

taining any  $\text{HNO}_3$ ),  $\text{H}_2\text{S}$  was passed through for 15 minutes, the mixture heated to boiling, the liquid decanted through a filter, and  $\text{AgNO}_3$  added: a precipitate of  $\text{AgBr}$  resulted which was apparently nearly as large as the amount taken. The residue from the  $\text{H}_2\text{S}$  treatment was washed and heated with  $\text{HNO}_3$  (1.20): the residue (of  $\text{AgBr}$  and  $\text{S}$ ) was less than one-fifth of the amount taken.

P. 119. *Delicacy of the Sulfite and Thiosulfate Tests.*—2 mg.  $\text{SO}_3$  as  $\text{Na}_2\text{SO}_3$  were dissolved in 8 cc. water and 2 cc. 10%  $\text{Na}_2\text{CO}_3$ ; 3 cc. 10%  $\text{Sr}(\text{NO}_3)_2$  solution were added, the mixture was acidified with acetic acid and the clear solution heated to boiling: a finely divided precipitate separated at once. After 15 minutes this was filtered off and treated as described in the Procedure: the precipitate of  $\text{BaSO}_4$  was distinct within 5 minutes after adding the bromine. The experiment was repeated twice with 1 mg.  $\text{SO}_3$  as  $\text{Na}_2\text{SO}_3$ : in each case the clear solution became slightly turbid on boiling, and a small but distinct confirmatory test was obtained. The experiment was repeated several times in the absence of sulfite: the solutions remained clear on boiling. In some cases a flocculent precipitate of  $\text{SrCO}_3$  formed while the mixture was being heated, but it dissolved on the addition of two or three drops of acetic acid.

Solutions containing 3 mg.  $\text{S}_2\text{O}_3$  as  $\text{Na}_2\text{S}_2\text{O}_3$  in 8 cc. water and 2 cc. 10%  $\text{Na}_2\text{CO}_3$  were treated as described in the preceding paragraph. To the resulting clear solutions were added 2 cc.  $\text{HCl}$  (1.20), and the mixtures were heated to boiling and allowed to stand: white precipitates of sulfur usually appeared within half an hour. The experiment was repeated twice with 2 mg.  $\text{S}_2\text{O}_3$ ; the solutions remained clear for about three hours, but were distinctly turbid in four hours. The experiment was repeated twice with 1 mg.  $\text{S}_2\text{O}_3$ : the solutions appeared to be nearly clear on standing over night, but became turbid when the mixtures were then shaken and allowed to stand half an hour longer. These experiments were repeated with an excess of 8 cc.  $\text{HCl}$  (1.20) instead of 2 cc.: in an experiment with 3 mg.  $\text{S}_2\text{O}_3$  the solution was clear after 1 hour, but became turbid over night, while in the experiments with 2 and 1 mg. no precipitates formed even on standing 24 hours. This shows that a large excess of acid interferes with the test.

To 1 mg.  $\text{S}_2\text{O}_3$  as  $\text{Na}_2\text{S}_2\text{O}_3$  dissolved in 10 cc. water were added 2 cc.  $\text{HCl}$  (1.12); the mixture was heated to boiling and allowed to stand: there was a small but distinct turbidity in half an hour which increased on standing.

*Effect of Excess of Acetic Acid on the Thiosulfate Test.*—100 mg.  $\text{S}_2\text{O}_3$  as  $\text{Na}_2\text{S}_2\text{O}_3$  in 8 cc. water and 2 cc. 10%  $\text{Na}_2\text{CO}_3$  solution were tested for sulfite by the process described in the preceding section: the solution remained clear on boiling. The experiment was repeated, except that an excess of 5 cc. 30% acetic acid was added: the solution became turbid when it was boiled, but the small sulfur precipitate did not increase in amount when the mixture was set aside at room temperature. The experiment was repeated with an excess of only 1 cc. 30% acetic acid: a faint turbidity appeared when the mixture was boiled; the mixture was slightly turbid after 1 hour, but was clear after three hours.

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[CONTRIBUTION FROM THE INSTITUTE OF ANIMAL NUTRITION OF THE PENNSYLVANIA STATE COLLEGE.]

