

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS, AND THE UNIVERSITY OF OKLAHOMA, NORMAN, OKLAHOMA]

LITHIUM CHLOROPLATINATE AND THE SEPARATION OF POTASSIUM FROM SODIUM AND LITHIUM BY THE UNMODIFIED ORIGINAL FRESenius METHOD

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Introduction

The determination of potassium as potassium chloroplatinate is of sufficient historical interest to warrant a somewhat detailed reference to the literature of the subject as a theoretical background to the present paper. The original work of Fresenius on the separation and determination of potassium in presence of sodium and lithium by the chloroplatinic acid process consisted of two contributions.^{2,3} Somewhat later there appeared an additional paper⁴ by Fresenius consisting of a duplication of the former work. This confirmatory work was necessitated by the intervening revision of the atomic weight of platinum by Seubert⁵ as will be explained later. Other important work dealing with Fresenius' process was contributed by Precht,⁶ Dupré,⁷ Morozewicz,⁸ and Fresenius and Brinton.⁹

By the original Fresenius method,^{2,3} of 1876–1877, potassium chloride was separated from sodium and lithium chlorides by converting the three chlorides to chloroplatinates, using an excess of chloroplatinic acid followed by the extraction of K_2PtCl_6 from the soluble sodium and lithium chloroplatinates using 80% ethyl alcohol. The value for the ratio $2KCl/K_2PtCl_6$ was found to be 0.3056. This value is the theoretical one based on the early atomic weight 197.18. In 1881 the Seubert⁵ revision of the atomic weight of platinum established the value 194.46. Consequently, the German potash industry solicited Fresenius to reinvestigate his process, which was undertaken in 1882.⁴ "As a result," Fresenius reported, "of all these determinations not the slightest doubt remains that for the calculation of the potassium chloride from the weight of potassium chloro-

¹ Holder of "The J. T. Baker Chemical Company Fellowship in Analytical Chemistry" for the year 1930–1931. This contribution is submitted in partial fulfillment of the requirements for the Ph.D. degree in the Graduate School of the University of Illinois.

² Fresenius, *Z. anal. Chem.*, 15, 224 (1876).

³ Fresenius, *ibid.*, 16, 63 (1877).

⁴ Fresenius, *ibid.*, 21, 234 (1882).

⁵ Seubert, *Ann.*, 207, 1 (1881).

⁶ Precht, *Z. anal. Chem.*, 18, 509 (1879).

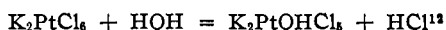
⁷ Dupré, *Diss.*, Halle, 1893.

⁸ Morozewicz, *Bulletin Inter. de L'Académie des Science de Cracovie*, 796 (1906).

⁹ Fresenius and Brinton, *Z. anal. Chem.*, 50, 21 (1911).

platinate dried at 130°, no other value than 30.56 to 100 is permissible and if the Seubert ratio 0.3069 is employed high results necessarily follow." The inference derived from this statement was that the Seubert revision of the atomic weight of platinum should be confirmed. This was done by Halberstadt,¹⁰ who substantially confirmed Seubert's value. The retention of the Fresenius value for the ratio $2\text{KCl}/\text{K}_2\text{PtCl}_6$ of 0.3056 therefore stamps the Fresenius method as empirical. Further studies of this method by Dupré⁷ and Fresenius and Brinton⁹ were attempts to clear up the difficulties involved. These failed to indicate methods eliminating the empiricism of the Fresenius method. The present value for the atomic weight of platinum, 195.23, was the result of the work of Archibald,¹¹ which gives for the theoretical factor 0.3067 as compared to the empirical factor 0.3056.

Variable Factors Influencing the Fresenius Method.—The basic facts accounting for the formation of impure precipitates of K_2PtCl_6 are summarized here. The chloroplatinic acid is often prepared under conditions giving the impurity $\text{H}(\text{NO})\text{PtCl}_6$. This product results from the incomplete removal of the nitric acid used in the solution of platinum black with aqua regia. The complete removal of this nitric acid using hydrochloric acid results in the accumulation of the impurity $\text{H}_2\text{Pt}(\text{OH})\text{Cl}_6$. Impurity in the precipitated K_2PtCl_6 results from the impure chloroplatinic acid as well as from the presence of water in the 80% alcohol, thus



