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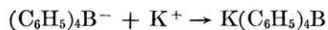and **John A. Gibson, Jr.**
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Qualitative Test for Potassium Using Sodium Tetraphenylboron

Sodium tetraphenylboron, $Na(C_6H_5)_4B$, reacts with potassium ions to form a white insoluble compound. The equation for the reaction may be written as follows:

$$(C_6H_5)_4B^- + K^+ \rightarrow K(C_6H_5)_4B$$

Sodium tetraphenylboron was first prepared by Wittig and co-workers (1, 2, 3) in 1949, and since that time a number of methods have been developed for use of this reagent in the quantitative determination of potassium. A comprehensive bibliography from 1949–58 is given by Barnard (4) and Barnard and Büechl (5).

A number of qualitative procedures are available using $Na(C_6H_5)_4B$ for the detection of K^+ by itself or in the presence of certain specific cations (6, 7, 8, 9, 10). The only methods using $Na(C_6H_5)_4B$ for the detection of K^+ in general cation unknowns (11, 12, 13) suggest testing for K^+ in the "soluble cation" group. These procedures further specify either the prior removal of NH_4^+, which also forms an insoluble compound with the reagent, or the distinction of K^+ from NH_4^+ by flame testing the precipitate. In this communication a method is described which uses $Na(C_6H_5)_4B$ to test for K^+ in original general cation unknown solutions. This test resulted from the observation that $K(C_6H_5)_4B$ is insoluble in NaOH while $NH_4(C_6H_5)_4B$ is soluble. The method, which eliminates all interfering ions by a one step treatment with NaOH, is specific for K^+, and hence the need for flame testing the precipitate is eliminated.

The concentration of the reagent was found to be a critical factor in the practical success of the test, an unnecessarily high concentration resulting in sensitivity to traces of K^+ in many common reagents. Most of the qualitative and quantitative procedures for the analysis of K^+ using $Na(C_6H_5)_4B$ recommend the use of a 1–4% solution of the reagent. (3.4% = 0.1 M.) This is needlessly high for the detection of K^+ in the concentrations (0.1 M) normally found in student unknowns. The solubility product at 25°C of $K(C_6H_5)_4B$ is 3×10^{-8} (14). Using one drop of 0.1 M reagent in five drops of test solution, one could theoretically detect about 10^{-6} M K^+. Probably because of supersaturation, neutral solutions containing less than 10^{-4} M K^+ were found to give no observable precipitate with 0.1 M reagent. This is in qualitative agreement with the sensitivity determinations reported by Amin (9), Crane (10), and Geilmann and Gebauhr (15). Concentrations of K^+ of the order of 10^{-4} M are often found in student unknowns as the result of traces of K^+ in reagents, or possibly from storage in soft glass reagent bottles. A number of Reagent Grade chemicals were found to give definite tests for K^+ using 0.1 M reagent.

The optimum concentration of reagent for present purposes was found to be 0.005 M. A curdy precipitate is obtained by using a more concentrated reagent, but with the 0.005 M reagent the result is a finely divided precipitate which is slow to settle. The sensitivity of the 0.005 M reagent is about 10^{-2} M K^+ in neutral solution which is equivalent to a dilution limit of about $1:2.5 \times 10^3$. The sensitivity appears to be considerably greater in NaOH of the concentration specified in the procedure below. Experience has shown that 0.005 M reagent will give a definite test for K^+ when present in student unknowns at a concentration of 0.1 M, but will not detect the traces of K^+ commonly found in such unknowns. A further advantage of

using these very dilute solutions of the reagent is that the cost is reduced to a negligible figure.

The reagent was prepared by dissolving in distilled water a weighed amount of solid $Na(C_6H_5)_4B$, which was purchased from the J. T. Baker Chemical Company. Some workers (16) advocate clarifying the reagent by addition of $AlCl_3$ which coagulates any $K(C_6H_5)_4B$ which may result from impurities and allows it to be filtered easily and quickly. Since no turbidity was observed when $0.005\ M$ solutions of the reagent were prepared, it was not felt necessary to add any $AlCl_3$. The reagent is unstable in acidic solutions (17). The addition of $AlCl_3$ makes the solution acidic by hydrolysis, and it is necessary to adjust the pH to about 8 with NaOH in order to obtain adequate storage stability (18). Water solutions of the reagent alone are sufficiently alkaline to be stable at room temperature for several weeks. Decomposition eventually occurs through various intermediates to give benzene as one of the products. A strong odor of benzene is observed from solutions of the reagent which have partially or completely decomposed.