## ADIABATIC DEVICE FOR BOMB CALORIMETER.

By J. A. FRIES.

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The value of an adiabatic equipment to a bomb calorimeter lies in the fact that such a device, if only simple enough, may be a means both of saving time and of greater accuracy in determining the heat of com-

bustion. It does away with much tedious computation, and the correct temperature of the calorimeter before and after a combustion is more readily obtained.

Adiabatic devices differing in principles have been described by Richards, Henderson and Trevert,<sup>1</sup> and Benedict and Higgins,<sup>2</sup> but since these, however valuable in themselves, are not made so as to be easily adjusted to bomb calorimeters that are already installed and in use, a simpler device was sought for to fill that want.

The problem was satisfactorily solved by applying to the bomb calorimeter the same principle which is used in the respiration calorimeter according to Atwater and Rosa. Any bomb calorimeter of the Atwater-Berthelot type can be made adiabatic without much expense by a simple device.

The materials which were used in the construction of the apparatus were such as could be picked up around the laboratory. Hence it is not so much the material as the principle which I want to emphasize.

The following is a description of the arrangement for making the bomb calorimeter adiabatic:

*Heating Device.*—This consists of a German silver wire about 3.5 meters long and 0.8 mm. in diameter, having a total resistance of about 6.1 ohms. This wire was strung through small brass eyelets screwed directly into the inner insulating fiber jacket of the modified Atwater-Berthelot bomb calorimeter which we are using. The eyelets were so arranged that there was one coil of wire near the bottom a little distance from the sides, the rest of the wire then going up and down along the sides making eight loops spaced as evenly as convenient and coming to within 30 mm. of the top of the inner fiber jacket. The two ends were fastened to insulated copper wire and brought out through the side of the fiber jackets. It was wired in this fashion in order to avoid any induction by the current. Both direct and alternating currents have been tried. At present we use only alternating current. The current which suits this particular wire, or resistance, and which will give the heat needed quickly enough is taken from a 110 volt circuit through five 32 c. p. carbon filament lamps in parallel. The distance between heating wire and fiber vessel is about 6 mm. on the average, leaving 15 to 20 mm. between wire and calorimeter.

With this device alone, however, it was found impossible to measure the true rise in temperature of the air quickly enough by means of mercury thermometers to make possible any use of it in connection with the heat measurements.

*Air Thermometer.*—Mercury thermometers being found useless for

<sup>1</sup> *Proc. Amer. Acad. Arts and Sci.*, 42, No. 21 (March, 1907).

<sup>2</sup> *THIS JOURNAL*, 32, 461 (1910).

measuring the air temperature, and electric thermometers being difficult and costly to instal, it was finally decided to use an air thermometer. Besides securing a quick registration of the resulting rise in temperature, it was also necessary to provide some way to regulate the heating effect upon the calorimeter and make it uniform. To use any kind of blower would complicate matters, but the problem was solved by placing the calorimeter inside a double walled copper jacket which constitutes the bulb of the air thermometer.