Absolute alcohol cannot be used to avoid the hydrolysis of K_2PtCl_6 for the reason that sodium chloride is thus formed from the Na_2PtCl_6 present



All these errors give rise to low results in the determination of the ratio $2\text{KCl}/\text{K}_2\text{PtCl}_6$. The effects of these errors are shown by the many methods for the analysis of K_2PtCl_6 . For example, the platinum may be reduced to metal, separated by filtration from the soluble potassium chloride and weighed as such. The filtrate from the platinum determination may be evaporated to dryness and the potassium chloride determined. In this case hydrogen is used to precipitate the platinum. The chloride aside from that combined as potassium chloride can be determined by thermal decomposition with absorption of the hydrogen evolved and precipitation

¹⁰ Halberstadt, *Ber.*, 17, 2962 (1884); *Z. anal. Chem.*, 25, 296 (1886).

¹¹ Archibald, *Z. anorg. Chem.*, 66, 169 (1910); *Proc. Roy. Soc. Ed.*, 29, 721 (1910).

¹² This reaction has led to the suggestion that K_2PtCl_6 should be separated in the presence of a small amount of hydrochloric acid.

¹³ This fact was not recognized by Precht,⁸ who proposed using absolute alcohol, but was corrected by Morozewicz.⁸ The use of absolute ethyl alcohol is attractive for the reason that it diminishes the solubility of K_2PtCl_6 and is a better solvent for Na_2PtCl_6 and Li_2PtCl_6 .

with silver. By the same method the total water can be determined. Water combined in the form $K_2PtOHCl_6$ is determined by ignition in an atmosphere of carbon monoxide followed by the determination of the carbon dioxide formed. Following these methods the exact determinations of the impurities in a precipitate of K_2PtCl_6 were studied by Dupré.⁷ Since the dissertation by Dupré was not published in any other form, and since the material is almost inaccessible, a summary of this thesis is given.

Summary and Conclusions from the Work of Dupré

1. The determination of potassium in the form of chloride by the reduction of the platinum with hydrogen, followed by filtration and evaporation of the potassium chloride solution, gives accurate results after taking into account the solubility of K_2PtCl_6 in alcohol. This method of determining potassium chloride is independent of atomic weights, factors and variations in the conditions of the separation. The method is slow, involved and not adapted to routine application.

2. The separation and determination of potassium as K_2PtCl_6 from the direct weight of the precipitate gives good results if the factor for potassium chloride is 0.3056. Precision in the result thus obtained is the only justification for the use of this empirical factor.

3. Potassium chloroplatinate obtained using the Fresenius method does not have the exact composition K_2PtCl_6 but contains more platinum and less chlorine than indicated. The determination of its potassium chloride content is not correct if calculated from the determination of either the platinum or chlorine using either the Fresenius factor or the correct atomic weight for platinum.

4. Precipitates of K_2PtCl_6 obtained by the use of either sodium or lithium chloroplatinates to precipitate potassium chloride solutions, "evidently" likewise contain too much platinum and too little chlorine.

5. The methods for the analysis of K_2PtCl_6 depending upon the calculation of potassium chloride from the weight of platinum by hydrogen, sodium formate or metallic magnesium, all lead to incorrect results. The determination of chlorine using finely divided silver or following ignition at 500–550° using excess of sodium oxalate likewise gives erroneous results.

Lithium Chloroplatinate as Precipitant for Potassium Chloroplatinate.—The present work describes a process for the precipitation of potassium chloroplatinate in the presence of sodium in which the potassium chloride in the precipitate can be calculated from its weight or by determination of the platinum content. The purity of the K_2PtCl_6 thus precipitated is further proved by the fact that it is stable at 260°, whereas the salt precipitated using chloroplatinic acid decomposes at temperatures much above 160°. The preparation of lithium chloroplatinate is de-

scribed. By this process there is obtained the theoretical factor for the ratios $2\text{KCl}/\text{K}_2\text{PtCl}_6$ and $\text{Pt}/\text{K}_2\text{PtCl}_6$.

At the time this work was begun the content of the dissertation by Dupré⁷ was not familiar to the authors. As a result the process employing lithium chloroplatinate was thought to be original. A copy of the thesis was subsequently obtained and the errors in Dupré's work were studied. He stated that lithium chloroplatinate was unsatisfactory.

