22. $N_2H_4.H_2C_2O_4$, acidic hydrazine oxalate.
    Sabanayev, *J. Russ. Phys.-Chem. Ges.*, **31**, 378.
  (Isomeric with $NH_2.CO.COOH.NH_3O$.)
  $HCO_2(NH_2)$, carbamic acid (hypothetic?)
  Salts of which prepared by:
    Basarow, *J. prakt. Chem.*, [2] **1**, 283.
    Mente, *Ann.*, **248**, 234 (1888).
    Naumann, *Ibid.*, **150**, 1 (1869).

As the properties of the compounds described were different for each pair, it seems probable that we are not dealing with the same compound under varying names and symbols.

POTASSIUM: ITS QUALITATIVE DETECTION AS THE COBALTINITRITE.

BY LEON T. BOWSER.

Received July 25, 1911.

In a previous note[1] a rapid method was outlined for the detection of potassium, even in very small amounts, by precipitating it as dipotassium sodium cobaltinitrite, $K_2NaCo(NO_2)_6$, in the presence of ethyl alcohol. A subsequent study of its possibilities resulted in such improvement as to render it far superior to any of the commonly applied tests, and from it has been evolved a very satisfactory method for the estimation of minute amounts of potassium. The present paper will deal only with the qualitative test, however, leaving the estimation to be dealt with in a later paper.

Many qualitative tests for potassium are known but practically every one has serious shortcomings. There are almost no potassium salts even fairly insoluble in water, hence most of the tests are applicable only to very concentrated solutions. Among the reactions applied are the following: Chloroplatinic acid, H_2PtCl_6, gives with neutral or acid solutions of potassium salts, in the presence of hydrochloric acid, a yellow, crystallin precipitate of potassium chloroplatinate, K_2PtCl_6. This precipitate is soluble in about 19 parts of water at 100° C. or in 111 parts at 10°, and comparatively recent work[2] has shown its solubility in absolute ethyl alcohol at 20° to be 0.0007 gram in 100 cc. of solution. The presence of alcohol is necessary in the use of this test unless concentrated solutions be employed. The reagent also gives a precipitate with certain non-alkali bases, which must be removed previous to testing for potassium, hence this reaction is but little used for qualitative work. Sodium perchlorate, $NaClO_4$, precipitates potassium perchlorate, $KClO_4$, from solutions of potassium salts, the precipitate being slightly soluble in water but almost insoluble in strong alcohol. Potassium may also be

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[1] THIS JOURNAL, **32**, 78 (1910).

[2] *Ibid.*, **30**, 747 (1908).

precipitated as the silicofluoride, the acid tartrate, the picrate, the phosphomolybdate and as potassium bismuth thiosulfate. Nearly every one of these reactions is far more sensitive in the presence of alcohol than of water.

Of the insoluble potassium salts there remains but one other available for qualitative purposes, namely, the cobaltinitrite. This salt, fairly complete references to the literature of which were given in an earlier paper,[1] has been known for fully half a century, but it is only within the last four years that its possibilities for the determination of potassium have been revealed to the analytical chemist. For qualitative purposes it had enjoyed some degree of usefulness, but that it possessed some unusually valuable characteristics seemed to have previously escaped attention. About the only serious attempt at a study of the reaction is that by W. C. Bray,[2] whose excellent paper served in a way as a basis for my note.[3]

The method I previously outlined was: To 5 cc. of the potassium solution add a little acetic acid, 5 cc. of sodium cobaltinitrite reagent, and then an equal amount of 95 per cent. alcohol, when the precipitate will be quickly thrown down. In this way potassium amounting to 2 parts per 100,000 could be detected within four minutes, the rapidity of the test being an important feature. It was stated that the use of alcohol did not render the precipitation any more delicate, merely hastened it so that minutes sufficed where hours were otherwise needed. The subsequent studies detailed in the present paper have proved this statement to be erroneous, and as will be shown the sensitiveness is actually increased ten times, while the time required is cut down to one or two minutes.

The merest accident led to a discovery of the fact that when two beakers are set side by side on a mirror, one containing the test being made.and the other a blank test on pure water, the first will show dimness from the precipitate present that is easily apparent by comparison with the other. A development of this idea, coincident with working out the best proportions of reagents for use, gave a sensitiveness of 2 parts per million, using 5 cc. of potassium solution. Numerous trials of large beakers, test tubes, colorimeter tubes, and tall, narrow beakers showed the latter to afford the best results. Those used were of about 50 cc. capacity, and the bases were comparatively small. Beakers with smooth, flawless bottoms are preferable, as they give no distortion of the image of the observer when looking down through the solution into the mirror.

