

3. The mutual influence of the spectra of two such groups as the carbonyl and benzene rings extends through carbon chains not more than two atoms long. At greater distances in the molecule the spectra become entirely independent of each other.

CAMBRIDGE, MASSACHUSETTS

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

THE SEPARATION AND DETERMINATION OF THE ALKALI METALS USING PERCHLORIC ACID. IV. THE PERCHLORATO-CHLOROPLATINATE METHOD FOR THE DETERMINATION OF POTASSIUM IN THE PRESENCE OF SODIUM

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Introduction

The separation and determination of potassium in the presence of sodium and lithium are most commonly carried out following the semi-extraction process of Fresenius.² Chloroplatinic acid is used to convert the aqueous solution of the mixed chlorides to the corresponding chloroplatinates, followed by the extraction of sodium and lithium chloroplatinates with ethyl alcohol to produce 80–85% of the latter. Many advantages result from the use of lithium chloroplatinate in place of chloroplatinic acid in the separation of potassium from sodium by the Fresenius process as shown by the present authors.³ Very distinct improvements in the perchlorate method in the separation of potassium from sodium have been developed as a result of previously published research from this Laboratory⁴ which seem to justify claims of superiority for the perchloric acid method over the chloroplatinate separation. In addition the use of perchloric acid facilitates the separation of sodium from lithium.⁵

The present paper demonstrates the advantage resulting from the simultaneous application of both perchloric and chloroplatinic acids to the separation and determination of potassium in the presence of sodium. Four distinct advantages result from this method of attack. Only enough chloroplatinic acid is employed to convert the potassium present to potas-

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² Fresenius, *Z. anal. Chem.*, **15**, 224 (1876); **16**, 63 (1877); **21**, 234 (1882).

³ Smith and Shead, *THIS JOURNAL*, **53**, 947 (1931).

⁴ Smith, *ibid.*, **45**, 2073 (1923); **47**, 762 (1925). Smith and Ross, *ibid.*, **47**, 774 (1925); **47**, 1020 (1925).

⁵ Willard and Smith, *ibid.*, **44**, 2816 (1922).

sium chloroplatinate. Following the Fresenius process the sodium must be converted to sodium chloroplatinate to take advantage of its solubility in alcohol. Since the ratio of chloroplatinic acid to sodium chloride, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}/2\text{NaCl}$, is approximately 4.8, the saving in platinum is apparent. A second improvement is that the process is completely a precipitation process and not, as with the Fresenius scheme, a semi-extraction method. Occlusion of sodium salts by the precipitated potassium chloroplatinate is therefore minimized. A third improvement results from the weighing of a mixture of potassium and sodium perchlorates in place of the corresponding chlorides. Lastly, as already shown,² the precipitated potassium chloroplatinate is stable after drying at $300\text{--}350^\circ$. Any error resulting from the occlusion of solvent by the potassium chloroplatinate is thus eliminated and the time required for its drying greatly reduced.

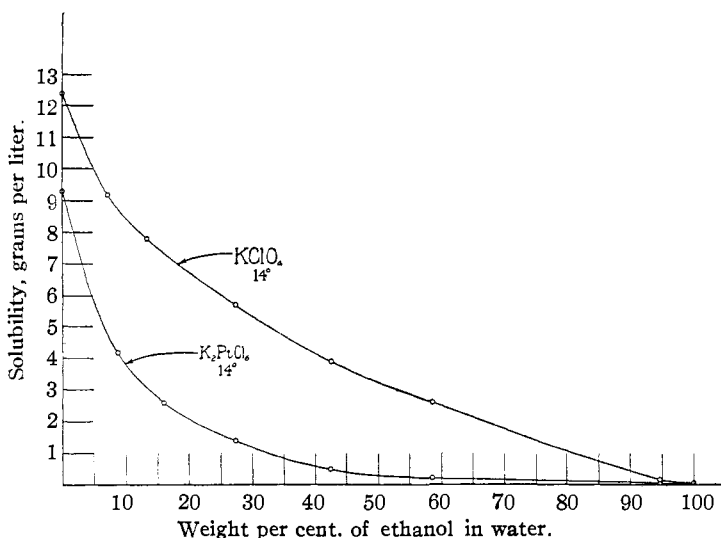


Fig. 1.—The solubility of K_2PtCl_6 and KClO_4 in alcohol-water solutions.

