A MICRO METHOD FOR THE DETERMINATION OF POTASSIUM AS IODOPLATINATE *

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The standard and most widely accepted method for the determination of potassium depends upon its precipitation as potassium chloroplatinate. The modification called the Lindo-Gladding procedure (1) is official with the Association of Official Agricultural Chemists. Methods based upon the precipitation of potassium as potassium of cobalti-nitrite (2), have been very useful in determination of potassium in the blood and serum when the technique described (3) is rigidly adhered to, but under slightly different conditions, or for material of varying salt composition, are questionable. This criticism applies also to modifications involving either the gasometric (4) or colorimetric (5) determination. The cobalti-nitrite precipitate is not of constant composition (6).

The method about to be presented depends upon the precipitation of the potassium chloroplatinate in the ash of physiological material and its subsequent determination by colorimetric or titrimetric procedure or by both.

The quantitative determination depends upon the conversion of potassium chloroplatinate to potassium iodoplatinate by the addition of potassium iodide. Because of the deep rich wine color of the iodoplatinate in solution, amounts as small as 0.1 mg. of potassium in this form can be estimated by colorimetric comparison with known amounts of potassium chloroplatinate also treated in this way. The principle was used in 1903 by Cameron and Failyer (7) for the determination of potassium in water. The presence of iodine in the compound permits the use of the

Potassium Determination

method of Peterson (8), in which potassium iodoplatinate is reduced in neutral solution to $K_2PtI_4$ with sodium thiosulfate. The probable reactions taking place are expressed in the following equations.

$$K_2PtCl_6 + 6KI = K_2PtI_6 + 6KCl$$
$$K_2PtI_6 + 2Na_2S_2O_3 = K_2PtI_4 + 2NaI + Na_2S_4O_6$$

$$(Pt^{++++} + 2S^{++} = Pt^{++} + 2S^{+++})$$

The color varies in proportion to the amount of potassium chloroplatinate present when potassium iodide is added to solutions of this salt. This proportion is maintained from 0.2 mg. per cent up to 10.0 mg. per cent, which is the highest concentration tried. Dilution does not affect the proportion. The color given by 1.6 mg. per cent and more cannot be read accurately in the colorimeter without previous dilution.

The rate of color development is proportional to the amount of potassium iodide present. The presence of acid also hastens color development, but after a time excess acid causes the liberation of iodine. The presence of free iodine destroys the proportional variation of the color. Heat also increases the rate of color formation. By the color development in 0.4 N potassium iodide (5 cc. of 2 N KI in 25 cc.) in the presence of either acid or hot water, full color is developed immediately.

The color so formed is permanent for 24 hours or longer. The only interfering substances found are iron, which forms a colored iodide, copper, which precipitates out as the iodide in acid solution, ferricyanide, which gives a green color, and alcohol, which reduces the potassium iodoplatinate. The hotter the solution, the less actual color is obtained, but this color is still in proportion to the amount of potassium present. Exposure to bright sunlight through glass for 30 minutes liberates iodine, which obviously invalidates the determination. Indirect light or darkness does not cause oxidation of the iodine salt.

By application of the optimal conditions defined above to the production of the wine-red color, the amount of potassium present in a solution can be determined colorimetrically within the reading error of the instrument, which is considered as ±4 per cent.

The potassium iodoplatinate is readily reduced in neutral solution by sodium thiosulfate. This reaction must take place
in a solution exactly neutral, as acid frees excess iodine and alkali suppresses the reaction. A final concentration of normal potassium iodide and heat are both used to insure a rapid formation of the iodine compound. Heat does not affect the actual titration with thiosulfate. Alcohol naturally must be avoided. Neutral salts such as potassium chloride have no effect. In the preliminary work the precipitate was separated and washed by centrifugation. This procedure gave good results, but an occasional analysis in a series gave large variation. This led to an improved filtration method which we have adopted here.

Because of the color of the reduced salt in solution, which is a lemon-yellow, the iodine salt is a self-indicator. The end-point is taken as the place at which 1 drop of the thiosulfate changes the color of the solution from a reddish to a greenish yellow.

By titration of the iodoplitate solution with 0.01 N sodium thiosulfate in a micro burette, 0.4 mg. potassium or more can be determined with an accuracy of ±2 per cent.

