

THE SEPARATION OF THE IONS OF COPPER, COBALT, NICKEL AND CADMIUM

John A. Froemke, Homer Stensrud, and Melvin Tschetter
Augustana College, Sioux Falls

INTRODUCTION

Better methods of separating ions as well as more definite confirmatory tests are sought by analysts. Much attention has been and is being given to the problem of replacing hydrogen sulfide in the laboratory. Although numerous other reagents have been suggested, this reagent still is in universal favor. First suggested by Fresenius (1) it is thought of as the general separatory reagent. None among the now numerous new schemes of separation has successfully replaced the Fresenius method.

In this paper the authors can list only a few of the new reagents which are being tried with more or less success. No attempt is made to discuss the few listed in the next paragraph, nor the large number which have been omitted.

The authors shall list these few as general representative non-hydrogen sulfide reagents: ammonium sulfide (2), ammonium phosphate with pyridine (3), and sodium benzoate with sodium fluoride (4). It is true that these methods eliminate the use of hydrogen sulfide, but they may introduce other objectionable features.

Froemke and his collaborators (5) reported that the identification of copper in the presence of cobalt, nickel and cadmium, as suggested in some of the newer schemes of analysis, was very difficult. They maintained that a more suitable means of separation and identification must be found, if some of these schemes of analysis were to replace the classical Fresenius method.

In the classical scheme of analysis, copper and cadmium are precipitated from an acid solution, while nickel and cobalt are precipitated in a basic solution. This cannot be done in the particular scheme under discussion. Here the copper is to be separated by first reducing it with the sulfite ion; then precipitating it with the thiocyanate ion. Final identification is made with potassium ferrocyanide or ammonium hydroxide. The results in the laboratory were rather disappointing; the method as outlined above cannot be recommended.

Since the non-hydrogen sulfide method offers advantages in the laboratory, the authors deemed it advisable to seek a better method of separating these particular ions. They began a systematic study of the properties of the ions and their compounds. Careful attention was given to the following: (a) the common inorganic compounds, (b) the solubility products of the general insoluble compounds (Table I), (c) the in-

stability constants of their complex ions, and (d) compounds formed with general qualitative and quantitative organic reagents.

TABLE I
THE SOLUBILITY PRODUCTS OF THE SULFIDES OF COPPER, CADMIUM, COBALT AND NICKEL

Compound	Solubility Product	Ratio ¹ copper to other ions	Reference
CuS	4×10^{-38}		6
CuS	1×10^{-42}		7
NiS	3×10^{-21}	$1 / 7.5 \times 10^{16}$	6
NiS	1×10^{-26}	$1 / 2.5 \times 10^{11}$	6
NiS	1×10^{-28}	$1 / 2.5 \times 10^9$	6
CoS	7×10^{-28}	$1 / 1.75 \times 10^{15}$	6
CoS	2×10^{-27}	$1 / 5 \times 10^{10}$	6
CdS	3×10^{-28}	$1 / 2.5 \times 10^9$	6

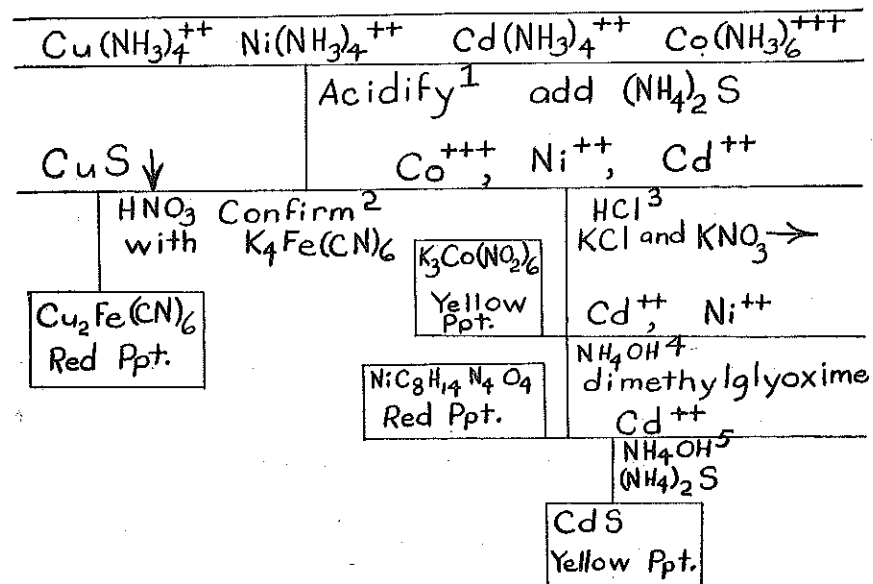
¹Ratio of the copper ion to the other ions was calculated from solubility data, using solubility products calculated by Latimer (6) from thermodynamic data.