It should be pointed out that the present work does not indicate that the platinum process is the best for the separation of sodium and potassium. The separation of potassium from sodium and lithium using perchloric acid has been the subject of an extended series of researches by one of the present authors¹⁴ and it has been shown that the use of perchloric acid for separations and determinations in the alkali group is superior to the platinum process in speed, accuracy and economy.

Experimental Part

Preparation and Purification of Materials

Lithium Carbonate.—An ordinary grade of lithium carbonate was suspended in a large volume of water in a flask and dissolved by conversion to the bicarbonate using a rapid stream of carbon dioxide during a period of several hours. The solution was filtered and the filtrate boiled to dissociate the lithium bicarbonate to the normal carbonate, which was precipitated, filtered and the mother liquor removed by centrifugal drainage. A portion of this product was dissolved and reprecipitated. The products thus obtained were used to prepare lithium chloroplatinate without further treatment. Both fractions were equally satisfactory.

Lithium Chloroplatinate.—Lithium carbonate was dissolved in either a slight excess or slight deficiency of reagent quality chloroplatinic acid, the solution filtered and the filtrate concentrated until upon cooling a slush of crystals and mother liquor was obtained. The crystals of hydrated lithium chloroplatinate ($\text{Li}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) were filtered using a sintered glass filtering crucible and drained centrifugally in the same container. They were dissolved in water and recrystallized in the same way. In case the lithium carbonate had been dissolved in a small deficiency of chloroplatinic acid, a little more of the latter was added to the filtered solution before crystallization. The light yellow crystals of $\text{Li}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ were found to be completely soluble in ethyl alcohol and were dried in a desiccator over anhydrous until ready for use. A yield of 65–70% of the total lithium chloroplatinate is easily obtained by this process. A second crop of 15% of the original quantity was then obtained.

Chloroplatinic Acid.—Crystals as purchased on the market.

Potassium Chloride.—This was from a stock of 100% KCl used in previous work, dried by fusion and proved to be pure by conversion to perchlorate by evaporation with a slight excess of pure perchloric acid. Occluded perchloric acid was removed by dissolving in hot water and evaporating to dryness. The crystals of potassium perchlorate now contained a small amount of occluded water which was removed by heating to constant weight at 350°. The final product gave no test for chloride. The purity of the potassium chloride was proved by the value obtained for the ratio KCl/KClO_4 . The data are tabulated in Table I.

¹⁴ Willard and Smith, *THIS JOURNAL*, **45**, 2072 (1923); Smith, *ibid.*, **47**, 762 (1925); Smith and Ross, *ibid.*, **47**, 774 (1925); **47**, 1020 (1925).

TABLE I

THE CONVERSION OF POTASSIUM CHLORIDE TO POTASSIUM PERCHLORATE AND THE DETERMINATION OF THE RATIO $KCl/KClO_4$

KCl, g.	KClO ₄ found		Error, KClO ₄ , mg.	Factor KCl/KClO ₄		
	15 min. 350° g.	Constant wt. 350° g.		Found	Calcd.	Error
0.15555	0.28915	0.28915	+0.1	0.53796	0.53816	-0.00016
.11580	.21530	.21530	+ .1	.53786		- .0003
.11645	.21650	.21650	+ .1	.53788		- .00028
.15925	.29620	.29620	+ .3	.53764		- .0004
			Average	.53788		- .00028

Alcohol.—Reagent alcohol was refluxed over lime and distilled, giving a 99.6% product.

Sodium Chloride.—From a stock of material comparable to the pure potassium chloride described above.

Procedure Followed in Determining the Conversion Factor $2KCl/K_2PtCl_6$.—Weighed samples of pure potassium chloride were dissolved in water in 150-cc. beakers and a small excess of a solution of lithium chloroplatinate in water added to convert the potassium chloride to chloroplatinate. The precipitated K_2PtCl_6 was dissolved by heating and the greater portion of the water evaporated until upon rapidly cooling the hot solution a finely divided precipitate was obtained. The beaker and moist contents were treated with 25 cc. of absolute alcohol and the K_2PtCl_6 filtered using platinum sponge filtering crucibles. The precipitates were washed by decantation with fresh portions of absolute alcohol and transferred to the filtering crucible. The precipitates were then washed in the crucible by the addition of 10–15 separate small portions of absolute alcohol followed by drying first at 130° for extended periods of time and finally at 260° during two and one-half hours. The results of five consecutive determinations are listed in Table II.