The Method

The process in brief is as follows.

The mixture of potassium and sodium chlorides obtained following the application of the J. Lawrence Smith method for decomposing an insoluble silicate (or a mixture of potassium and sodium nitrates) is converted to perchlorates by evaporation to dryness in a platinum dish or crucible with an excess of 70–72% perchloric acid. A 30-cc. Pyrex beaker may be used for the evaporation. The mixed perchlorates of potassium and sodium are dissolved by heating with a few cubic centimeters of water and again evaporated to dryness and heated for fifteen to thirty minutes at 350° , cooled and weighed. Anhydrous sodium perchlorate is faintly hygroscopic and the container plus the sample should be weighed covered.

The mixture of potassium and sodium perchlorates is dissolved in hot water (5 cc.

is sufficient for all ordinary samples) and 5 cc. of 95% or stronger ethanol is added and the solution warmed to just below the boiling point. Small portions of a 10% solution of chloroplatinic acid dissolved in ethanol are added until potassium chloroplatinate begins to precipitate. After digesting for a minute at just below the boiling point, the slow addition of precipitant is continued until all the potassium present is precipitated and the supernatant liquid is colored slightly yellow. Enough ethanol is added to make an 80–85% concentration of alcohol (not less than 30 cc. of alcohol in case 5 cc. of water was used) and the solution is digested for five minutes on an electric hot-plate with stirring at just below the boiling temperature. The precipitate and solution are cooled to room temperature, filtered, washed with 85% or stronger alcohol and the filtrate set aside for recovery of the slight excess of platinum used or for the direct determination of sodium. The filtering crucible and precipitate are dried for five minutes at 100–130° to remove the alcohol and finally for fifteen minutes at 300–350°, cooled and weighed. The potassium chloride originally present is calculated using the theoretical factor $2\text{KCl}/\text{K}_2\text{PtCl}_6 = 0.3067$.

Solubilities Involved in the Perchlorato-Chloroplatinate Process.—Five cubic centimeters of water at 25° dissolves more than 10 g. of sodium perchlorate. The addition of alcohol in equal proportion does not greatly diminish this solubility. Lithium perchlorate is less soluble in water (2.98 g. in 5 cc.) but is much more soluble in ethyl alcohol than is sodium perchlorate. The comparative solubilities of potassium perchlorate and potassium chloroplatinate in various strengths of aqueous ethanol are given in Table I taken from the data of M. Pierrot.⁶

TABLE I

THE COMPARISON IN SOLUBILITY OF POTASSIUM PERCHLORATE AND POTASSIUM CHLOROPLATINATE IN VARIOUS CONCENTRATIONS OF AQUEOUS ETHANOL AT 14°

Material	0.0	Concentration of ethanol, % by weight of alcohol								
		7.1	8.7	13.2	15.9	27.3	42.4	58.5	94.7	100
		Solubility g./1000 cc.								
KClO ₄	12.4	9.2		7.8		5.7	3.9	2.6	0.15	0.071 ^a
K ₂ PtCl ₆	9.3		4.2		2.6	1.4	0.5	0.2	0.02	0.018 ^a

^a Solubility determinations in absolute alcohol: KClO₄ by Willard and Smith, *THIS JOURNAL*, **45**, 286 (1923). Solubility of K₂PtCl₆ calculated from accepted solubility data, 1 part of K₂PtCl₆ to 42,600 parts of ethanol.

From an examination of Table I it will be observed that the solubility of potassium chloroplatinate in water is very highly suppressed with increasing addition of ethyl alcohol as compared to the diminution in the solubility of potassium perchlorate under the same conditions. For solutions of equal parts of ethyl alcohol and water, 32.5 mg. of potassium perchlorate dissolves in 10 cc. This amount is increased approximately ten-fold at the boiling point of such solutions.

