TABLE V.—AIR TEMPERATURE ABOVE OR BELOW THE CALORIMETER TEMPERATURE.

At time of ignition. ° C.	1 minute after ignition. ° C.	Average during 4 minutes. ° C.	Calories per gram benzoic acid.
+0.34	—0.25	+0.13	6323.0
+0.11	—0.15	+0.01	6315.0
+0.16	+0.05	+0.16	6316.3
+0.13	—0.25	+0.13	6323.3

acid being 6320 calories according to the U. S. Bureau of Standards. These results show that the adiabatic arrangement is very sensitive and capable of giving very good results.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

A STUDY OF COBALTINITRITES AND THEIR APPLICATION TO ANALYTICAL CHEMISTRY.

BY LAURIE LORNE BURGESS AND OLIVER KAMM.

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A. Silver-Potassium Cobaltinitrites: A New Qualitative Test for Potassium.

The quantitative determination of the alkali metals has long been one of the most troublesome of analytical problems. In 1900, Adie and Wood[1] demonstrated the possibility of employing the cobaltinitrite method for potassium as a rapid and accurate volumetric process, and since that time much work has been done to bring it to perfection. The solution of this problem is of prime importance to agricultural chemists and consequently the activity in this field has been confined mainly to them. Notwithstanding a good deal of careful work, results obtained have proven far from satisfactory. For this reason we have undertaken a rather extensive theoretical study of the subject, hoping to overcome the difficulties now encountered in its application to analytical work. Our method of attack has been from the physico-chemical standpoint, for we believe that this problem will be solved only after having obtained a proper knowledge of the behavior of these complex substances when in solution. It was during the course of such an investigation that a series of new compounds was prepared, and it is the purpose of this article to recommend one of them as a new qualitative test for potassium.

In this preliminary paper we do not intend to give a historical review of the subject. It may be necessary, however, to mention the work of Drushel,[2] Bowser,[3] and Shedd,[4] all of whom have attempted to apply the dipotassium sodium cobaltinitrite, $K_2NaCo(NO_2)_6$, to the quantitative

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[1] *J. Chem. Soc.*, 77, 1076 (1900).

[2] *Am. J. Sci.*, 24, 433 (1907); 26, 329; 26, 555 (1908); *Chem. News*, 97, 124 (1908).

[3] *J. Ind. Eng. Chem.*, 1, 791 (1909); *Chem. News*, 101, 100 (1910); THIS JOURNAL, 32, 78 (1910).

[4] *J. Ind. Eng. Chem.*, 1, 302 (1909); 2, 379 (1910).

determination of potassium. The use of the same reaction as a qualitative test will be found described in most text-books on "Qualitative Analysis." Bray[1] has shown that the test is delicate enough to detect sixty parts of potassium per million, provided a large excess of reagent is used. Recently, Bowser[2] has increased its sensitiveness by precipitating in the presence of ethyl alcohol. A similar reaction, depending upon the formation of the tripotassium salt, $K_3Co(NO_2)_6$, is commonly used in the analytical laboratory for the detection of cobalt in the presence of nickel. As little as two parts of cobalt per million may be detected in this way. The method was originally proposed by Fischer[3] in 1848.

The reagent used in these qualitative tests is a solution of the sodium salt, $Na_3Co(NO_2)_6$, which may be prepared as described by Adie and Wood.[4] We have found it preferable, however, to use a solution of the pure substance, thus eliminating the large excess of sodium and cobaltous salts as well as acetic acid which, as will be shown later, interfere with the sensitiveness of the reagent. The pure sodium salt may be prepared by precipitation with ethyl alcohol as described by Cunningham and Perkin.[5] In the following experiments we have used a freshly prepared 25% solution of pure sodium cobaltinitrite.

