# A Rapid Determination of Potassium with Hexanitrodiphenylamine (Dipicrylamine) Reagent.

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During the past few years, the feasibility of the use of Hexanitrodiphenylamine or dipicrylamine as a reagent in the quantitative determination of potassium has been reported from several sources. Most of the reports give procedures for the gravimetric method, in which the potassium is precipitated and weighed as the potassium salt of dipicrylamine, expressed as $H_K$. The drying at a certain temperature, cooling in a dessicator and weighing of the $H_K$ are all quite time consuming. Colorimetric methods such as those of Kielland[1] and of Kolthoff and Bendix[2] are particularly suitable for the determination of microquantities of potassium, and a potentiometric titration method is reported by T. Kiba[3], but these methods require elaborate apparatus and are not particularly suited for rapid, simple application.

Perhaps the quickest, simplest, and in general the most satisfactory method is the direct titration of the $H_K$ with standard acid. Kolthoff and Bendix give an acidimetric method, in which the potassium salt, $H_K$, (after being precipitated and washed as for the gravimetric method) is dissolved in acetone, converted to the amine with a measured excess of standard acid, and after evaporating off the acetone and then removing the precipitated amine by filtering through a glass filter, the excess acid is back titrated with standard sodium hydroxide using bromothymol blue as indicator.

After studying the above methods, the authors found that when acid is added to the acetone solution of the $H_K$, the reddish solution becomes yellow with the precipitation of the amine. On measuring the volume of acid added until the disappearance of the reddish color, it was found that the titration was quantitative. The addition of an excess amount of the acid followed by the back titration with sodium hydroxide until the permanent appearance of the reddish color of the $H_K$ did not affect the accuracy of the titration. Working with sample solutions of KCl containing approximately 20 mg. of potassium, the results for a series of twelve determinations checked satisfactorily as shown in Table I. The KCl solution was calculated to be 0.252% in $K_2O$, and the relative errors ranged from −1.98% to +1.19%, corresponding to an average of 0.87%.

**Experimental Materials:** Magnesium Dipicrylaminate, $H_{Mg}$. A 3% solution $H_{Mg}$ was prepared by dissolving 12 g. of dipicrylamine with 5 g. of MgO in 400 c.c. of distilled water. After stirring the solution well, it

(1) Kielland, *Ber.*, **71** B (1938), 220.
(2) Kolthoff and Bendix, *Ind. Eng. Chem.*, Anal. Ed., **11** (1939), 94.
(3) T. Kiba, *J. Chem. Soc. Japan*, **60** (1939), 1073.

Table 1. Titration of $H_K$ with N/10 $H_2SO_4$.

| Sample No. | 0.1102 N $H_2SO_4$ (c.c.) | 0.09378 N NaOH (c.c.) | Corrected Vol. $H_2SO_4$ (c.c.) | $K_2O$ % Present | $K_2O$ % Found | Relative Error (%) |
|---|---|---|---|---|---|---|
| 1 | 6.85 | 2.54 | 4.79 | 0.252 | 0.250 | −0.79 |
| 2 | 8.75 | 4.60 | 4.84 | ,, | 0.252 | 0.00 |
| 3 | 5.68 | 0.95 | 4.87 | ,, | 0.253 | +0.40 |
| 4 | 5.55 | 0.96 | 4.73 | ,, | 0.247 | −1.98 |
| 5 | 5.85 | 1.20 | 4.83 | ,, | 0.251 | −0.40 |
| 6 | 5.70 | 1.00 | 4.85 | ,, | 0.253 | +0.40 |
| 7 | 7.50 | 3.10 | 4.86 | ,, | 0.254 | +0.79 |
| 8 | 6.10 | 1.60 | 4.74 | ,, | 0.247 | −1.98 |
| 9 | 5.53 | 0.92 | 4.77 | ,, | 0.249 | −1.19 |
| 10 | 8.00 | 3.70 | 4.85 | ,, | 0.253 | +0.40 |
| 11 | 6.00 | 1.40 | 4.81 | ,, | 0.250 | −0.79 |
| 12 | 6.60 | 2.00 | 4.90 | ,, | 0.255 | +1.19 |

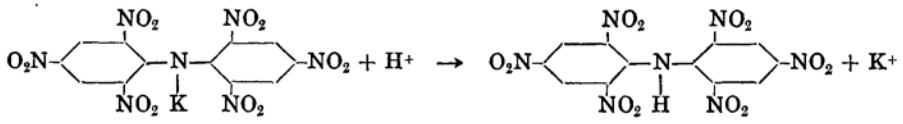
was allowed to stand overnight and was then filtered through a No. 1 G 4 glass filter.

Washing Solution A. Distilled water was cooled to 0°C. in a 100 c.c. wash bottle placed in an ice bath.

Washing Solution B. A solution of potassium dipicrylaminate saturated at 0°C. was prepared by dissolving an excess of the $H_K$ (about 0.5 g. per 500 c.c.) in distilled water and then filtering the solution after cooling to 0°C. The solution was then kept at that temperature in a 100 c.c. wash bottle placed in an ice bath.

Standard Potassium Chloride Solution. A solution of potassium chloride was prepared by dissolving 0.9977 g. of dried KCl (Takeda, "zur Analyse") in 250 c.c. of distilled water. This solution was calculated to be 0.252% in $K_2O$ and to contain 20.65 mg. of potassium per 10 c.c.

**Experimental Procedure.** 10 c.c. of the standard KCl solution were pipetted into a 100 c.c. beaker. With constant stirring, 10 c.c. of the $H_{Mg}$ solution, corresponding to an excess of 20%, were added dropwise to precipitate the potassium as $H_K$. After cooling for about 15 minutes over an ice bath, the precipitate was filtered with a No. 1 G 4 glass filter, washed with about 1 c.c. of washing solution A, then with 3 or 4 c.c. of washing solution B and finally with about 1/2 c.c. of washing solution A. The $H_K$ was then dissolved with a minimum of acetone. If more than 5 c.c. of the latter are required, the excess must be evaporated off, because it prevents a sharp color change at the titration end point. Before each titration, the acetone solution was diluted to about 15 or 20 c.c. with distilled water. It was found that the color change of from yellow to red was shaper than that of from red to yellow, so as shown in Table I, a slight excess of acid was added, and the latter was then back titrated with standard sodium hydroxide. The reaction of the $H_K$ conversion to the amine is as follows:



**Conclusion.** By revising the methods reported by Kolthoff and Bendix and by T. Kiba, a simple, rapid determination of potassium with Hexanitrodiphenlyamine as the reagent was found. The potassium, after being precipitated as the potassium salt of dipicrylamine, is dissolved in acetone, and the resulting solution is directly titrated with standard acid. By taking advantage of the color change of the solution from the red of the potassium salt to the yellow of the precipitated amine, no indicator is necessary in the titration. The relative errors ranged from −1.98 to +1.19%, and the average for a series of twelve determinations was 0.87%. However, it is believed that the simplicity and rapidity of the method justify its application in routine analyses, where the accuracy of more sensitive methods may be sacrificed.

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