorate is known to become increasingly less soluble in more concentrated alcohol, these data show that 95% ethyl alcohol causes the least dissociation of sodium perchlorate. Since 95% ethyl alcohol is the most commonly occurring strength, this fact is a fortunate circumstance operating to simplify the process.

Outline of Procedure.—1.48 to 1.63 g. of sodium chloride (containing potassium chloride) sufficient to give a sodium concentration of 0.25–0.28 normal is dissolved in water in a 150-cc. beaker and converted to sodium and potassium perchlorate using twice the perchloric acid required. The residue thus obtained is freed from excess perchloric acid by heating, the last part of the operation being carried out on a wire gauze over a free flame, the beaker being rotated with the cover glass supported on glass hooks and the beaker walls brushed carefully by the flame to remove perchloric acid condensed on the inside walls of the beaker and under side of the cover glass. If evaporation of the sodium perchlorate solution has been carried out above 35°, the residue is anhydrous upon deposition from the water–perchloric acid solution.

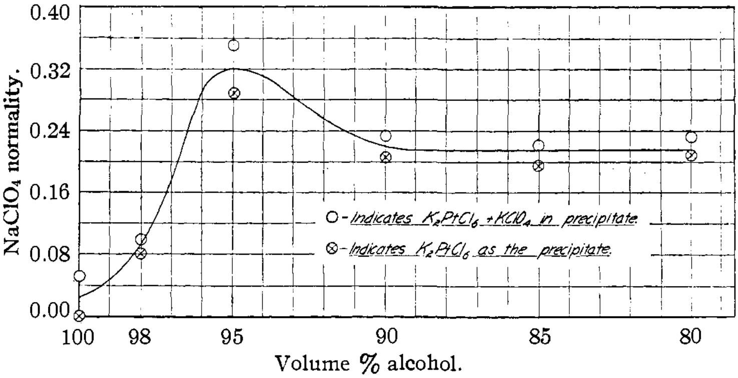

Fig. 1.—Selective precipitation of K_2PtCl_6 from $KClO_4$ and $NaClO_4$ solutions: influence of alcohol strength.

The beaker is cooled, the inside rinsed with a few ml. of water, and the evaporation and heating repeated for the second time. By this operation the perchloric acid occluded in the first obtained anhydrous sodium perchlorate is freed and the residue is acid free. Dissolve the salts by adding 95 ml. of 95% ethyl alcohol and heating if desired up to near the boiling point on the hot-plate. (The heating of such solutions is perfectly safe since free acid is not present.) Chloroplatinic acid, 0.2 g. in 5 ml. of 95% ethyl alcohol, is added to this solution, preferably hot, and after a few minutes' digestion and vigorous stirring the mixture is cooled to 0° and allowed to stand with frequent stirring at this temperature for an hour or longer.

The precipitated solution is filtered through a sintered glass or quartz filtering crucible, the potassium chloroplatinate washed once with 95% alcohol and finally with cold absolute alcohol until free from sodium perchlorate (9–10 portions of 1 ml. each) and finally dried and weighed. The potassium chloroplatinate is stable at 350° and its weight may be checked by solution in hot water and precipitation of the platinum by acidification with hydrochloric acid and decomposition with a few milligrams of magnesium ribbon. The precipitated platinum is then filtered on a small ashless filter which is dried, ignited and weighed, from which value the amount of potassium chloride originally present is calculated using the theoretical factor.

Experimental Analyses.—The first variable requiring study was the determination of the required excess of chloroplatinate ion. Weighed amounts of sodium chloride were treated with weighed amounts of potassium chloride in the form of a dilute solution in water using a weight buret to increase the accuracy of obtaining the small amounts of potassium chloride. Solutions were prepared for analysis as above described and various weights of chloroplatinic acid were added and the effects determined. The results of these analyses are given in Table I. Precipitations were carried out in 100 cc. of 95% alcohol.

TABLE I

THE INFLUENCE OF EXCESS CHLOROPLATINIC ACID ON THE SEPARATION OF SMALL AMOUNTS OF POTASSIUM IN THE PRESENCE OF LARGE AMOUNTS OF SODIUM

KCl, g.	NaCl, g.	Excess $H_2PtCl_6 \cdot 6H_2O$, g.	$NaClO_4$, normality	K_2PtCl_6 found, g.	KCl calcd., %	KCl found, %	Error KCl unpptd., %
0.0010	1.4705	0.0025	0.25	0.0003	0.068	0.006	90
.0020	1.4600	.0038	.25	.0011	.137	.019	83
.0039	1.4225	.0096	.24	.0061	.266	.131	58
.0012	1.4281	.0680	.24	.0028	.084	.052	38
.0024	1.4724	.1000	.25	.0071	.163	.148	9

Results from Table I indicate that an excess of somewhat greater than 100 mg. of $H_2PtCl_6 \cdot 6H_2O$ in 100 ml. of solution should provide a sufficient excess of precipitant; 200 mg. of precipitant per 100 ml. of solution was therefore chosen as a safe working basis. Results obtained in final tests of the new method of analysis are given in Table II.