When a drop of this reagent is added to a solution containing 1% of potassium, a yellow precipitate is formed immediately, which consists of tripotassium cobaltinitrite, $K_3Co(NO_2)_6$, or of the dipotassium salt, $K_2NaCo(NO_2)_6$, according to the amount of reagent used.[6] In the presence of silver ion, however, the corresponding silver salts are formed. The entire series is represented here.

$$Na_3Co(NO_2)_6 \longrightarrow Na_2KCo(NO_2)_6 \longrightarrow NaK_2Co(NO_2)_6 \longrightarrow K_3Co(NO_2)_6.$$
$$Ag_3Co(NO_2)_6 \longrightarrow Ag_2KCo(NO_2)_6 \longrightarrow AgK_2Co(NO_2)_6.$$

It would appear that as we replace sodium in the trisodium salt with potassium, we obtain less soluble substances. In the same manner if we replace sodium in the sodium-potassium derivatives, with silver, we obtain even less soluble salts—the silver-potassium cobaltinitrites. The delicacy of the latter reaction is shown by the following experiment: A drop of reagent added to a very dilute solution of potassium (less than 100 parts per million) produces no perceptible precipitate. If the test is repeated in the presence of 0.01 *N* silver nitrate, a copious yellow precipitate is formed immediately. In the absence of potassium nitrate but using the same concentration of silver as before, it is found that the

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[1] THIS JOURNAL, 31, 613–621–633 (1909).

[2] *Ibid.*, 33, 1566,1752 (1911).

[3] *Pogg. Ann.*, 74, 124 (1848).

[4] *Loc. cit.*

[5] *J. Chem. Soc.*, 95, 1562 (1909).

[6] *Ibid.* (See also Gilbert, "Inaugural Dissertation," Tübingen, 1898.)

trisilver and the silver-sodium salts are not precipitated. Because of this fact it is possible to use these silver-potassium cobaltinitrites as a delicate qualitative reaction for potassium. In applying the test, it is essential that the solution be neutral or only slightly acidified with acetic acid. Halogens may be removed by the addition of silver nitrate, a large enough excess being added so as to obtain approximately a 0.01 *N* solution. Interference due to the presence of other substances is discussed below.

In the usual scheme of analysis the test may be applied after the removal of the heavy metals. The filtrate from the latter is acidified with an excess of nitric acid, evaporated to dryness and the ammonium salts volatilized. The residue is extracted with water and the solution tested for potassium in the manner already described.

The silver-potassium cobaltinitrite precipitate is very insoluble, in fact, it serves to detect even less than one part of potassium per million. It comes down in a very finely divided condition, and examination under the microscope shows it to be amorphous. It exhibits a marked tendency to pass into the colloidal condition when washed with pure water but is coagulated by solutions of electrolytes. Alcohol serves the same purpose. The color of the precipitate varies from yellow to orange according to the conditions of the precipitation. Its composition also appears to be dependent upon these conditions; the larger the excess of silver present in the original solution the more will be found in the precipitate. There is also a slight tendency for sodium to be carried down; the nature and extent of this contamination is under investigation at the present time.

The delicacy of this qualitative test for potassium is shown by the following table. The fourth column represents approximately the time required for the decomposition of the precipitate, a phenomenon which accounts for the varying results obtained when determining the solubility of any cobaltinitrite. As would be expected, the precipitate is more stable in the presence of an increased volume of reagent.

TABLE I.

