

A STUDY OF, AND A MODIFIED METHOD FOR, VOGEL'S REACTION FOR COBALT.

F. J. ALLEN and A. R. MIDDLETON, Purdue University.

Among the more sensitive tests for cobaltous ion and one particularly suitable for detection of traces of cobalt in nickel salts is the reaction with thiocyanate, usually called Vogel's reaction. When an aqueous solution of a nickel salt, to which excess of ammonium thiocyanate has been added, is shaken with a mixture of equal parts of amyl alcohol and ethyl ether, even minute amounts of cobalt form a blue compound which dissolves in the ether-alcohol layer. Nickel remains entirely in the aqueous layer. Iron, if present in traces only, causes the color to appear purple but the interference of this element can be overcome as shown below. Although easily performed and requiring only reagents ordinarily available, especially in the modified procedure to be described, this test is mentioned in few textbooks of chemical analysis and seems to be not very widely known.

HISTORICAL. In 1877 Morrell¹ noted that cobalt salts, when added to a neutral or acid solution of ammonium thiocyanate in alcohol, give a blue color becoming pink on dilution. He proposed the use of this reaction for determining alcohol. Two years later Zimmerman² proposed a separation of iron from cobalt and nickel by excess of ammonium thiocyanate and precipitation of the iron as hydroxide by sodium carbonate solution added to the point of discharge of the red color of ferric thiocyanate. About the same time Wolff³ studied the absorption spectra of cobalt thiocyanate solutions. Slightly later Vogel⁴ proposed the reaction as a test for cobalt, removing iron by Zimmerman's method and dissolving the blue compound into a mixture of equal parts of amyl alcohol and ether. He stated that by the characteristic absorption spectrum of the blue ether-alcohol layer 1 part of CoCl_2 in 400 parts of FeCl_3 or in 200 parts of NiCl_2 could be detected easily.

Vogel's work remained practically unnoticed until 1900 when Treadwell⁵ called attention to it and showed that the reaction is capable of detecting 0.02 mg. of cobalt in presence of large amounts of nickel. He also isolated the blue compound dissolved in the ether-alcohol layer and found its composition to be that of a double salt, $\text{Co}(\text{SCN})_2 \cdot 2\text{NH}_4\text{SCN}$. At about the same time Rosenheim and Cohn⁶ by migration experiments showed that the blue compound contains a complex anion since cobalt migrated to the anode. They prepared nickel double thiocyanates in crystalline form having the general formula, $\text{Ni}(\text{SCN})_2 \cdot 4\text{RSCN}$, and found that in their solutions complex anions were not present, as nickel migrated only to the cathode. In Treadwell's Analytical Chemistry this reaction is included among the tests for cobalt. He prescribes neutral

¹ Z. analyt. Chem., 16, 251.

² Ber., 12, 2254.

³ Ber., 12, 2314.

⁴ Z. analyt. Chem., 18, 38.

⁵ Z. anorg. Chem., 26, 108.

⁶ Z. anorg. Chem., 27, 280.

solution and suppresses iron, when present, by ammonium acetate and tartaric acid.

In this laboratory it was observed some years ago that when ethyl alcohol is substituted for amyl alcohol and potassium thiocyanate for the ammonium salt, a blue color is developed in the aqueous layer which does not pass into the ether layer until mineral acid is added. It was found that under these conditions cobalt could be readily detected in nickel salts in which the procedure recommended by Treadwell failed to show the presence of this element. Of many salts examined only one, a Kahlbaum's "kobalt-frei" NiSO_4 , failed to show the presence of cobalt. Since nickel salts usually contain iron, a purple instead of blue color appeared in the ether layer. It was found that shaking with a few small crystals of sodium thiosulfate quickly reduced the iron and a pure blue color remained.

It appeared desirable to study this modification of the Vogel reaction in greater detail in order to fix more certainly the conditions of concentration under which it is most delicate and reliable and to compare the delicacy of the test in neutral and in acid solution. It seemed probable that in acid solution the blue ether-soluble compound might be the acid of a complex anion, e.g., $\text{H}_2\text{Co}(\text{SCN})_6$, and that such an acid might be isolated from the ether solution. Two such complex acids have been obtained in crystalline form, $\text{H}_2\text{Hg}(\text{SCN})_4$ ¹ and $\text{HAu}(\text{SCN})_4 \cdot 2\text{H}_2\text{O}$.²

EXPERIMENTAL. A solution of cobalt nitrate was prepared by dissolving electrolytic nickel-free cobalt in nitric acid, removing excess of acid by evaporation and diluting with water. This solution was standardized (1) by igniting the nitrate and weighing as Co_2O_3 ; (2) by conversion to anhydrous sulfate. The cobalt content per cc. as found by the first method was 8.401 mg. and by the second 8.391 mg.; average, 8.396 mg. By accurate dilution solutions were prepared containing respectively, 1.0, 0.1, 0.01 and 0.001 mg. of cobalt per cc. Standard solutions of ammonium, potassium and sodium thiocyanates and of hydrochloric and sulfuric acids were also prepared.