After some preliminary tests it became evident to the authors that the separation of copper was only one phase of the problem. The solution could be found only by investigating both the general separation and identification of the four ions under discussion. This was accomplished in the following manner: (a) the effect of the separation of the copper on the identification of the other ions, and the effect of such separation of each of the other ions was studied in turn; (b) the most favorable conditions for the separation of the ions were determined, and (c) suitable confirmatory tests were sought.

PROCEDURE

The general scheme of analysis used by the authors is given in Figure 1.

FIGURE 1. FLOW SHEET SHOWING THE SEPARATION OF COPPER, NICKEL, COBALT AND CADMIUM



¹Acidify to pH 3-4. Methyl orange indicator. Use 1/3 HCl and 2/3 acetic acid.

²Neutralize solution; make acid and buffer, pH 4 to 6.

³Acidify with HCl to pH of 1-2. Saturate with dry salts (1/3 KCl and 2/3 KNO_2).

⁴Add 9M NH_4OH till pH is approximately 9. Saturate with KCl and add excess dimethylglyoxime to remove any excess nickel.

⁵Add more NH_4OH to pH 11-12. Then add a few drops of $(\text{NH}_4)_2\text{S}$.

The copper was separated from the other ions with ammonium sulfide in a solution having a pH range of 3 to 4 (see table II). Then cobalt was precipitated with potassium nitrite in the presence of potassium chloride. Nickel was then removed with dimethyl glyoxime. Finally the test was made for cadmium. Only standard tests of such a nature as to cause very little interference were used (See Table III).

TABLE II
THE SEPARATION OF COPPER AT DIFFERENT pH VALUES AND FINAL CONFIRMATORY TESTS

pH range	Indicator	Confirmatory Tests				Remarks
		Cu	Cd	Ni	Co	
0-2	Methyl Violet	good	fair	poor	poor	Too much copper in filtrate
3-5	Congo Red	good	good	poor	poor	pH range to large, more copper is usually removed
3-4.4	Methyl Orange	good	good	good	good	Best general results
5-6	Universal indicator paper	good	poor	poor	poor	Some nickel, cadmium, and cobalt also precipitate with copper
6.5-7	Universal indicator paper	fair	poor	poor	poor	Too much of ions precipitate with copper

TABLE III
BEST CONFIRMATORY TESTS

Ion	pH	Confirmatory Test	Concentration*		Remarks
			Test	Limit	
Cu	9-10	$\text{Cu}(\text{NH}_3)_4$.025 M	Fair Test
Cu	4-6	$\text{Cu}_2\text{Fe}(\text{CN})_6$.001 M	Very sensitive Test
Co	1-3	$\text{K}_3\text{Co}(\text{NO}_2)_6$ (8)		.001 M	Excess KCl should be added
Ni	8-10	Complex Nickel Compound (9)		.001 M	Make Basic until $\text{Ni}(\text{OH})_2$ Dissolves
Cd	11-12	CdS		.005 M	Add only a drop or two of $(\text{NH}_4)_2\text{S}$

*Concentration limit denotes the general student limit- not that of an experienced analyst.

As the nickel-cobalt separation has been discussed by a number of investigators, and has proved itself, the authors were mainly interested in the total effect. Consequently the complete separation was studied, and is being reported.

THEORY

All analysts agree with the proposition: "The separation of any ion must not interfere with the subsequent identifications of other ions in solution." As this cannot be attained in the laboratory, the alternative is to select reagents which cause a minimum of interference.

