

A HYMOLAL SALT TEST FOR POTASSIUM

E. A. WILDMAN, Earlham College

During 1933 there appeared on the market a new detergent ("Gardinol," "Drene," "Dreft") that is said to be a mixture of sodium alkyl sulfates in which the alkyl radicals are those of the alcohols formed by the reduction of cocoanut oil fatty acids. For convenience in naming the compounds of this class they have been called "hymolal salts."¹

Such alkyl sulfates of lithium, ammonium, sodium, magnesium, and calcium are readily soluble in water at 20° C. The potassium salt is remarkable in being very slightly soluble. A chance observation of this fact several months ago led us to use a 1% solution of the sodium hymolal salt as the reagent for potassium in our course in qualitative analysis. The result was that potassium was reported correctly throughout the entire course by every student.

More recently there has been an opportunity to examine the properties of these salts in so far as they have a bearing on the potassium test. A 3% solution of the reagent was found to be more satisfactory than either a greater or a smaller dilution. All tests were made by adding 1 cc. of this reagent to 5 cc. of the solution to be tested. At 20° C. the ammonium, sodium, and magnesium salts are readily soluble under such conditions, but the potassium salt produces a dense white precipitate of silky fibers within less than one minute after mixing, when the potassium ion is present in amounts of 1 mg. or more per cc.

Unfortunately ammonium ion forms a hymolal salt precipitate when it is present in concentrations exceeding about 25 mg. per cc. Consequently, if a complete analysis is being made the ammonium salts must be removed as usual. Unfortunately, also, the presence of any considerable amount of magnesium ion delays the precipitation of potassium so much that when the two ions are present in equal amounts by weight, the potassium salt comes out only when the mixture is allowed to stand as long as over night, regardless of the concentration. Sodium ion has much less restraining effect.

Cooling with ice water hastens the crystallization of the potassium salt greatly, both when pure and when magnesium is present. When pure a 1 mg. per cc. solution forms the precipitate in 15 seconds, but if 1 mg. of magnesium is also present 1 minute is required. The corresponding periods of time for 0.25 mg. per cc. solutions are 50 seconds and 3 minutes respectively.

Cooling solves the difficulty due to the restraining effect of magnesium, but it might seem to introduce another because of the decrease in solubility of the sodium salt (the reagent) with lowering of temperature. It is soluble to the extent of 100 mg. per cc. at 20° C. (10%),

¹ Killefer, D. H. Sulfonated Higher Alcohols. *Ind. and Eng. Chem.* 25:138. Items in News Ed. of *Ind. and Eng. Chem.* 12:98, 316. 1934.

but at 0° C. the solubility is less than 5 mg. per cc. (equivalent to about 0.5 mg. of sodium ion). The latter is the concentration of the reagent in the actual test when performed with the quantities specified above. Over 10 minutes are required for the precipitate to form, however, so there is no interference from this course unless there is sufficient additional sodium ion in the solution to produce a marked common ion effect. This effect shortens the time of precipitation to 5, 2, and 1 minutes when the reagent is added to solutions containing, respectively, 1, 5, and 10 mg. per cc. of sodium ion. When potassium and sodium ions are in the same solution in equal amounts the potassium precipitate comes down in the same time as it would if the sodium were not present. Even when sodium ion concentration is five times that of potassium ion it does not hold the latter back to a significant extent, but it does so sufficiently to be confusing when ten times the concentration of potassium.

The data presented up to this point indicate that potassium is precipitated in one twentieth of the time necessary for sodium when both are present in the amount of 1 mg. per cc. and in one-fourth of the time needed for the latter if the potassium is held back by an equal amount of magnesium. This allows a reasonably satisfactory opportunity to distinguish between sodium and potassium. The distinction is made much more sharp, however, by the fact that magnesium holds back the precipitation of sodium as well as of potassium, and to a much greater extent, as is shown by the following data. A potassium precipitate is formed, when the solution is cooled, in 20 seconds after the reagent is added to a solution of 5 mg. each per cc. of potassium and magnesium ions. In the case of a solution that contains 5 mg. each per cc. of sodium and magnesium ions no precipitate at all is formed within an hour and twenty minutes. It seems, therefore, that the presence of a moderate amount of magnesium not only makes the cooling of the solution in order to get a potassium precipitate in a reasonable time necessary, but also it compensates for this inconvenience by sharpening the distinction between potassium and sodium.

A considerable excess of magnesium, such as five times as much as of potassium, makes the hymolal salt test practically impossible because of the long delay in the formation of the precipitate—thirty minutes or more when the two are present in the amounts of 5 and 1 mg. per cc. respectively. The only practicable methods of removing the magnesium before testing for potassium involve adding reagents that carry sodium ion and make the latter so concentrated that a sharp distinction between it and potassium is not possible.

The test is not applicable, therefore, in cases in which a small amount of potassium ion is mixed with a large amount of both or either one of the other two.

Lithium belongs in the fifth group in the qualitative analysis scheme in addition to the three elements already mentioned, but it is often not included because of its relative lack of importance as an element. It has a number of properties that relate it closely to magnesium. As may be expected because of this fact its behavior in respect to the hymolal salt test is intermediate between that of sodium and that of magnesium, but more like the latter.

In sensitivity the hymolal salt test exceeds that with perchloric acid. The former produces a definite precipitate with as low a potassium concentration as one-sixteenth of a milligram (0.0625 mg.) per cc. (in 2 minutes) when it is the only ion present, whereas the practical limit for the perchloric acid test is 2 mg. per cc. It is much less sensitive than the cobaltinitrite test, the limit for which is about 0.001 mg.

The practical advantages of the hymolal salt test are: (1) its cheapness, two hundred and fifty tests cost one cent, whereas the same cost obtains eight tests with sodium cobaltinitrite and three tests with perchloric acid, and (2) the avoidance of testing in a highly colored solution on the one hand and the danger of a perchloric acid and alcohol mixture on the other. Disadvantages are: (1) the restraining effect of magnesium, (2) the necessity for ice water cooling in many cases, and (3) its failure to detect potassium in the presence of a large excess of magnesium or sodium.

In our laboratory unknowns are prepared so as to contain approximately 50 mg. of each cation present. The following is a procedure for the detection of potassium:

Divide the filtrate from Group IV into three equal parts. Use two of the portions for the magnesium and sodium tests before making the potassium test. Remove ammonium salts as usual from the third portion. Take up the residue in about 15 cc. of water that contains a few drops of acetic acid. Filter if not clear. To 5 cc. of the unknown solution add 1 cc. of a 3% solution of the hymolal salt reagent. A white precipitate within one minute indicates potassium. If no precipitate is obtained or if it were previously found that magnesium is present cool the test tube in ice water. A significant amount of potassium forms a precipitate within about one minute unless there is a very large quantity of magnesium. In the latter case use the cobaltinitrite test.