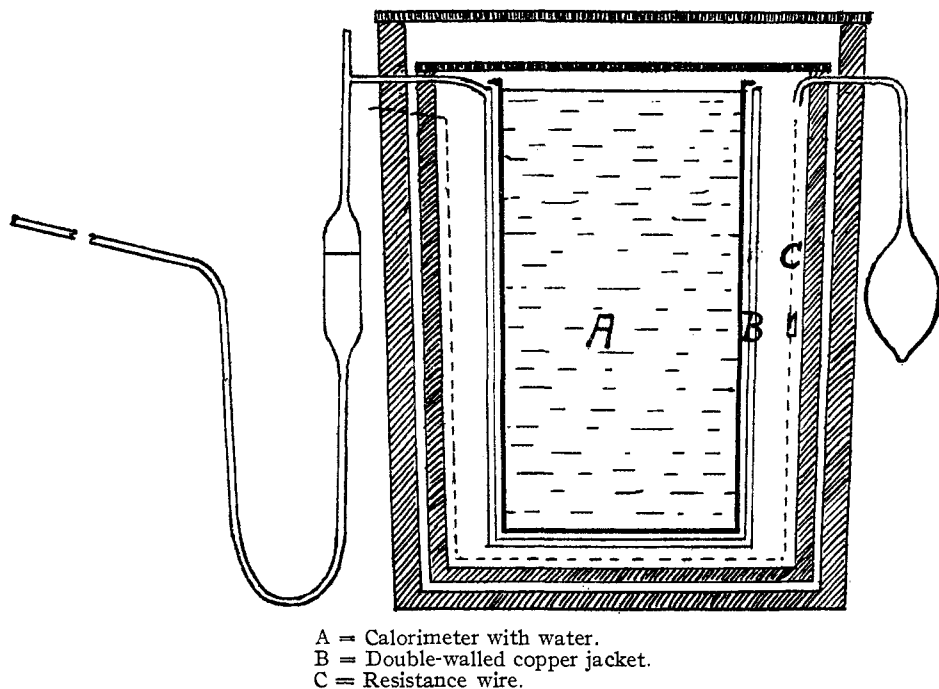
*Copper Jacket.*—This double walled cylindrical copper jacket was made of polished sheet copper about 0.25 mm. thick and has a 4 mm. air space between the walls and bottoms. In the bottoms there are three holes through which project three screw heads on which the calorimeter rests. The diameter of this jacket is such that when the calorimeter is in place there is an air space of about 4 mm. between the calorimeter and copper at the sides and 5 mm. at the bottom, and the upper edge of the copper is on the same level as the upper edge of the calorimeter. The copper jacket rests on three corks and is held in position by corks at the sides, and the calorimeter is kept in its position within the jacket by means of a few pasteboard blocks glued on the sides of the copper. Care must be taken that the different metals do not touch at any point.<sup>1</sup> At the upper edge a small brass tube is soldered into the copper and connected by good rubber to a piece coming through the fiber walls from the outside. When this air-tight jacket has once been placed in position, it remains as a permanent part of the apparatus.

*Tube and Water Reservoir.*—The thermometer consists, besides the copper jacket, of a glass tube, bore about 2 mm., which is placed at an angle of about 14 degrees. It is bent in U shape at the end near the jacket and from the bend to the extremity is 85 cm. long. The tube is supported against a fixed strip of wood, which also serves as a support for the calibrated paper scale. Between the brass tube coming from the apparatus and the end of the glass tube, the bulb of a 25 cc. pipet is inserted. This pipet bulb serves as a reservoir for the water (colored with litmus) which serves as the indicating column, and the total water in the system should not be quite sufficient to fill the bulb. This is to prevent the water from being drawn into the jacket should the temperature ever go below the range of the thermometer.

With the copper jacket and tube, as described, one degree change in temperature equals 12.5 cm. on the glass tube. This was considered sensitive enough, although the air thermometer can be made more or

<sup>1</sup> It may be stated that in order to make it convenient to lower the calorimeter filled with water into the copper jacket a depression is made on each side at the upper edge of the jacket so that the fingers can grip conveniently over the edge of the calorimeter when handled.

less sensitive by using a smaller or larger bore tube, or by placing it at a different angle.



*Calibration of the Air Thermometer.*—This air thermometer is sensitive both to heat and barometric pressure, but since the latter rarely changes materially during the short time required for a heat determination no correction for pressure is necessary.

In order, however, to provide for the use of the full range of the Beckmann thermometer the glass tube must be a little longer than is needed for the given number of degrees, so as to allow for some changes in the atmospheric pressure. Should the barometric pressure change considerably during the day the air thermometer can be adjusted to the existing temperature and pressure conditions in a moment by opening the air valve on the brass pipe just outside the fiber jacket. The amount of water in the tube should be such that when the air valve is open the water column stands a little above the bend of the tube. To prepare the scale representing centigrade degrees a good mercury thermometer on which  $0.01^{\circ}$  can be estimated by aid of a lens is placed in the copper jacket, the covers are put on, and the apparatus allowed to stand until the conditions have reached constancy. The air valve is then closed, the thermometer lifted up and read and the position of the water column marked.

Heat is then applied by means of the electric current and the water column is kept constant at another point until the mercury thermometer standing in the copper jacket has reached a maximum. This point is marked and the corresponding rise in temperature of the jacket is noted. This operation is repeated until a sufficient number of points have been established to permit the making of the scale which should be graduated at least to  $0.1^{\circ}$ . If the calibration is extended over considerable periods of time during unsettled weather conditions, the barometric pressure should be noted and corrected for, if necessary.

