

## Detection of Cobalt (II) by Succinimide and Isopropylamine<sup>1</sup>

FRANK J. WELCHER and JOHN A. BUEHLER, Indiana University  
and Anderson College.

Analytical chemists are constantly seeking to find new reagents that will be specific for particular metallic ions. In searching the literature one finds numerous reports where the metallic ions have been used to detect and determine organic compounds of a specific type.

Thus, in 1933, Koppanyi and coworkers (1) reported that barbiturates could be detected by forming a colored complex with cobalt (II) in the presence of isopropylamine, using chloroform and methyl alcohol as solvents. The test was claimed to be specific for barbiturates with the exception of creatinine and theobromine. A reddish-violet color developed and was used to prove the presence of barbiturates in urine. Koppanyi continued to study the reaction and found that all barbiturates that were tested, ten in number, gave the test (2). However, it was soon discovered that many other structures gave the test, and that other bases could be used in place of isopropylamine, such as sodium hydroxide, lithium hydroxide, barium hydroxide, isobutylamine, and ammonia (3, 4, 5,6). Further studies showed that compounds containing an imide group in a cyclic structure gave the test.

The authors considered the possibility of using one of the barbiturates or imides to detect cobalt in aqueous solutions, rather than in organic liquids, since the usefulness of the test could thereby be greatly extended.

Several organic reagents such as, phenylethylbarbiturate, isoamyl-ethylbarbiturate, diethylbarbiturate, phthalimide and succinimide were studied. It was found that the barbiturates were too insoluble in water to form solutions of sufficient concentrations to give the color reaction with cobalt. Phthalimide was also too insoluble. Previous work was carried out in organic solvents, and it appears that the complex is more stable and shows less tendency to dissociate than in a water medium. In order to obtain the color, a large excess of one of the reagents is required. Succinimide was finally chosen, since it is very soluble in water, and a one molar solution could be easily prepared. The test was carried out in the presence of the ions listed in Table I.

<sup>1</sup> 1. Contribution No. 699 from the Chemistry Department of Indiana University.

TABLE I

Ion	Color without Cobalt (II) in solution	Color with Cobalt (II) in solution
Silver (I)	colorless	violet
Mercury (I)	slightly gray	violet
Lead (II)	colorless	violet
Arsenic (III)	colorless	violet
Antimony (III)	colorless	violet
Tin (II)	colorless	violet
Mercury (II)	colorless	violet
Bismuth (III)	colorless	violet
Copper (II)	blue	blue
Cadmium (II)	colorless	violet
Aluminum (III)	colorless	violet
Iron (III)	reddish-brown	brown
Chromium (III)	gray-green	gray
Manganese (II)	slightly brown	violet
Nickel (II)	pale green	violet
Cobalt (II)	reddish-violet to bluish-purple	
Zinc (II)	colorless	violet
Calcium (II)	colorless	violet
Strontium (II)	colorless	violet
Barium (II)	colorless	violet
Magnesium (II)	colorless	violet
Sodium (I)	colorless	violet
Potassium (I)	colorless	violet
Ammonium	colorless	violet

In addition to the cations commonly included in the classical qualitative scheme of analysis, a large number of less common cations were also tested. The results are shown in table II.

TABLE II

Ions	Color Without Cobalt (II) in Solution	Color With Cobalt (II) in Solution
Cesium (I)	colorless	violet
Rubidium (I)	colorless	violet
Scandium (III)	colorless	violet
Yttrium (III)	colorless	violet
Lanthanum (III)	colorless	violet
Cerium (III)	colorless	violet
Neodymium (III)	colorless	violet
Ruthenium (III)	colorless	violet

TABLE II—(Continued)

Ions	Color Without Cobalt (II) in Solution	Color With Cobalt (II) in Solution
Palladium (II)	colorless	violet
Rhodium (III)	pink	violet
Osmium (IV)	colorless	violet
Iridium (IV)	colorless	violet
Platinum (IV)	colorless	violet
Indium (IV)	colorless	violet
Germanium (IV)	colorless	violet
Titanium (IV)	colorless	violet
Gold (III)	yellow	bluish

The test was also tried with a number of anions as shown in Table III.