Potassium chloroplatinate is so slightly soluble in a 50% solution of ethyl alcohol in water (4 mg. in 10 cc.) that this concentration was chosen for the first addition of chloroplatinic acid. It was found that the temperature coefficient of increase in solubility of potassium chloroplatinate

⁶ Pierrot, *Compt. rend.*, **172**, 1041 (1921).

with increase in temperature is very slight. No need for excess of chloroplatinic acid for its common ion effect in reducing the solubility of potassium chloroplatinate is shown by the data. The addition of alcohol serves as an effective substitute when above 80%.

Preparation of Materials for Use in Testing the Accuracy of the Perchlorato-Chloroplatinate Process

Perchloric Acid.—Chemically pure 70–72% material distilled *in vacuo* and supplied by the G. Frederick Smith Chemical Company of Columbus, Ohio.

Potassium Chloride.—A portion of the same stock previously described² and demonstrated to be 100% pure. The fused product only was employed to eliminate the possibility of occluded moisture.

Sodium Chloride.—Samples were taken from a stock used in previous investigations published from this Laboratory. It had been repeatedly crystallized from water solution by the addition of gaseous hydrochloric acid with intermediate filtrations using centrifugal drainage. This preparation had been carried out by Dr. T. R. Ball, at present at Washington University, St. Louis, and was fused before weighings to eliminate the possibility of occluded moisture.

Chloroplatinic Acid.—Purchased from two different laboratory chemical supply houses and used as received.

Ethyl Alcohol.—Anhydrous alcohol as purchased in the market.

The Stability of Chloroplatinic Acid in Hot Alcoholic Solution.—The platinum in a hot alcoholic solution of chloroplatinic acid might be reduced to a lower stage of valence or to metallic platinum especially in the presence of reducing agents such as traces of aldehydes commonly present in alcohol. This possibility in the present method is practically eliminated for two reasons: first, the negligible increase in solubility of potassium chloroplatinate in hot as compared to cold alcohol solutions and second, the use of such a slight excess of chloroplatinic acid the latter being unnecessary either to convert sodium perchlorate to sodium chloroplatinate or for the common ion effect of excess precipitant. Samples of commercial anhydrous ethyl alcohol or the more common 95% alcohol either untreated or dried with lime followed by metallic calcium serve equally as well for this method. No determinations were lost because of the reduction of the chloroplatinic acid. Qualitative tests in all these types of alcohol showed traces of aldehyde or similar reducing agents.

Filtrates from the precipitation of potassium chloroplatinate containing sodium perchlorate, a slight excess of chloroplatinic acid and perchloric acid, when diluted further with water and allowed to digest for periods of thirty to sixty minutes at steam-bath temperature, precipitate their platinum completely as platinum black, a reduction conveniently employed in the direct determination of sodium. The filtrate from the potassium separation is so treated, the platinum filtered and washed and the sodium perchlorate determined by conversion to sulfate or by precipitation as sodium chloride following the method of Willard and Smith,⁵

Smith and Ross⁴ or by direct weight as sodium perchlorate as described in the next section.

The Conversion and Determination of Sodium Chloride as Sodium Perchlorate and its Stability at 350°.—By comparison of the two conversion factors, $\text{Na}_2\text{O}/2\text{NaCl}$ (0.5303) and $\text{Na}_2\text{O}/2\text{NaClO}_4$ (0.2531), weighing sodium as perchlorate instead of chloride is seen to carry a distinct advantage. Conditions for the correct determination of potassium as perchlorate have been clearly demonstrated by Smith and Ross.⁴ To avoid a contamination of potassium perchlorate by either occluded perchloric acid or moisture it must be dried at 350°. If sodium perchlorate can be shown to be stable at 350°, and suitable for weighing in this form, the mixture of sodium and potassium chlorides, frequently weighed after drying at 500°, can be weighed more satisfactorily in the form of perchlorate. This becomes more important since it is recognized that weighing mixtures of sodium and potassium chlorides following drying below their fusion temperature does not eliminate moisture. At the melting point these chlorides are too volatile to permit this treatment without prohibitive loss in weight. It is obvious that an indirect determination of sodium by difference is unsatisfactory for precise work. This practice is, however, commonly applied since the potassium determination is more important than that of sodium. The following experiments in the conversion of sodium chloride to perchlorate for final weighing are, therefore, described.