Being affected by two factors, heat and pressure, a fixed scale is of no value, a movable one must be used, one that can be set to any point within several degrees. In order to have the degrees of equal length upon the tube, care must be taken in selecting one having a uniform bore.

*Sensitiveness.*—The long space on the scale equal to a tenth of a degree makes it easy to estimate to a hundredth of a degree by the naked eye at some little distance away. The heating effect of the electric current, previously referred to, may be seen from the following table which gives the time of the current in seconds, and the rise in temperature of the air thermometer at different intervals. These results may vary somewhat with the temperature condition of fiber jackets and surrounding air, as well as with changes in voltage.

TABLE I.

Current in seconds.	Rise in temperature in		
	30 seconds. °C.	1 minute. °C.	Total. °C.
20	0.28	0.58	0.76
25	0.35	0.78	1.05
30	0.52	0.95	1.35
35	0.52	1.17	1.63
40	0.52	1.37	1.81
45	0.52	1.58	2.00

In about  $1\frac{1}{2}$  minutes after the current is off, the water column has practically ceased to rise and in 3 to 4 minutes the maximum rise is reached. Here it remains constant for some minutes before it begins to fall again, so that unless one wishes to take the readings of the calorimeter temperature for a longer period than 3 or 4 minutes after the maximum has been reached, it is not necessary to hold the temperature of the air thermometer constant by further short contacts.

When a charge is ignited in the bomb, the Beckmann thermometer will begin to show a rise in 10 seconds, increasing so that the most rapid rise is between 30 and 60 seconds after ignition. In 30 seconds after ignition of a substance in the bomb the heat from the calorimeter is beginning to show on the air thermometer.

The air thermometer begins to show the effect of the heating current in less than 8 seconds, and sooner when the air between copper and fiber jacket is stirred by means of a rubber bulb. The effect which this heating has upon the calorimeter may be seen from the following observations, giving the change in calorimeter temperature per minute which took place during a given period of time with a given difference between the average of the air and calorimeter thermometers.

During these tests the calorimeter contained the bomb and 2000 grams of water, which was stirred as during a heat determination.

TABLE II.—TEMPERATURE VARIATIONS IN CALORIMETER DUE TO DIFFERENCE BETWEEN ITS TEMPERATURE AND THE SURROUNDING AIR TEMPERATURE.

Minutes.	Temperature of calorimeter water.	Average of air thermometer.	Difference.	Change in calorimeter temperature per minute.
1st to 4th	24.182°	24.40°	0.22°	0°
5th to 11th	24.190	24.97	0.78	+0.0025
12th to 16th	24.207	25.25	1.04	+0.0035
1st to 9th	24.086	23.96	-0.13	-0.0008
10th to 13th	24.080	24.00	-0.08	-0.0004
14th to 5th	26.040	25.20	-0.84	-0.0050
6th to 8th	26.023	25.73	-0.29	-0.0035
9th to 14th	26.017	25.96	-0.06	-0.0008

In these short tests the temperature of the calorimeter was about 0.5° above that of the fiber jackets in the case of the first five, and about 2.5° above in the last three.

From the foregoing figures we see that with the air thermometer 0.22° above that of the calorimeter no change was observed in the calorimeter temperature during four minutes. When heat was applied so that the air thermometer registered 0.78° on an average more than the calorimeter temperature there was a rise of 0.0025° per minute, etc. On the other hand we see a drop in the temperature of the calorimeter when the air thermometer was allowed to fall below that of the calorimeter. At the upper limit of the scale and with the abnormally great difference in temperature between the calorimeter and fiber jackets the drop in the calorimeter temperature was relatively somewhat greater than in the first cases.

*Tests of the Apparatus.*—The purpose of the adiabatic device is to prevent loss of heat from the calorimeter when its temperature is raised above that of the surrounding media during a determination. A test, therefore, of the efficiency of the arrangement would be to be able, by the use of it, to hold the calorimeter temperature constant when it is higher than the room temperature and that of the rest of the apparatus.