The best procedure is as follows: Pipet 5 cc. of the potassium solu-

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[1] *Jour. Ind. Eng. Chem.*, 1, 791 (1909).

[2] THIS JOURNAL, 31, 621 and 633 (1909).

[3] *Loc. cit.*

tion into a beaker of the type described, 5 cc. of distilled water into another as nearly like it as possible, and set both on a well polished mirror lying on the desk. Into each introduce 2.5 cc. sodium cobaltinitrite reagent and 5 cc. of 95 per cent. alcohol; then rotate the solutions an instant to insure thorough mixing. Looking down through the solutions into the mirror, the observer sees in the blank a bright, sharp image of himself, in the other a decidedly dim one, the dimming being caused by partial cutting off of the rays of light by the finely divided precipitate. The smaller the amount of potassium in a solution the brighter the image seen through it, until at less than 2 parts per million no decided difference can be observed between the potassium solution and the distilled water. In any case the precipitate gradually disappears and within a few minutes a potassium solution cannot be differentiated from a blank. This makes it imperative that the comparison be made quickly, else a very slight trace may never be noticed at all.

The procedure in regard to reagents differs from that given in my note to some extent, as instead of 5 cc. sodium cobaltinitrite solution only 2.5 cc. are used, while acetic acid is omitted entirely. It was found important to use as little reagent as possible, since its dark color tends to obscure the image, if in too great excess. Less than 2 cc. gives an unsatisfactory precipitation, while more than 3 cc. makes the solution too dark, but 2.5 cc. serves the purpose nicely. Experiments to determin the necessity for the addition of acetic acid showed that better results followed if it was omitted, which accords closely with the observation of Bray.[1] Any moderately strong daylight answers very well for the purposes of this test. Very sharp results may be secured if the solution be set in the direct rays of the sun, but it should be removed almost instantly, as within a short time both precipitate and reagent will be decomposed.

The following tests will serve to show the sensitiveness of the method. Volume of potassium solution taken was 5 cc. in every case.

TABLE I.

Mg. K.	Parts per million.	Precipitate perceptible.
0.15 or more	30 or more	heavy ppt. at once
0.10	20	at once
0.08	16	"
0.06	12	"
0.03	6	"
0.025	5	"
0.020	4	soon
0.015	3	"
0.010	2	within 2 minutes
0.005	1	no ppt.

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[1] *Loc. cit.*

From these results it may be seen that in most cases the presence of potassium is shown at once, while even at a dilution of 2 or 3 parts per million the precipitate will form within a minute or two. The extreme sensitiveness attained is 2 parts per million, a delicate enough test for all ordinary purposes.

It is essential that no ammonium salts be present, since they are readily precipitated by this method. Table II illustrates their behavior:

TABLE II.

Mg. NH_3.	Parts per million.	Precipitate perceptible.
0.50	100	At once
0.25	50	"
0.10	20	faintly at once
0.05	10	shortly
0.025	5	never

The extreme sensitiveness attainable in this case was found to be about 10 parts per million, or one-fifth that of potassium.

Bray states that a moderate amount of the alkaline earth elements or lithium does not interfere with the test (as conducted without alcohol), and my own results have shown that save for ammonium there is no metallic salt which interferes in any way with the precipitation so conducted. By reason of these advantages any solution may be tested directly for potassium without removing anything save ammonium. Due care must be taken in case the solution is alkaline to make it slightly acid with acetic acid. If a free acid other than acetic be present in the solution it should be neutralized by means of sodium hydroxide and then made slightly acid with acetic acid.

Summarized, the procedure is as follows: Place 5 cc. of the potassium solution in a tall beaker of 50 cc. or 100 cc. size, set on a mirror beside it 5 cc. of pure water in a similar beaker, and add to each 2.5 cc. of sodium cobaltinitrite reagent and 5 cc. of 95 per cent. alcohol. If upon looking down through the solutions into the mirror an equally sharp image of the observer can be seen in each beaker there is no potassium present; if the test solution shows a dimmer image than the blank, potassium is present amounting to two or more parts per million. The only precautions necessary are to avoid making the test in an atmosphere dense with ammoniacal fumes, to be certain of the absence of ammonium from the solution, and to be certain that the solution is neutral or slightly acid with acetic acid.

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THE OXIDATION OF HYDRAZOIC ACID.

BY HAROLD EATON RIEGGER.

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It has been shown[1] in this laboratory that hydrazoic acid may be

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[1] Browne, THIS JOURNAL, **27**, 551–5 (1905); Browne and Shetterly, *Ibid.*, **29**, 1305–12 (1907); **30**, 53–63 (1908); **31**, 221–37 (1909); **31**, 783–99 (1909).