TABLE II

RESULTS OF DETERMINATIONS

Expt.	KCl, g.	K ₂ PtCl ₆ Found			Factor 2KCl/ K ₂ PtCl ₆	KCl found, g.	Error, KCl, mg.
		4 hrs., 130°, g.	12 hrs., 130°, g.	2.5 hrs., 260°, g.			
1	0.10845	0.35315	0.35315	0.35310	0.30687	0.10838	-0.07
2	.12460	.40585	.40570	.40560	.30720	.12433	- .27
3	.11450	.37325	.37325	.37325	.30676	.11449	- .01
4	.07820	.2546030715	.07809	- .11
5	.17395	.5664530709	.17375	- .2
				Average	.3070		
				Calcd.	.30673		

The lithium chloroplatinate used for the conversion of KCl to K_2PtCl_6 in Table II was made from lithium carbonate which had been twice precipitated from its bicarbonate solution by boiling. The $Li_2PtCl_6 \cdot 6H_2O$ was recrystallized once and dried in a desiccator over phosphorus pentoxide.

Two and one-half grams was dissolved in 25 cc. of water and sufficient of this solution added to give approximately a 20% excess.

The filtrate and washings from the five determinations in Table II varied from 40 to 47 cc. No correction was applied to the values obtained for the weight of K_2PtCl_6 left in the filtrate and washings. Such a correction if applied would result in an average correction to the potassium chloride found of 0.12 mg. Applying the correction would reduce the value found for the conversion factor $2KCl/K_2PtCl_6$ to practically the theoretical value.¹⁵

The precipitates of K_2PtCl_6 obtained in Table II were dissolved in the filtering crucibles using a minimum quantity of hot water and the filtrates caught in 125-cc. Erlenmeyer flasks for determination of their platinum content. The platinum sponge filtering crucibles were then dried and weighed. Their final weight was compared with the original weight, and a small correction applied for the insoluble impurities accumulated throughout the analyses. This correction averaged 0.25 mg. Failure to have applied this correction would have tended to make the results obtained agree more closely with the theoretical value.

To the K_2PtCl_6 from the experiments of Table II dissolved in water as above described, a little hydrochloric acid was added and the platinum reduced to metal by the use of hydrogen under slight pressure which was kept in contact with the solutions at a temperature of approximately 80° for a period of twelve hours or until the solutions were colorless. The platinum sponge thus obtained was filtered using the same filtering crucibles in which the K_2PtCl_6 had been filtered, washed with hot water, dried and ignited. The results of these analyses are included in Table III.

TABLE III
THE DETERMINATION OF PLATINUM IN K_2PtCl_6 AND DETERMINATION OF THE RATIO
 Pt/K_2PtCl_6

Expt.	K_2PtCl_6 , g.	Pt found, g.	Pt calcd., g.	Pt error, mg.	Factor found, Pt/K_2PtCl_6
1	0.35310	0.14200	0.14179	+0.21	0.40215
2	.40560	.16290	.16288	+ .02	.4016
3	.37325	.15005	.14989	+ .16	.4020
4	.25460	.10195	.10224	- .29	.4013
5	.56645	.22680	.22747	- .67	.4004
				Average	.40162
				Calcd.	.40157

From examination of Table III it is found that practically the theoretical weight of platinum was obtained from the analysis of the K_2PtCl_6 shown in Table II. The slight error is found to be of the same direction and magni-

¹⁵ A second series of results for the ratio $2KCl/K_2PtCl_6$ determined with a new preparation of Li_2PtCl_6 in which the K_2PtCl_6 was dried at 160-170° gave the following values for the factor: 0.30625, 0.30671, 0.30660, 0.30707, 0.30683; mean, 0.30668.

tude as that found in the case of the determination of the factor $2\text{KCl}/\text{K}_2\text{PtCl}_6$. The low values found in the case of the last two experiments of Table III are the only ones obtained in both Tables I and II which do not show the trend predicted.