Of the three tests of longer duration given below, one (a) was made near the upper limit of the scale, with a difference of about 1.5° between the calorimeter and the rest of the apparatus. In another trial (b),

near the lower limit of the scale, there was a difference of about  $0.5^{\circ}$  between the calorimeter contents and the fiber jackets and covers. A third trial (*c*) is given in which the temperature of the bomb contents was adjusted practically to that of the room and the rest of the apparatus. In this case no heat was applied, the water being stirred as in a determination of heat of combustion. Under these conditions there should be no change in the temperature anywhere. Having no automatic heat regulator in the room, perfect test conditions could not be obtained but they were sufficiently so for our purpose.

TABLE III.

Minutes.	(a)		(b)		(c)	
	Calorimeter temperature.	Air thermometer.	Calorimeter temperature.	Air thermometer.	Calorimeter temperature.	Air thermometer.
1st	25.189 <sup>o</sup>	25.35 <sup>o</sup>	21.358 <sup>o</sup>	21.47	21.491 <sup>o</sup>	21.48 <sup>o</sup>
3rd	25.189	25.34	21.358	21.47	21.491	21.48
5th	25.189	25.34	21.358	21.47	21.491	21.49
7th	25.189	25.34	21.358	21.47	21.491	21.49
9th	25.190	25.33	21.359	21.47	21.491	21.49
11th	25.190	25.30	21.358	21.44	21.492	21.49
13th	25.190	25.29	21.357	21.46	21.492	21.49
15th	25.190	25.29	21.357	21.46	21.493	21.49
17th	25.190	25.28	21.357	21.47	21.493	21.49
19th	....	...	21.357	21.48	....	...
21st	....	...	21.357	21.49	....	...
24th	....	...	21.357	21.50	....	...

In (*a*) and (*b*) of the above tests the calorimeter and its contents were warmer than the rest of the apparatus when placed in position. After being placed in position and the stirrer started the heat was applied gradually until the air thermometer registered as noted in the table.

At the beginning of test (*a*) when the air thermometer registered  $0.16^{\circ}$  above that of the calorimeter the temperature of the latter remained constant for 5 minutes. After that there was a tendency of the calorimeter temperature to rise, but it remained constant when the difference in temperature was gradually falling, until at the end of the test it was but  $0.10^{\circ}$ . With a difference of  $0.11^{\circ}$  in the beginning of test (*b*) the temperature of the calorimeter remained constant for 9 minutes. Only a slight cooling of the air caused a drop in the calorimeter temperature, but with a difference of  $0.13^{\circ}$  the temperature again remained constant.

The fact that it is necessary to have the air thermometer read  $0.10$ – $0.16^{\circ}$  higher than the calorimeter in order to keep the latter at a constant temperature may be ascribed to the fact that there is a constant radiation of heat from the water surface and top of the calorimeter to the colder air and covers. It being impracticable to extend the copper jacket over the top, extra heat must be supplied through the sides and bottom of

the calorimeter to compensate for the loss of heat at the top and keep the whole system in equilibrium.

This necessary difference in temperature will no doubt vary with each instrument while, as the foregoing results show, and as would be expected, it is greater the greater the excess of the calorimeter temperature is over that of the surroundings. When working under uniform conditions, a little experience will soon show what excess is necessary.

In test (c) of Table III, no heat was applied, but the water in the calorimeter was stirred as during the other tests. After the fourth minute the air thermometer remained constant, but the calorimeter temperature rose  $0.002^\circ$  in 17 minutes. This slight rise in the calorimeter temperature can only be ascribed to one of two causes. It must either be due to heat generated by the stirrer or else due to increase in barometric pressure affecting the reading of the air thermometer. The writer inclines to the latter explanation, although during these tests the weather was rainy and, hence, there is a possibility that the heat produced by friction of the stirrer may have exceeded the loss of heat due to evaporation of water, which under ordinary winter conditions, judging from common observations only, appears to exceed that produced by friction of the stirrer.

*Rise in Temperature Due to Combustion.*—For the particular bomb calorimeter in question the rise in temperature due to a definite number of calories generated in the bomb may be seen in the following table:

TABLE IV.—RISE IN CALORIMETER TEMPERATURE WHEN HEAT IS GENERATED IN THE BOMB.