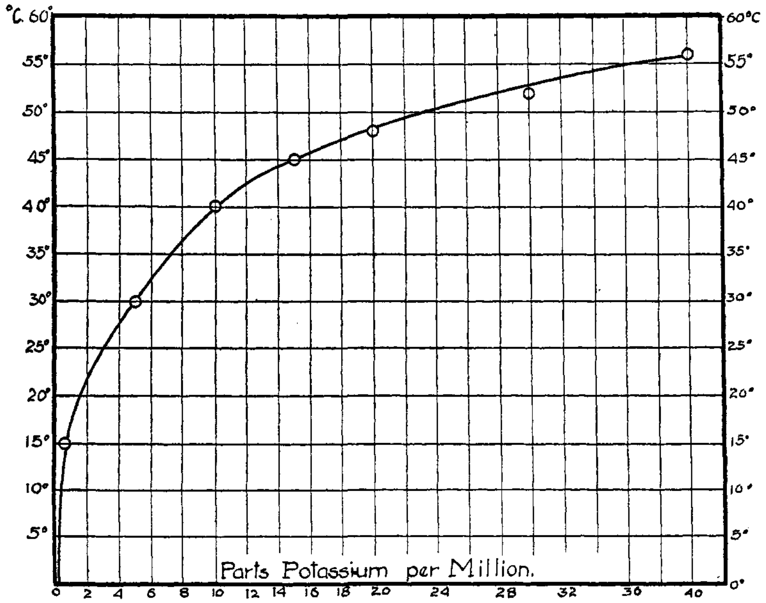
Parts potassium per million.	Vol. $Na_3Co(NO_2)_6$ used.	Precipitate appeared after.	Precipitate lasted.
3.0	1 drop	almost immediate	60 min.
2.0	1 drop	almost immediate	30 min.
1.0	1 drop	15 sec.	5 min.
0.5	0.5 cc.	2 min.	30 min.
0.2	1.0 cc.	turbidity after a few min.	

All of the above tests were made at a temperature of 15°, and the same concentration of silver nitrate (0.01 *N*) was used in every case.

It is thus seen that the silver-potassium cobaltinitrite precipitate serves as an extremely delicate qualitative reaction for potassium. Its advantages over the old method are: (1) It is more sensitive.[1] (2) The test may be made with the use of a single drop of reagent added to 100 cc. of the solution.

When a mere trace of potassium is to be detected, the temperature of the solution must be considered, because of the rapid decomposition of the complex ion, $Co(NO_2)_6^{---}$. The latter is very unstable in dilute solutions and its rate of decomposition increases rapidly with increasing temperature. For example, at 15° we may detect one-half part of potassium per million. At a temperature of 30°, however, the limit of sensitiveness is five parts per million, while above 40° no precipitate is obtained with ten parts, a single drop of reagent being used in each case.

The results of a series of experiments of this kind have been plotted, using the temperature as ordinate and the concentration of potassium as abscissa. The curve obtained represents graphically the effect of increasing temperature upon the delicacy of the test. The points on the curve represent the temperatures at which a known amount of potassium will just fail to produce a precipitate, the concentration of silver nitrate being 0.01 *N*. With the use of this curve we may make an approximate analysis of a solution containing potassium, by observing the temperature at which a temporary precipitate is formed. Only a few drops of



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[1] Although Bowser's modification is delicate enough to detect two parts of potassium per million, it possesses a distinct disadvantage in that no definit precipitate, but only a temporary turbidity, is formed in such dilute solutions.

reagent are added in order to avoid an excessive amount of sodium nitrite whose presence will interfere with the delicacy of the test. The explanation for this is given above.

The only substances interfering with this qualitative reaction for potassium are those that also interfere with the usual test in which the tripotassium salt is formed. Ammonia should be absent because it forms not only a triammonium salt[1] but also a less soluble salt containing silver. Rubidium, cesium, thallium, lead, and mercurous salts also interfere, as will be shown below. Barium forms sparingly soluble cobaltinitrites but the other alkaline earth metals do not. In concentrations below 0.1 *N*, barium will not interfere under the usual conditions.

In the dilute solutions used, sodium salts will not appreciably affect the delicacy of the test. When only a trace of potassium occurs in the presence of a tenth normal solution of sodium, the precipitate forms more slowly than usual, and it may be necessary to add a larger volume of reagent in order to secure complete precipitation. An increase in the amount of silver increases the delicacy of the test. Thus, any effect which is due to sodium may be counteracted by increasing the concentration of the silver. It is only when dealing with very dilute solutions of potassium, *i. e.*, ten parts per million or less, that the effect of the sodium or of the silver ion need be considered.