The reduced salt tends to become reoxidized on standing in the air, especially in acid solution. Advantage is taken of this fact to check the titration value with a colorimetric comparison after complete oxidation. Quantitative transformation to potassium iodoplitate is hastened by the addition of acid and a mild oxidizing agent, 0.2 per cent H₂O₂.

Both the ashing of the sample and the precipitation of the potassium chloroplatinate are carried out according to the well known Lindo-Gladding method for potassium. A few minor modifications have been introduced to make the procedure applicable to such small amounts of material as must be used. With materials such as amino acids which contain large amounts of nitrogenous substances in comparison to the potassium content, a preliminary ashing in glass with sulfuric acid and superoxol is recommended. Otherwise, 5 to 10 per cent of the potassium is lost. When a small amount of protein is present, as in pathological cerebrospinal fluids, the results may be 50 per cent low unless the protein is first removed. The potassium chloroplatinate is precipitated in the presence of redistilled alcohol and the wash liquids are saturated with the salt. In this way the last 0.01 mg. is precipitated.

Ammonia also forms a chloroplatinate which has the same
solubilities and properties as potassium chloroplatinate. Because of this, great care should be taken that all ammonia is expelled from the ash. A sulfuric acid ashing should be carried out on all samples just before the precipitation of the chloroplatinate to insure the volatilization of absorbed ammonia.

Analytical Procedure.

1. Reagents.

Trichloroacetic acid, 20 per cent.
Superoxol (30 per cent hydrogen peroxide) Merck, Blue Label.
Sulfuric acid, approximately 4 N.
Hydrochloric acid, approximately 1 N.
Chloroplatinic acid, 10 per cent platinum.
Alcohol, redistilled over lime.
Alcohol, redistilled over lime, saturated with potassium chloroplatinate.
Potassium chloride, 10 per cent, saturated with potassium chloroplatinate.
Potassium iodide, 2 N, iodate-free, recrystallized from alcohol.
Sodium thiosulfate, 0.01 N. This is standardized against potassium iodate.
Hydrogen peroxide, 0.2 per cent (made up just before use).

2. Preparation of the Sample.

(a) Blood Serum or Plasma.—The determination is made on the protein-free filtrate. 1 volume of 20 per cent trichloroacetic acid is added to 1 volume of serum or plasma and diluted to 5 volumes. 5 cc. of the filtrate, equivalent to 1 cc. of the serum or plasma, are taken for the colorimetric determination. Twice this amount is taken for the titrimetric determination.

(b) Whole Blood.—1 volume of whole citrated blood is precipitated with 2 volumes of 20 per cent trichloroacetic acid and diluted to 5 volumes. 1 cc. of the human blood filtrate, which is equivalent to 0.25 or 0.35 mg. of potassium, is taken for the colorimetric procedure and twice the amount for the titrimetric determination. 2 to 5 cc. of dog blood filtrate are necessary to supply the correct amount of potassium.

3. Ashing of Sample.

(a) Salt Solutions.—These are ashed directly.

(b) Serum, Plasma, and Cerebrospinal Fluid.—An amount of the sample containing from 0.15 to 0.80 mg. of potassium is
placed in a Folin digestion tube. 0.6 cc. of 4 N sulfuric acid is added and the mixture is evaporated to a small volume. A drop or more of superoxol (30 per cent hydrogen peroxide) is added at intervals and the ashing is continued until a clear, colorless solution is obtained while sulfuric acid fumes are escaping. Care should be taken that all hydrogen peroxide has been dispelled before one continues. The sample is then transferred to a platinum crucible, evaporated to a small volume, and ashed according to the regular procedure described in (c).

(c) Whole Blood, Urine, and Stool.—An amount of the sample containing from 0.15 to 0.8 mg. of potassium is transferred to a platinum crucible. 4 drops of 4 N sulfuric acid solution are added. The sample is evaporated to dryness on a hot plate. The dish is heated carefully over a micro burner until all sulfuric acid fumes are given off and the ash becomes white. 1 drop of 4 N sulfuric acid is added and the sample re-ashed at red heat. With samples containing a larger percentage of potassium than that in blood, such as stool, it is often easier to ash more of the sample than is required for one determination. This is dissolved in a definite volume of water and aliquots are taken for the determination.