Weighed samples of pure sodium chloride were placed in a 30-cc. Pyrex beaker, dissolved in water and a small excess of pure 70–72% perchloric acid added. The samples were evaporated dry and the excess perchloric acid expelled. After heating during two and one-half hours in an electric muffle at 350°, the samples were cooled in a desiccator and weighed. In the latter operation a small watch-glass was used as a beaker cover. The results are shown in Table II. Sodium perchlorate crystallized from solution above 30° in the form of the anhydrous salt. A monohydrate is obtained by crystallizing from solution below 25°. The transition point

TABLE II

THE CONVERSION OF SODIUM CHLORIDE TO PERCHLORATE WITH DRYING AT 350°

NaCl taken, g.	NaClO ₄ found, g.	NaClO ₄ calcd., g.	Error in NaClO ₄ , g.	NaCl taken, g.	NaClO ₄ found, g.	NaClO ₄ calcd., g.	Error in NaClO ₄ , g.
0.2013	0.4217	0.4217	0.0000	0.2496	0.5234	0.5228	+0.0006
.3098	.6493	.6490	+ .0003	.3993	.8375	.8365	+ .0010
.3371	.7069	.7062	+ .0007	.0804	.1688	.1684	+ .0004
.3376	.7074	.7072	+ .0002	.0428	.0899	.0898	+ .0001
.1985	.4160	.4158	+ .0002	.0979	.2045	.2051	— .0006
.3941	.8285	.8286	+ .0002	.1367	.2863	.2864	— .0001
.3460	.7258	.7248	+ .0010	.2293	.4805	.4804	+ .0001
						Av.	+ .0002

lies between these limits. It is easy, therefore, to favor the formation of the anhydrous salt and thus avoid its subsequent dehydration. The time of drying at 350° was purposely and unnecessarily extended to completely test the stability of sodium perchlorate. The melting point of sodium perchlorate is 482°.

The Determination of Potassium Chloride Using the Perchlorato-Chloroplatinate Process.—Samples of fused c. p. potassium chloride were weighed and dissolved in a few cc. of hot water in a 150-cc. beaker and converted to perchlorates by evaporation to dryness following the addition of 2 cc. of 70% perchloric acid. The samples were again dissolved by the addition of a few cc. of hot water and a second time evaporated dry and heated finally over a wire gauze to remove the last trace of occluded perchloric acid. The potassium perchlorate was then dissolved in a known volume of 50% ethyl alcohol, warming on the hot-plate nearly to the boiling point to limit the volume of solvent required. The samples were then precipitated as potassium chloroplatinate by the addition of reagent in several portions, with intermediate digestion for a minute on the hot-plate at just below the boiling point. The alcohol used to dissolve the chloroplatinic acid was sufficient to make a final alcohol concentration greater than 80%. Excess of precipitant is easily recognized by the appearance of a yellow color in the solution being precipitated. After five minutes' digestion during precipitation, the solutions and precipitates are cooled to room temperature and filtered using a platinum Monroe filtering crucible or a sintered quartz or glass filtering medium. The precipitates were washed with absolute alcohol and dried for twelve hours at 135° and finally for fifteen minutes at 350°, cooled, dried and weighed after each treatment. The chloroplatinic acid was added in weighed amount calculated to give a 10% excess and the excess platinum finally determined in the filtrates from the potassium separation as previously described. The results of these analyses in the absence of sodium are given in Table III.

TABLE III

THE PRECIPITATION OF POTASSIUM CHLOROPLATINATE FROM PERCHLORATE SOLUTION USING CHLOROPLATINIC ACID AND ETHYL ALCOHOL

KCl taken, g.	KClO ₄ soln. in 50% alcohol, cc.	H ₂ PtCl ₆ 6H ₂ O used, g.	Pt in filtrate		Potassium chloroplatinate		Filtrate and washings, cc.	Loss in wt. of K ₂ PtCl ₆ , 135° → 350°		KCl found, g.	Error, mg.
			Metal, g.	Acid, calcd., g.	135°, g.	350°, g.		mg.	%		
0.07775	8	0.35	0.0315	0.0836	0.25075	0.2504	42.5	0.35	0.14	0.07685	-0.8
.1347	8	.55	.0254	.0674	.43965	.43895	43.6	0.65	.15	.1347	.0
.30455	16	1.2	.0495	.1311	.99195	.99175	66.2	1.20	.12	.30435	-.2
.1216	8	0.5	.0143	.0379	.39775	.3971	48.8	0.75	.19	.1219	+.3
.1887	14	.85	.0741	.1963	.6155	.6151	54.1	.60	.10	.1888	+.1
Mean solubility of K ₂ PtCl ₆ , 0.84 mg./100 cc.					Av.		51 cc.		0.14%		-0.12