In general, an excess of reagent increases the sensitiveness of the test provided that there has been no decomposition of the cobaltinitrite. This decomposition takes place in accordance with the following reactions, resulting in the increase in the concentration of nitrite ion.

$$Co(NO_2)_6^{---} \rightleftarrows Co^{+++} + 6NO_2^-$$
$$Co^{+++} + NO_2^- \rightleftarrows Co^{++} + NO_2 \text{ (gas)}$$

The effect of the presence of a soluble nitrite, such as sodium nitrite, is to prevent the complete precipitation of the potassium. This is explained by the formation of the complex ion, $Ag(NO_2)_x$, with a consequent decrease in the concentration of silver ion. We have found that a certain definit concentration of the latter must be present in order to precipitate the silver-potassium salt from a solution containing a given concentration of potassium. Since the addition of a nitrite removes silver ion from solution, we can, by adding a sufficiently large amount of the former, decrease the concentration of the latter to such an extent that the silver-potassium salt will fail to be precipitated.

The following experiment will illustrate this point: When a drop of reagent is added to a 0.01 *N* solution of silver nitrate containing ten parts of potassium per million, an immediate precipitate is formed. If, however, the experiment is repeated in the presence of a 0.1 *N* solution

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[1] Erdmann, *J. prakt. Chem.*, 97, 404 (1866). Rosenheim and Koppel, *Z. anorg. Chem.*, 17, 35 (1898).

of sodium nitrite no immediate precipitate is obtained under the same conditions, *i. e.*, we have decreased the concentration of the silver ion to such a small value that not enough is present to produce a precipitate. If a larger amount of potassium is present, or if an increased volume of reagent is added, a precipitate will be obtained. This is exactly what the law of mass action would lead us to expect.

Another interesting point may be brought out here. The silver-cesium salt mentioned below is less soluble than the corresponding potassium salt. We would, therefore, expect it to be precipitated by a smaller concentration of silver ion than is needed to precipitate the potassium salt. This was actually found to be the case, *i. e.*, when enough sodium nitrite was added to prevent the precipitation of the potassium salt, an equivalent amount of cesium, rubidium or thallium was still precipitated because of the smaller concentration of silver ion necessary.

It may be suggested that the silver-potassium cobaltinitrites could be used as a delicate qualitative test for cobalt. They do not, however, offer any distinct advantage. The usual reaction, *i. e.*, the formation of $K_3Co(NO_2)_6$, is very sensitive, due to the large concentration of potassium salts which decreases the solubility of the precipitate.

B. Other Insoluble Salts in this Series.

The fact that potassium forms extremely insoluble cobaltinitrites led us to believe that other alkali metals would form similar silver salts. Considering the series Li, Na, K, Rb and Cs, in which the elements are arranged in the order of increasing atomic weights, we find that the lithium and sodium salts are very soluble while the potassium salts are rather insoluble. We would, therefore, expect the rubidium and cesium cobaltinitrites to be even less soluble, and Rosenbladt[1] has shown that this is the case. The following table shows the concentrations at which no precipitate was obtained when one drop of reagent was used. The results are, of course, only comparative, the test being more delicate when a larger volume of reagent is used.

TABLE II.

	Concentration necessary for precipitation.
K	100 to 150 parts per million
Rb	70 to 80 parts per million
Cs	70 to 80 parts per million
Tl	30 to 50 parts per million

Rubidium, cesium and thallium also form insoluble silver salts. Solutions of their salts so dilute that the reagent itself gives no precipitate readily form the characteristic insoluble yellow silver cobaltinitrites when in the presence of 0.01 *N* silver nitrate. They are all less soluble than the corresponding silver-potassium salts, and like the latter may

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[1] *Ber.*, 19, 2531 (1886).

readily be precipitated from solutions containing less than one part per million (temp. 15° C.).

Ammonium salts also form an insoluble silver-ammonium cobaltinitrite. The latter may be precipitated from solutions containing less than five parts of ammonia per million. This would serve as a delicate qualitative test for ammonia in the absence of potassium.