4. Precipitation of Potassium Chloroplatinate.

To the ash so prepared are added 1 drop of N hydrochloric acid and 0.30 cc. of platinic acid (10 per cent platinum). This is thoroughly mixed and 5 cc. of alcohol are added. After standing for 20 minutes, the precipitate is transferred to a micro filter (9). The filter is made by mounting a 1 inch funnel in a Witt filtering apparatus, which is essentially a suction flash with a ground glass removable top, so that the filtrate may be recovered in a small inner tube. A glass pearl is dropped into the funnel and a mat about 1/2 of an inch thick of fine grained asbestos is put over the bead. This makes essentially a micro Caldwell crucible. The excess platinum is filtered off by suction and saved for recovery. The precipitate and the filter are then washed four or five times with alcohol saturated with potassium chloroplatinate. The contaminating salts, which are precipitated with the chloroplatinate in alcohol, are washed out with 3 or 4 washings of 10 per cent potassium chloride saturated with potassium chloroplatinate.
5. Quantitative Determination of Potassium Chloroplatinate.

The amount of potassium in the chloroplatinate so obtained can be determined in the following ways.

(a) Colorimetric Determination.—A 25 cc. volumetric flask is placed in a Witt filtering apparatus and the precipitate dissolved in situ by the repeated addition of small amounts of hot water which is first used to rinse the platinum crucible. This is followed by addition of 5 cc. of 2 N potassium iodide and 1 cc. of 1 N HCl. The mixture is cooled and made to the volume. The deep wine-red color can be compared against known standards at once.

<table>
<thead>
<tr>
<th>Authors' method</th>
<th>Amount present</th>
<th>Error</th>
<th>Remarks</th>
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<td>per cent</td>
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<td>-1.3</td>
<td>Colorimetric procedure (centrifuged). Artificial blood salts.</td>
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<tr>
<td>0.405</td>
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<td>+1.0</td>
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Colorimetric determination is convenient for 0.1 mg. to 4 mg. of potassium in the form of potassium chloroplatinate.

(b) Titrimetric Procedure.—The funnel containing the precipitate is removed from the Witt filtering apparatus, inverted, and the precipitate together with the asbestos returned to the original crucible by means of a small glass rod inserted in the stem of the funnel. The sides of the funnel are washed with 1 to 2 cc. of hot water and 1 cc. of 2 N potassium iodide. The mixture is heated almost to boiling for 3 to 5 minutes. It is not necessary to remove the asbestos. The solution is then titrated hot with 0.01 N sodium thiosulfate delivered from a micro burette calibrated to 0.01 cc.
TABLE II.
Potassium Determinations on Physiological Material.

<table>
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<tr>
<th>Material</th>
<th>Authors' method</th>
<th>Gravimetric method</th>
<th>Remarks</th>
<th>Material</th>
<th>Authors' method</th>
<th>Gravimetric method</th>
<th>Remarks</th>
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<tr>
<td>Cow blood</td>
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<td>0.089</td>
<td>0.086</td>
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</table>
The end-point is a lemon-yellow color free from red. 1 cc. of thiosulfate is equivalent to 0.39 mg. of potassium. The titrimetric procedure is convenient for 0.4 to 1.0 mg. of potassium and potassium chloroplatinate.

(c) Combination.—The titrimetric result can be checked colorimetrically by reoxidation of the solution. 1 cc. of the normal hydrochloric acid solution and 0.10 cc. of a 0.2 per cent hydrogen peroxide solution are added to the mixture. This is allowed to stand exposed to the air from 30 minutes to 1 hour. The solution is made up to 50 cc. and compared against a suitable colorimetric standard.

The results obtained by this procedure are given in Tables I and II.

Determinations were made in triplicate or quadruplicate with good agreement. It is needless to say that known solutions of potassium sulfate were determined correctly; that a mixture of
salts of the same composition as the blood and salts of known purity gave theoretical values for potassium; and that potassium added to various unknowns was recovered. In addition, varying amounts of material yielded the same percentage analysis for potassium. All results with the present method were checked by gravimetric determination according to the Lindo-Gladding method. The results for blood, serum, milk, and urine were also checked by this method.

SUMMARY.

A procedure is outlined for the determination of 0.1 mg. or more of potassium. Potassium chloroplatinate is precipitated and converted to iodoplatinate. Quantitative determination is made either by colorimetric comparison with known standards, or by titration with sodium thiosulfate. By this method 0.1 mg. can be determined, ±4 per cent, and 0.4 mg., ±2 per cent.

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A MICRO METHOD FOR THE DETERMINATION OF POTASSIUM AS IODOPLATINATE
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