It will be seen from the results of Table III that using a perchlorate solution, chloroplatinic acid precipitates potassium chloroplatinate equal in purity to that produced by lithium chloroplatinate in chloride solutions of potassium.³ The precipitated potassium chloroplatinate in the former case differs from the latter only in the formation of free perchloric acid in place of hydrochloric acid. The presence of hydrochloric acid is also thus proved to cause impure precipitates of potassium chloroplatinate by the original Fresenius method. Potassium chloroplatinate is not free from moisture after drying at 135° for twelve hours. Results obtained by dry-

ing for fifteen minutes at 350° , or to constant weight, show that precipitates dried at the lower temperature contain an average of 0.12% occluded solvent. Using chloroplatinic acid as above described, determinations of potassium, sodium and lithium from the same sample can be obtained, which is not true using lithium chloroplatinate. A distinctive feature incorporated in the present method lies in the fact that absolute alcohol can be employed to transfer and wash precipitates of potassium chloroplatinate. This is not possible by the Fresenius method because of the formation of sodium chloride from sodium chloroplatinate. Assuming an average case with 50 cc. of filtrate and washings, only 0.14 mg. of potassium chloride remains unprecipitated, corresponding to 0.08 mg. of potassium oxide. Drying precipitates of K_2PtCl_6 obtained by this method at 135° instead of 350° gives high results almost exactly compensating for the loss of potassium due to solubility.

The Separation of Potassium in Presence of Sodium from Solutions of their Perchlorates Using Chloroplatinic Acid.—Samples of mixtures of weighed portions of potassium and sodium chlorides were converted to perchlorates and prepared for the determination of potassium in exactly the same manner as described in connection with Table III. Potassium chloroplatinate was precipitated in the same manner using a 10% excess of chloroplatinic acid and the precipitates filtered and washed with absolute alcohol and dried for five minutes at 135° and for fifteen minutes at 350° . Results are given in Table IV, calculated from the weight of K_2PtCl_6 using the factor 0.3067 (theoretical).

TABLE IV

THE SEPARATION OF POTASSIUM FROM SODIUM IN ALCOHOLIC PERCHLORATE SOLUTION USING CHLOROPLATINIC ACID

KCl taken, g.	NaCl taken, g.	K_2PtCl_6 , g.	KCl found, g.	Filtrate and washings, g.	Error, KCl, mg.
0.13475	0.2018	0.43725	0.1342	38	-0.55
.1095	.1086	.3572	.1096	42	+ .1
.0633	.3846	.2065	.0634	64	- .1
.0522	.2238	.1635	.0502	44	- .2
.02850	.1495	.0936	.0287	43	+ .2
.0037	.0083	.0113	.0035	..	- .2
.01625	.0174	.05215	.0160	..	- .25
.0279	.0228	.08965	.0275	..	- .4
.0609	.0333	.1954	.0599	..	-1.0
.08635	.1342	.2799	.0858	..	-0.55
.05085	.2293	.1643	.0504	..	- .45
.0333	.0979	.1109	.0340	..	+ .7
.0089	.0429	.0289	.0089	..	.0
.0170	.0045	.0558	.0171	..	+ .1
.02135	.1985	.07045	.0216	..	+ .25
				Av.	- .14

It is seen from the results of Table IV that the separation of potassium chloroplatinate in the presence of sodium gives as accurate a potassium determination as obtained in Table III in the absence of sodium. The method is accurate to an average of approximately 0.15% in both cases. It is interesting to note that for the combined determinations of Table IV, less than 3 g. of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was required, whereas, if the original Fresenius method had been used, approximately 12 g. would have been necessary. The method is very rapid as compared to the original Fresenius process both because of the method of precipitation and the short time (twenty minutes) required to dry the precipitated K_2PtCl_6 . The precipitate is obtained as finely divided, light lemon-yellow colored crystals, which filter with ease and are very easily transferred from precipitating beaker to filtering crucible.