Silver, lead, and mercurous mercury all form cobaltinitrites. Of these the silver salt, $Ag_3Co(NO_2)_6$,[1] and the lead salt, $Pb_3[Co(NO_2)_6]_2$,[2] have been described in the literature, but we have not been able to find any reference to their double salts with the alkali metals. The mercurous cobaltinitrite, probably $Hg_3Co(NO_2)_6$, has not, as far as we know, been described. It appears to be the least soluble of all the simple salts of the cobaltinitrite series.

Some of the double salts in the lead series are the lead-ammonium, the lead-potassium, the lead-rubidium, the lead-cesium and the lead-thallium salts. All of them are more soluble than the corresponding silver derivatives, but are less soluble than are the simple cobaltinitrites. It may be interesting to note here that we have also prepared a lead-silver cobaltinitrite, which apparently stands intermediate between the lead and the silver series. It is less soluble than either the silver or the lead salt.

Rosenheim and Koppel[3] have prepared the barium salt, $Ba_3[Co(NO_2)_6]_2$. We have found that barium also forms a barium-silver salt. It is less soluble than the simple barium salt and may be precipitated from a tenth normal solution of barium provided the concentration of silver is more than 0.01 *N*. It decomposes more readily than any of the other cobaltinitrites studied.

The barium and lead salts mentioned above are very sensitive to the conditions of the precipitation, and their study may be of importance from this standpoint. They are crystallin in nature.

Cunningham and Perkin[3] have described certain cobaltinitrites containing organic radicles, such as the anilinocobaltinitrite, $(C_6H_5NH_3)_3$-$Co(NO_2)_6$. We have found the corresponding silver salts to be less soluble.

Summary.

1. New silver-potassium cobaltinitrites are described.

2. They are recommended as a delicate qualitative reaction for potassium. Directions for applying the test, its delicacy, and all interferences have been given in detail.

3. The corresponding silver salts with ammonium, rubidium, cesium,

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[1] Cunningham and Perkin, *loc. cit.*

[2] Rosenheim and Koppel, *loc. cit.*

[3] *Loc. cit.*

thallium and lead are mentioned, and the possible use of some of them in analytical work, indicated.

4. A corresponding series of double salts with lead and the alkali metals has been prepared.

In conclusion we wish to state that we are continuing the study of cobaltinitrites and their application to analytical work—particularly the application of the silver-potassium cobaltinitrites to the quantitative determination of potassium.

A COLORIMETER FOR RAPID WORK WITH WIDELY VARYING STANDARDS.

BY CHARLES H. WHITE.

The intensity of the color of a solution depends upon three elements, or factors. They are the quantity of coloring matter used, the volume of the solvent in which it is held, and the thickness of the solution through which the light passes before entering the eye. It is well known that if we keep two of these quantities constant and vary the third in a determinate way until two solutions are alike in color, we can estimate the quantity of coloring matter in one, if the quantity in the other is known. These three variables form the basis of the three classes of methods in colorimetry, and of the three types of colorimeters. When two solutions are brought to agreement in color by the addition of coloring matter to one, the amount added is the measure of that in the other. If the agreement is effected by dilution, the coloring matter is then proportional to the volumes. If they are brought to equality by changing the thickness of the sections observed, the quantity of coloring matter is then inversely proportional to the measurements of these sections.

This instrument is a modification of a colorimeter devised by the writer for the determination of carbon in steel.[1] With it comparisons are made by the third method; that is, the thickness of the section of solution examined is the variable. It consists essentially of two wedge-shaped hollow glass prisms of exactly equal dimensions and open at the large end for the introduction of the solutions to be tested. The wedges are held in a vertical position side by side in a camera and may be raised or lowered by rack and pinion actuated by thumb screws. The prisms are screened from view on the side towards the operator except for a narrow horizontal slit across the middle of the camera through which the solutions are observed when a test is being made. The carriers are graduated to correspond to the length of the wedges, the zero of the scale being opposit the index when the sharp edge of the wedge is opposit the narrow opening in the screen through which the color is observed. The screens are

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[1] *Trans. Am. Inst. Min. Eng.*, 38, 559–564.