Heat generated. Calories.	Rise first minute.	Total rise.
5000	$1.60^\circ$	$2.06^\circ$
4500	1.35	1.86
4000	1.10	1.65
2000	0.56	0.80

The rise in temperature during the first minute may vary slightly according to the nature of the substance ignited.

*Manipulation.*—While the bomb is gotten ready for a determination, both covers of the apparatus are kept in position and a good mercury thermometer is allowed to stand in the copper jacket. When the bomb has been charged with oxygen, and the necessary amount of water, a little warmer than the apparatus, has been put in the calorimeter, the air valve is closed, the temperature of the air in the apparatus is taken, and the scale set so that the end of the water column will indicate that temperature. The covers are now removed, calorimeter and bomb placed in position and stirrer started. After a couple of minutes raise the air thermometer readings, by making short contacts, to  $0.10^\circ$  to  $0.15^\circ$  above the reading of the Beckmann thermometer in the calorimeter



water. Take a reading or two to be sure that the calorimeter temperature remains constant. Ignite the charge and at the same time close the switch on the heating circuit.

The length of time during which the current should be on depends upon the amount of heat generated in the bomb. If, for instance, we expect about 4500 calories, a glance at Table IV shows that the total rise in temperature will be  $1.86^{\circ}$  and about  $1.35^{\circ}$  at the end of the first minute. From Table I we see that the current on for 40 seconds with perhaps one or two additional short contacts will meet the conditions. Whether the total current should be on continuously for that length of time, or whether under any conditions it would be of advantage to make shorter contacts with some seconds of time between, experience will soon decide.

Readings of the thermometers are taken as usual every minute. The maximum temperature will be obtained in from 3 to 5 minutes according to the charge. In most cases 4 minutes decides the maximum rise, but a couple more readings should be taken to make sure that the temperature is constant.

*Computation.*—The computations are much simplified by this method of determination. Only the reading of the Beckmann thermometer taken at the time of ignition and the maximum reading after ignition, usually at the fourth minute, receive the thermometer corrections. The true temperature difference is multiplied by the water equivalent of the apparatus, and from this product is subtracted the heat due to the iron wire or other material used for ignition and the acid formed during the combustion.

*Cooling the Apparatus for the Next Determination.*—As determinations are usually made with the bomb calorimeter, considerable time elapses between the ignitions, and the copper jacket and air wall acquire the room temperature without any further attention. To hasten the lowering of the temperature, a small toy fan, 5 inches in diameter, and driven by 2 to 3 dry batteries, can be placed above the apparatus for a few minutes, or a beaker or other vessel with cold water may be set down in the copper jacket for a little while. The covers are then put on, the mercury thermometer replaced and the apparatus allowed to stand to be ready for the next determination.

*Energy Determinations Influenced by Air Temperature.*—The following table gives the difference in temperature between the calorimeter and the surrounding air space at different times during the determination and also the results obtained for the heat of combustion of benzoic acid.

These four determinations show a range of air temperature conditions within which it is easy to keep the apparatus and the results come practically within the limit of analytical error, the theoretical value of benzoic

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 COBALTNITRITES AND THEIR APPLICATION TO ANALYTICAL CHEMISTRY.**

BY LAURIE LORNE BURGESS AND OLIVER KAMM.

Received March 5, 1912.

**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<sup>1</sup> 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,<sup>2</sup> Bowser,<sup>3</sup> and Shedd,<sup>4</sup> all of whom have attempted to apply the dipotassium sodium cobaltinitrite,  $K_2NaCo(NO_2)_6$ , to the quantitative

<sup>1</sup> *J. Chem. Soc.*, 77, 1076 (1900).

<sup>2</sup> *Am. J. Sci.*, 24, 433 (1907); 26, 329; 26, 555 (1908); *Chem. News*, 97, 124 (1908).

<sup>3</sup> *J. Ind. Eng. Chem.*, 1, 791 (1909); *Chem. News*, 101, 100 (1910); *THIS JOURNAL*, 32, 78 (1910).

<sup>4</sup> *J. Ind. Eng. Chem.*, 1, 302 (1909); 2, 379 (1910).