TABLE II

THE SEPARATION OF SMALL AMOUNTS OF POTASSIUM IN PRESENCE OF LARGE AMOUNTS OF SODIUM

Volume of solution precipitated, 100 ml. Acid used, 0.20 g. of $H_2PtCl_6 \cdot 6H_2O$ per determination. Temperature of precipitation, 0°.

KCl, g.	NaCl, g.	$NaClO_4$ normality	K_2PtCl_6 calcd., g.	K_2PtCl_6 found, g.	Pt found, g.	Pt calcd., g.	KCl found, g.	KCl found, %.	Error KCl, g.
0.0021	1.4483	0.244	0.0069	0.0073	0.0029	0.0029	0.0022	0.152	+0.0001
.0020	1.4598	.25	.0065	.0068	.0027	.0026	.0021	.142	+ .0001
.0021	1.3888	.235	.0069	.0073	.0029	.0029	.0022	.153	+ .0001
.0019	1.4394	.243	.0063	.0069	...	...	.0021	.145	+ .0002
Blank	1.48	.25	...	.0006	...	...	.00018	.012	....

From an examination of Table II it is seen that 0.15% of potassium chloride in sodium chloride can be determined readily by one precipitation with an accuracy of 5% if the blank correction for the determination of the trace of potassium in the sodium chloride used to test the results is disregarded. Applying the blank correction, the results obtained are as accurate as are those obtained in analyses of the ordinary rather than the semi-micro type. While the analyses of Table II deal with comparatively large amounts of potassium chloride, the method has been applied with equal success to much smaller amounts of potassium approaching that of the blank determination given above. The method has already been shown to apply admirably to large amounts of potassium[1] and by examination of the last table of results in that paper, it will be seen that in the cases in which the method did not apply for small amounts the cause is found in either the use of too high concentrations of sodium salts or the incorrect strength of solvent alcohol. If the directions are properly followed, no free perchloric acid is left, and so there is no danger in heating the alcoholic solutions.

Summary

1. The method of Smith and Shead[1] has been extended to include the determination of small quantities of potassium in the presence of large amounts of sodium.

2. The salts of sodium and potassium, in the modified procedure, are converted to the neutral anhydrous perchlorates, dissolved in 95% alcohol, and treated with a moderate excess of chloroplatinic acid. The precipitate of potassium chloroplatinate can be weighed as such, or converted to platinum and the potassium calculated from this.

3. The method involves the direct precipitation of potassium (one operation) and no previous concentration to isolate the potassium for subsequent purification is required.

4. The method involves the use of but 0.20 g. of chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) per determination. The demand for, and cost of recovery of, platinum is therefore a small factor.

5. In analyses of samples of sodium chloride containing no more than 0.15% of potassium chloride, results obtained by the method should not be in error by more than 0.01%.

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The Systems (a) Ammonium *d*-Tartrate–Lithium *d*-Tartrate–Water, and (b) Ammonium Lithium *d*-Tartrate–Ammonium Lithium *l*-Tartrate–Water

BY ALAN NEWTON CAMPBELL AND LOUIS SLOTIN

Pasteur's first method of resolution of optically active substances has so far only been found applicable to a relatively few cases, the reason being that most inactive forms at room temperature are true racemates and not conglomerates. A study of the mixed solubilities will always tell whether or not the transition point lies in an attainable region. Such studies have been carried out by van't Hoff and by Findlay. So far as is known to the present authors, the only racemic salts whose transition points are known are sodium ammonium racemate,[1] sodium potassium racemate,[2] and rubidium racemate.[3]

It was thought therefore that it would be of interest to investigate the effect on the transition temperature of the substitution of lithium for so-

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(1) Van't Hoff and van Deventer, *Z. physik. Chem.*, **1**, 165 (1887).
(2) Van't Hoff, *ibid.*, **17**, 505.
(3) Van't Hoff and Muller, *Ber.*, **31**, 2206 (1898).