The Stability toward Heat of Potassium Chloroplatinate Precipitated by Lithium Chloroplatinate.—The observation has been made repeatedly and was familiar to Fresenius and all subsequent investigators that the precipitate of K_2PtCl_6 obtained using chloroplatinic acid is not stable much above 130° . This temperature was not thought to be sufficiently high to eliminate entirely occlusion of water and the temperature of 160° is sometimes recommended as it was by Dupré.⁷ No statement was found which would indicate that precipitates of K_2PtCl_6 obtained following the Fresenius method can be heated at a temperature above 160° without decomposition. A temperature higher than this is never advised.

Potassium chloroplatinate when pure is known to be stable at 400° , as demonstrated by Noyes and Weber.¹⁶ The K_2PtCl_6 used in their work had been prepared from chloroplatinic acid made from platinum black by electrolytic oxidation in the presence of hydrochloric acid as described by Weber.¹⁶ It was thought appropriate, therefore, to determine the various ratios $2\text{KCl}/\text{K}_2\text{PtCl}_6$, $\text{Pt}/\text{K}_2\text{PtCl}_6$ and $4\text{Cl}/\text{K}_2\text{PtCl}_6$ using chloroplatinic acid from various sources, including acid prepared by the Noyes and Weber process. The data are reported in Table IV.

TABLE IV
VARIOUS CONVERSION FACTORS DETERMINED FOR K_2PtCl_6 USING H_2PtCl_6 FROM VARIOUS SOURCES

Source of chloroplatinic acid	Factor determined	Values obtained						Average	Calcd.	Error, %
Commercial	$\text{Pt}/\text{K}_2\text{PtCl}_6$	0.40117	0.40067	0.39928	0.40098	0.40083	0.40080	0.40157	-0.25	
	$2\text{KCl}/\text{K}_2\text{PtCl}_6$.30495	.30540	.30525	.30554	.30613	.30546	.30673	-0.38	
B.S. elec. oxid.	$2\text{KCl}/\text{K}_2\text{PtCl}_6$.30346	.30465	.30440	.30347	.30407	.30401	.30673	-0.89	
Recovered										
Pt + HNO_3										
+ HCl	$2\text{KCl}/\text{K}_2\text{PtCl}_6$.30366	.30321	.30283	.30336	.30269	.30342	.30673	-1.08	
	$4\text{Cl}/\text{K}_2\text{PtCl}_6$.28444	.28936	.29074	.28980	.28966	.28980	.29174	-0.63	
	$\text{Pt}/\text{K}_2\text{PtCl}_6$.39766	.39901	.39606	.39850	.39753	.39775	.40157	-0.95	

The determinations of the various ratios of Table IV followed the procedure given for the determinations using lithium chloroplatinate as precipitant. The results in the first two horizontal rows were obtained using 99.6% ethyl alcohol. The remaining results were obtained using 80% alcohol with a solubility correction applied on the basis of one part of K_2PtCl_6 dissolved in 26,400 parts of alcohol, the corrections calculated averaging 1.5 mg. The last sample of chloroplatinic acid in Table IV

¹⁶ Noyes and Weber, *Bull. Bureau Standards*, 4, 345 (1908); Weber, *THIS JOURNAL*, 30, 29 (1908).

was prepared from scrap platinum dissolved in aqua regia and later precipitated as platinum black and again dissolved in aqua regia followed by the removal of the nitric acid by evaporation with hydrochloric acid. It had been made and used in connection with previous work by others published from these laboratories.

It will be noted by examining Table IV that the values obtained using chloroplatinic acid purchased in the usual manner from a reagent supply company gave values for the determination of the Fresenius factor $2\text{KCl}/\text{K}_2\text{PtCl}_6$ which duplicated the value 0.3056 as given by Fresenius. The chloroplatinic acid made from scrap platinum showed the poorest quality and the three factors obtained leave no doubt that the K_2PtCl_6 precipitated using this acid was impure. The errors found were all in the predicted direction, namely, too little platinum and chlorine and a molecular weight of K_2PtCl_6 less than the theoretical.

A point of particular interest lies in the fact that the Fresenius method calls for the use of 80–85% alcohol for reasons cited above, whereas in the absence of sodium, absolute alcohol may be used, thus avoiding a correction due to the solubility of K_2PtCl_6 . The correct Fresenius factor was obtained using 99.6% alcohol in the case of the first sample of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ of Table IV.