TABLE III

Anions	Color Without Cobalt (II) in Solution	Color With Cobalt (II) in Solution
Chloride	colorless	violet
Bromide	colorless	violet
Iodide	colorless	violet
Fluoride	colorless	violet
Thiocyanate	colorless	violet
Thiosulfate	colorless	violet
Sulfate	colorless	violet
Sulfite	colorless	violet
Phosphate	colorless	violet
Arsenate	colorless	violet
Tungstate	colorless	violet
Chromate	yellow	brown
Oxalate	colorless	violet
Carbonate	colorless	violet
Borate	colorless	violet
Silicate	colorless	violet
Chlorate	colorless	violet
Nitrate	colorless	violet
Nitrite	colorless	violet
Acetate	colorless	violet
Tartrate	colorless	violet
Citrate	colorless	colorless
Ferrocyanide	pale yellow	dark brown
Ferricyanide	green-yellow	brown

The only cations that seriously interfere with the test are copper (II), iron (III), and chromium (III). Copper can be removed by adding granulated zinc, and a good test for cobalt obtained in the presence of the deposited copper metal. Interference by the ferric ion is eliminated by adding a large excess of potassium fluoride to form the hexafluoroferrate complex. Cobalt can be detected in a solution that contains iron in the form of the fluoride complex. The only ion that seriously interferes is chromium. If chromium is present, the cobalt test is applied at the point in the qualitative scheme of analysis where both cobalt and nickel sulfides are dissolved in aqua regia and separate tests made for nickel and cobalt ions. Cobalt may be detected in the presence of nickel by this method with good results.

It appears that there are four anions that interfere with the test for cobalt; these are, citrate, chromate, ferricyanide, and ferrocyanide. The citrate, ferro- and ferricyanides may be removed by oxidation and the chromate reduced with formaldehyde.

#### Procedure

The concentrations of all solutions used were 10 milligrams of the ion to be tested per milliliter.

Add 0.25 ml of the solution to be tested to a spot plate. Then add 0.5 ml of a one molar succinimide solution, and finally 0.05 ml of isopropylamine. If cobalt is present, a reddish-violet or bluish purple color develops.

In the presence of copper proceed as follows: Add several grains of granulated zinc and shake the mixture until the copper color of the solution disappears. Test a few drops of the solution with ammonium hydroxide, if the solution remains colorless when ammonium hydroxide is added then proceed with the test for cobalt.

In the presence of iron proceed as follows: Add a large excess of potassium fluoride (solid) until the yellowish-brown color of the ferric ion disappears. Then proceed with the test for cobalt.

#### Sensitivity

The lower limit of sensitivity seems to be a solution that contains 0.5 milligrams of the cobalt ion per milliliter, provided the final volume of the solution after the test is completed is no more than one milliliter. In order to obtain a distinct test, the final concentration of the cobalt ion after the test reagents are added should not be less than 0.125 mg/ml.

The sensitivity of the test was determined in the presence of several ions that have color. Table IV shows the results of this study.

TABLE IV

Ion	Final Conc. in mg/ml of the ion.	Final Conc. in mg/ml of the Cobalt ion.
Nickel (II)	.25	0.5
Manganese (II)	2.5	0.5
Bismuth (III)	2.5	0.125

The results in Table IV show that the ions which do not contribute color have no effect on the sensitivity of the test. Ions like nickel and manganese decrease the sensitivity of the color and therefore require a higher concentration of cobalt before a positive test is obtained for cobalt.

### Conclusion

Although this test is not as sensitive as many that have been used, it does permit the detection of cobalt in the presence of fifty-eight different cations and anions without the necessity of difficult and time consuming separations. In fact, the test appears to be specific under the conditions given.

The authors believe that a new color reaction has been introduced for cobalt (II) that is suitable for the detection of cobalt in the presence of most of the cations commonly detected in the classical scheme of qualitative analysis. Of the ions in this classical scheme only one ion interferes, but this difficulty may be overcome by testing for cobalt at the position in the scheme where nickel and cobalt are usually tested. The authors have used this test with their students and obtained excellent results. It is quick, serves as an excellent spot test, and is relatively inexpensive.

The authors are currently exploring the possibility that this test may serve as a useful quantitative determination for cobalt.

### References

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