The separation of copper in this paper is based mainly on the solubility product principle (see Table I). It would seem to be merely a matter of calculating the proper hydronium ion concentration

$$K_1 = 1.1 \times 10^{-23} = \frac{C_{\text{H}^+}^2 \times C_{\text{S}^{2-}}}{C_{\text{H}_2\text{S}}}$$

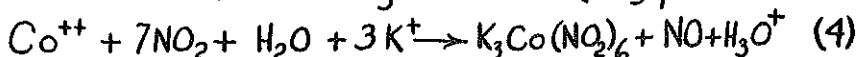
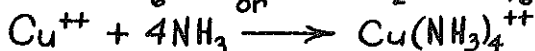
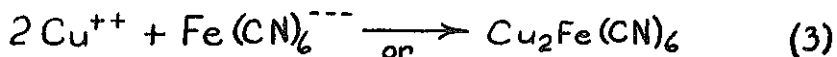
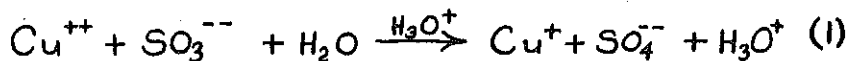
$$\text{S.P.} = 3.5 \times 10^{-38} = (\text{Cu}^{++})(\text{S}^{2-})$$

from the solubility product and ionization constant data. This unfortunately is not the case. At least three reasons can be given: (1) Nickel sulfide and cobalt sulfide appear as α and β forms. A similar suggestion has been given for copper (See Table I). (2) Activity coefficients cannot be calculated with any degree of accuracy, as neither the concentrations of the solutions nor the number of components is always known. (3) In acid the precipitation may well be by means of the HS^- ion instead of the simple S^{2-} ion. This would require new data and might change the entire approach to the problem.

The authors found that confidence in the general trend, rather than in the absolute figures, was justifiable. Separation of copper from the other three was to be preferred to the general separation of copper and cadmium with hydrogen sulfide in an acid solution, and to the general separation of cobalt and nickel in a basic medium. Many independent investigators have noted that the classical method leaves much to be desired. Stieglitz (10) gave the conditions under which nickel and cobalt might appear with copper and cadmium during precipitation in an acid medium.

The final confirmatory test for copper should be made with potassium-ferrocyanide. Preferably the solution should be slightly acid and buffered. This test is more sensitive than the reaction involving the ammonium complex ion (Equation 3, Figure 2). Cobalt (8) is best precipitated with potassium nitrite in the presence of excess potassium ion (Equation 4, Figure 2). As the cobalt may be in the lower valence state, the solution should be acidic. Best results are obtained when the pH is approximately 1-3 since oxidation of the cobaltous ion is easily accomplished. Removal of cobalt is complete enough so as not to interfere with the tests for either nickel or cadmium.

FIGURE 2. TEST REACTIONS.



Nickel is best precipitated from an ammoniacal solution, using the well-known dimethyl-glyoxime reagent (9). As the solubility product of $\text{Ni}(\text{OH})_2$ is only 1×10^{-18} , sodium hydroxide should not be used to make the solution basic. Complete removal of nickel is possible, although the addition of potassium chloride can be used to reduce the amount of nickel present before the dimethyl-glyoxime treatment. KCuCl_3 (11) is probably formed. Finally, cadmium is precipitated from an ammoniacal solution with ammonium sulfide. As the other ions have been sufficiently removed, this test is very satisfactory.

SUMMARY

A method for the separation of the ions of copper, cobalt, cadmium and nickel is presented. Standard reagents are used, but special attention is given to the pH at all points in the separation.

BIBLIOGRAPHY

1. Fresenius, Qualitative Analysis. (1840).
2. Cornog, J. J., J. Chem. Ed., **15**, 420 (1938).
3. Dobbins, J. J. and Goldreath, J., J. Chem. Ed., **22**, 119 (1945).
4. West, P. W., Wick, M. M. and LeRosen, A. L., Qualitative Analysis. The MacMillan Co., New York (1953).
5. Froemke, J. A., Lutz, G., Odland, R., and Phillips, R., Proc. S. Dak. Acad. Sci., **32**, 115 (1953).
6. Latimer, H. M., Oxidation Potentials. Prentice-Hall, New York (1938).
7. Kolthoff, I. M., J. Phys. Chem., **35**, 2720 (1931).
8. Fisher, N. W., Pogg. Ann. **74**, 124 (1848).
9. Tschugaeff, L., Ber., **1905**, 2520 (1905).
10. Stieglitz, J., Qualitative Analysis. The Century Co. New York. Vol. I, 208 (1911).
11. Sidgwick, N. V., Chemical Elements and Their Compounds. Oxford Press, London, Volume I, 163 (1950).