The Separation of K_2PtCl_6 from Na_2PtCl_6 Using Li_2PtCl_6 as Precipitant

In the practical separation of potassium and sodium using lithium chloroplatinate as precipitant two modifications of the procedure previously employed had to be applied. One consisted in using 80% ethyl alcohol in place of 99.6% strength. The reaction $\text{Na}_2\text{PtCl}_6 = \text{NaCl} + \text{PtCl}_4$ is known to occur⁷ in the latter case. The sodium chloride formed is insoluble. The second modification consisted in restricting the filtrate from the K_2PtCl_6 in order to avoid the necessary correction for its solubility in 80% alcohol. This correction is undesirable since a variable excess of chloroplatinate ion makes the magnitude of this correction uncertain.

The use of the filtrate from the K_2PtCl_6 to transfer the precipitate to the filtering crucible made it possible to limit the filtrate and washings to a volume of 15 cc. That a complete transfer of the precipitate was obtained was shown by washing the beaker with distilled water which, after concentration to a small volume, was colorless. Using lithium chloroplatinate prepared as previously described, 80% alcohol as solvent and weighed quantities of potassium and sodium chloride, a series of separations was carried out using the theoretical factor $2\text{KCl}/\text{K}_2\text{PtCl}_6 = 0.3067$. The theoretical factor was obtained from the data. The K_2PtCl_6 precipitates were dried for an hour at 185° and finally for an hour at 200° . No de-

composition resulted, as was proved by their complete solubility in hot water. Results are found in Table V.

TABLE V
THE SEPARATION OF POTASSIUM FROM SODIUM USING Li_2PtCl_6 AS PRECIPITANT AND 80%
ALCOHOL AS SOLVENT

KCl, g.	NaCl, g.	K_2PtCl_6 , g.	KCl found using fac- tor 0.3067, g.	Error, KCl, g.	Calcd. factor $\frac{2\text{KCl}}{\text{K}_2\text{PtCl}_6}$	Deviation from calcd., %
0.10565	0.190	0.34315	0.10525	-0.0004	0.30788	+0.37
.18160	.160	.59285	.18185	+ .00025	.30632	- .13
.21375	.130	.69815	.21410	+ .00035	.30617	- .18
.20110	.100	.65530	.20095	- .00015	.30688	+ .05
.11965	.090	.39060	.11980	+ .00015	.30632	- .13
			Mean ^a	- .00015	.3064	- .11

^a Excluding the value for the first entry.

Reference to Table V shows that the theoretical factor for the ratio $2\text{KCl}/\text{K}_2\text{PtCl}_6$, namely, 0.3067, is obtained with an error of -0.1% . This theoretical factor was obtained using the detailed directions of the original Fresenius method with the one alteration, the substitution of lithium chloroplatinate for chloroplatinic acid. To include the value for the first determination of Table V would bring the mean value for the conversion factor closer to the theoretical.

Discussion of Results

In accord with the results obtained by all previous investigators the original Fresenius method using chloroplatinic acid, is found to be empirical. Using chloroplatinic acid purchased from a standard supply house, the Fresenius factor 0.3056 was obtained as compared to the theoretical 0.3067. Chloroplatinic acid from other sources or prepared from platinum residues may be less satisfactory.

The substitution of lithium chloroplatinate for chloroplatinic acid makes possible the use of the theoretical factor. The use of the lithium salt obviously does not permit determination of lithium in the presence of sodium and potassium. It introduces lithium chloride into the filtrate from the potassium determination, which complicates the separation and direct determination of sodium. Several methods, however, are available for the separation of sodium from lithium.¹⁴ The direct determination of sodium in the filtrate from the K_2PtCl_6 precipitation is seldom made, which minimizes this objection.

Lithium chloroplatinate to be used in the separation of potassium from sodium should be prepared from lithium carbonate purified by two precipitations from lithium bicarbonate and subsequent conversion to the normal carbonate, which is insoluble in water. An excess of lithium carbonate

should be used in its conversion to lithium chloroplatinate using reagent quality of chloroplatinic acid.

The lithium chloroplatinate is twice recrystallized. One recrystallization improves the results but does not correct completely the errors resulting in low values for the ratio $2\text{KCl}/\text{K}_2\text{PtCl}_6$.

It is of interest to compare the advantages afforded by the use of the chloroplatinate method for alkali metal separations with the disadvantages.

Advantages.—1. The insolubility of K_2PtCl_6 in 80% alcohol. One part of K_2PtCl_6 is dissolved by 26,400 parts of the alcohol.