The following cations have been found to form precipitates with $0.005\ M$ reagent: Ag^+, Hg_2^{+2}, Hg^{+2}, and NH_4^+. A number of other cations, which do not appear in the usual schemes of cation analysis, have been reported to form insoluble compounds with the reagent. These cations are Tl^+ (19, 20, 21, 22), Ce^{+4} (20), Cu^+ (20), Rb^+ (3), and Cs^+ (3). Using $0.005\ M$ reagent, no interference was found with Pb^{+2}, As^{+3}, Sb^{+3}, Sn^{+2}, Sn^{+4}, Bi^{+3}, Cu^{+2}, Cd^{+2}, Co^{+2}, Ni^{+2}, Al^{+3}, Cr^{+3}, Zn^{+2}, Fe^{+2}, Fe^{+3}, Mn^{+2}, Ca^{+2}, Ba^{+2}, Mg^{+2}, Sr^{+2}, Na^+, and Li^+, when the concentration of the above ions was $0.5\ M$. The following anions in concentrations of $0.5\ M$ were found to give no interference using $0.005\ M$ reagent: S^{-2}, $S_2O_3^{-2}$, SO_3^{-2}, SO_4^{-2}, ClO_4^-, ClO_3^-, ClO^-, BrO^-, IO_3^-, NO_2^-, NO_3^-, $C_2H_3O_2^-$, CO_3^{-2}, $C_2O_4^{-2}$, AsO_3^{-3}, AsO_4^{-3}, BO_3^{-3}, CN^-, SCN^-, CNO^-, $Fe(CN)_6^{-4}$, $Fe(CN)_6^{-3}$, PO_4^{-3}, CrO_3^{-2}, $Cr_2O_7^{-2}$, MnO_4^-, F^-, Cl^-, Br^-, and I^-. A number of organic alkaloids, amines, and quaternary ammonium salts have been reported to form precipitates with the reagent (10). Enough K^+ is present in some soapy water to give a test with $0.005\ M$ reagent.

In analysis for K^+ in Group V, the only interference is from NH_4^+. However, $NH_4(C_6H_5)_4B$ can be distinguished from $K(C_6H_5)_4B$ by the fact that the former is soluble in warm NaOH while the latter is insoluble. If precipitation with $Na(C_6H_5)_4B$ is made in acid solution, and NaOH then added to determine whether the precipitate is $NH_4(C_6H_5)_4B$ or $K(C_6H_5)_4B$, Mg^{+2} and traces of other cations will form insoluble hydroxides with NaOH and lead to false conclusions regarding the presence of K^+. Therefore the most satisfactory procedure is to test for K^+ on the original solution after first removing all interfering ions with NaOH. The decantate can then be tested for K^+ by adding one or two drops of $Na(C_6H_5)_4B$. In strongly alkaline solution

$NH_4(C_6H_5)_4B$ does not precipitate, even when allowed to stand in a closed container for a period of several weeks. Concentrations of NH_4^+ as great as $1.0\ M$ do not interfere with the test for K^+ using the procedure described below.

The following procedure has been tested by the 120 students in our sophomore course in qualitative analysis and found to be satisfactory.

To 5 drops of the original unknown solution add an equal volume of $3\ N$ NaOH. Centrifuge and test for complete precipitation by adding one more drop of NaOH. Add two drops of $0.005\ M\ Na(C_6H_5)_4B$. If K^+ is present a white precipitate forms immediately.

It has been found that $6\ N$ NaOH prepared from a c.p. reagent gives a precipitate with $0.005\ M\ Na(C_6H_5)_4B$. Even with $3\ N$ NaOH a very slight turbidity is sometimes observed, depending on the source of the NaOH. Since the NaOH is actually diluted to $1.5\ N$ after the test for K^+ is completed, the use of $3\ N$ NaOH should cause no interference with the test. However in order to verify this assumption, it is recommended that a blank be run on the NaOH supplied for the test.

Using the above procedure, results for K^+ in student unknowns have improved considerably. The test is far superior to both the cobaltinitrite test and the flame test, particularly if large amounts of sodium are present.

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