The Determination of Small Amounts of Potassium in Presence of Large Amounts of Sodium.—The present method requiring no conversion of sodium chloride to sodium chloroplatinate immediately suggests its application to the determination of small amounts of potassium in the presence of large amounts of sodium. This determination is generally possibly only in two operations. For example, the potassium present is concentrated by first precipitating as cobaltinitrite, $\text{K}_2\text{NaCo}(\text{NO}_2)_6$, followed by solution in hydrochloric acid and conversion to perchlorate.⁷ The present method was therefore examined in the determination of less than 0.5% of potassium in sodium chloride. The results obtained indicated the need for further investigation of this subject for reasons indicated by the following equation



As the amount of sodium perchlorate increases, the increase of perchlorate ions reaches sufficient magnitude to direct the reaction from right to left rather than the reverse and either the K_2PtCl_6 does not form at all or there is obtained a mixed precipitate of K_2PtCl_6 and KClO_4 . Successful separations of 5 mg. of potassium chloride in the presence of 2000 mg. of sodium chloride were attempted. More data are being collected on this subject. No difficulty in applying the present method is encountered as long as the ratio of potassium chloride to sodium chloride is 1%, using a one-gram sample or less of the mixed chlorides. The attempt to follow out the present procedure (slightly modified in some instances) gave results shown in Table V.

Results given in Table V are seen to be satisfactory only in the case of the first two determinations. The adjustment of the present method to analyses in the range used in this table is now being investigated. No violent reactions were met with in the study of this method. Owing to the relatively high concentration of water present in all solutions of the per-

⁷ Bennett, *Analyst*, **41**, 165 (1916).

TABLE V

THE DETERMINATION OF SMALL AMOUNTS OF POTASSIUM PRESENT WITH LARGE AMOUNTS OF SODIUM

5 cc. 70% HClO_4 used to convert chlorides to perchlorates. 0.12 g. of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ used for each precipitation.

KCl taken, g.	NaCl taken, g.	Hot solvent used to dissolve mixed perchlorates		K_2PtCl_6 , g.	KCl calcd., g.	Error, KCl, mg.
		H_2O cc.	$\text{C}_2\text{H}_5\text{OH}$ (Anhyd.), cc.			
0.00935	1.2819	3	45	0.02965	0.0091	-0.25
.0053	1.4592	2	35	.01685	.0052	-0.1
.0158	1.4611	.	60	.00975	.00605	-3.0
.0189	1.9165	7	42	.04675	.0144	-4.5
.00545	1.9038	5	55	.01235	.0038	-1.7
.0044	2.1821	2	35	.00735	.0023	-2.1
.00465	2.0017	2	35	.01395	.0043	-0.35
.00125	1.2832	2	35	.00305	.0095	-0.3

chlorates in alcohol, no explosion is possible. Converting mixtures of sodium and potassium chlorides or nitrates to perchlorates by evaporation with perchloric acid to dryness is perfectly safe. This method should, therefore, not fail of application because of prejudice from this source.

Summary

1. Potassium and sodium in the form of their perchlorate solution in 50% ethyl alcohol and water mixture may be precipitated by the addition of an alcoholic solution of chloroplatinic acid and the potassium quantitatively separated in the form of potassium chloroplatinate.

2. Since sodium perchlorate is soluble in alcohol, only enough chloroplatinic acid is required to react with the potassium, thus effecting a saving in cost.

3. The method gives precipitates of theoretical composition stable upon drying at 350° .

4. Stronger alcoholic solutions may be used by this method than are possible starting with the mixed alkali chlorides. Anhydrous alcohol can be used to wash the precipitate.

5. Sodium and potassium can be weighed with advantage as mixed perchlorates after heating at 350° .

6. This is a precipitation process, not a semi-extraction method, and, therefore, more efficient.

7. Platinum is recovered from the filtrates by simply digesting for thirty to sixty minutes at $80-90^\circ$. The direct determination of sodium is thus facilitated.