2. The low conversion factors $2\text{KCl}/\text{K}_2\text{PtCl}_6 = 0.3056$ (The Fresenius factor) or 0.3067 (Theoretical) and $\text{K}_2\text{O}/\text{K}_2\text{PtCl}_6 = 0.1906$.

3. The chloroplatinate process is a semi-extraction operation since the mixture of alkali chloroplatinates is taken up with alcohol from a concentrated solution in water. Occlusion of sodium and lithium chloroplatinates in the K_2PtCl_6 is therefore practically eliminated.

Disadvantages.—1. The cost of recovery of platinum. Aside from the cost of platinum and the interest on the value invested, the recovery is costly in time and attention.

2. The factor $\text{H}_2\text{PtCl}_6/2\text{KCl}$ is high, greater than 3.5. This value is greatly increased for the reason given in 3.

3. The necessity for the conversion of NaCl to Na_2PtCl_6 . The failure to complete this conversion results in the precipitated K_2PtCl_6 being contaminated by NaCl .

4. The direct determination of sodium in the filtrate from the potassium must follow the separation of platinum from the solution.

5. The method is empirical if H_2PtCl_6 is used.

6. Using H_2PtCl_6 , the K_2PtCl_6 must be dried at 130° . Occluded moisture is not expelled completely at this temperature.

The low conversion factor in the original Fresenius method is due to the errors resulting from several sources. Reduction of platinum in H_2PtCl_6 is known to occur in warm alcohol solution. It was shown by Dupré⁷ that precipitation of K_2PtCl_6 using a cold alcoholic solution of H_2PtCl_6 gave high results, indicating a low conversion factor $2\text{KCl}/\text{K}_2\text{PtCl}_6$. Presumably the addition of alcohol to the slightly acid solution that results from the precipitation of aqueous potassium chloride by aqueous H_2PtCl_6 also results in the reduction of platinum with the same effect. It is at least noteworthy that the use of lithium chloroplatinate for chloroplatinic acid avoids the formation of hydrochloric acid through precipitation of K_2PtCl_6 . The hydrolysis of chloroplatinic acid to form such a product as $\text{H}_2\text{PtOHCl}_5$ would result in a high value for the ratio $2\text{KCl}/\text{K}_2\text{PtCl}_6$. Nitroschloroplatinic acid, $\text{H}(\text{NO})\text{PtCl}_5$, if present in the H_2PtCl_6 , would have the opposite effect. The use of lithium chloroplatinate corrects these errors, as previously shown.

Summary

1. The preparation of lithium chloroplatinate suitable for a reagent in the precipitation of potassium has been described.

2. Potassium chloroplatinate of the theoretical composition is precipitated if lithium chloroplatinate is used in place of chloroplatinic acid, with 80% ethyl alcohol as solvent.

3. Precipitates of potassium chloroplatinate formed by the lithium salt are stable at 200–260°, whereas those obtained by the usual process are unstable at temperatures above 160°.

4. A critical discussion has been given of the errors involved in the old process and an explanation offered for the better results obtained by the new procedure.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY OF MCGILL UNIVERSITY]

THE DIELECTRIC CONSTANT OF WATER AS DETERMINED BY A RESONANCE METHOD

BY E. P. LINTON¹ AND O. MAASS

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The object of this paper is not so much the determination of the dielectric constant of water, as an investigation of the adequacy for this purpose of the resonance method when employed in the manner previously described.² Certain criticisms have been put forward with regard to this method, the principal one being that when a measurable amount of conductivity can be assigned to the dielectric under investigation, the dielectric constant value obtained is irrelevant. It will be shown in this paper that criticism of the value found for the dielectric constant of water was justified, but that the error involved was due to a cause other than the conductivity of the water and that the method can be used for the measurement of the dielectric constant of water provided its conductivity is below a certain specified value.

It was suspected that any influence of conductivity was to be found in the absorption of the electric oscillations, with consequent distortion of the point of resonance. The set-up previously described was therefore altered to include a radiotron tube of greater power and measurements were made with dielectrics whose conductivity could be varied to a known extent by the addition of a small amount of electrolyte. Apart from this a method was devised for calibrating the tuning condenser. The effect of using the harmonic instead of the fundamental for the point of resonance

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² Cuthbertson and Maass, *THIS JOURNAL*, 52, 483 (1930).