A. Treadwell-Vogel Test (Neutral solution). The effect of varying the concentrations of the various components of the test solution was studied and the conditions determined under which the test is most delicate. The optimum conditions were found to be high concentration of thiocyanate, small total volume and small volume of the ether-alcohol layer. For example, 5cc. of 4 normal Na, K, or NH₄ thiocyanate, 2.5 cc. of saturated ammonium acetate and 0.5 cc. of cobalt nitrate (0.001 mg. per cc. Co) when shaken with 1 cc. of 1:1 mixture of amyl alcohol and ethyl ether gave a faint but distinct blue color in the ether-alcohol layer when this was observed against a white background. Under these conditions 0.0005 mg. of Co in a total aqueous volume of 8 cc. is clearly detectable. Treadwell's statement that 0.02 mg. of cobalt is detectable is conservative. Not much difference was observed in the effectiveness of the three alkali thiocyanates but it was noticed that

¹ Rosenheim and Cohn, loc. cit.

² Bjerrum and Kirschner, Die Rhodanide des Goldes—Mem. acad. roy. sci. lettres Danemark, 8me serie, V, No. 1, p. 20.

traces of iron interfered less when the sodium salt was used. This is in accord with the observation of Rosenheim and Cohn¹ that of the three alkali-ferric thiocyanates, $R_3Fe(SCN)_6$, prepared by them the sodium salt is most stable and least decomposed by aqueous ether into $Fe(SCN)_3$, which is soluble in ether and $NaSCN$ insoluble in ether.

B. *The Vogel Test in acid solution.* The effect of varying a single component of the test solution while keeping the others constant is shown in the tables following.

TABLE 1. Effect of acid concentration.

0.01 mg. Co, 1 cc. 4 N NH_4SCN , 0.3 cc. C_2H_5OH , 1.2 cc. $(C_2H_5)_2O$; total volume 5 cc.

H_2SO_4 normality in 5 cc.	Color in alcohol-ether layer	HCl normality in 5 cc.	Color in alcohol-ether layer
0.0	none	0.0	none
0.2	faint blue	0.2	faint blue
0.4	faint blue	0.4	faint blue
0.6	deeper blue	0.6	deeper blue
0.8	maximum blue	0.8	maximum blue
1.0	maximum blue	1.0	maximum blue
1.5	maximum blue	1.5	maximum blue
3.0	weaker blue	3.0	weaker blue
6.0	pale blue	5.0	none
9.0	greenish blue		

TABLE 2. Effect of thiocyanate concentration.

0.01 mg. Co, 0.8 cc. 5 N HCl, 0.3 cc. C_2H_5OH , 1.2 cc. $(C_2H_5)_2O$; total vol., 5cc.

Normality of thiocyanate in 5 cc.	Color in alcohol-ether layer
0.0	none
0.08	none
0.4	faint blue
0.8	maximum blue
1.36	maximum blue

¹ Loc. cit.

TABLE 3. Effect of ethyl alcohol. TABLE 4. Limit of sensitiveness.

0.01 mg. Co, 1cc. 4 N NH_4SCN ,
0.8 cc. 5N HCl, 1 cc. ether; total
vol. 5 cc.

1 cc. 4 N NH_4SCN , 1 cc. 5 N HCl,
0.3 cc. alcohol, 1.2 cc. ether; total
vol. 5 cc.

Per cent alcohol in 5 cc.	Color in ether or ether-alcohol layer.	mg. Co	Color, ether-alcohol layer
0.0	faint blue	0.0	none
1.0	slightly bluer	.001	very faint blue
2.0	slightly bluer	.002	pale blue
4.0	maximum blue	.003	pale blue
6.0	maximum blue	.004	clear, sky blue
8.0	maximum blue	Repetition using KSCN and NaSCN in place of NH_4SCN gave the same tints for each concn. of Co.	
16.0	maximum blue		
20.0	maximum blue		

TABLE 5. Comparison of sodium, potassium and ammonium thiocyanates in neutral solution.

1 cc. 4 N alk. thiocyanate, 2 cc. ether, 0.5 cc. $\text{C}_2\text{H}_5\text{OH}$; total vol. 5 cc.
(The sodium and potassium salts gave identical results).

mg. Co	Color, KSCN or NaSCN		Color, NH_4SCN	
	aqueous layer	ether layer	aqueous layer	ether layer
0.1	sky blue	none	sky blue	very faint blue
1.0	deep blue	very faint blue	deep blue	deep blue
1.5	deep blue	pale blue	deep blue	deep blue
55.0	indigo blue	deep sky blue	indigo blue	slightly paler than aqueous layer

TABLE 6. Comparison of 1:1 amyl alcohol-ether with 1:4 ethyl alcohol-ether in acid solution.

1 cc. 4 N NH_4SCN , 1 cc. 5 N HCl; total vol. 5 cc.

mg. Co	Color, amyl alcohol-ether	Color, ethyl alcohol-ether
0.001	none	faint blue
.002	faint blue	distinct blue

TABLE 7. Ethyl alcohol in neutral solution as a reagent for cobalt.

1 cc. 4 N NaSCN ; total vol. 5 cc.

Per cent $\text{C}_2\text{H}_5\text{OH}$ in total volume	Color 0.01 mg. Co	Color 0.1 mg. Co
20	none	none
30	barely perceptible blue	pale blue
40	pale blue	bright blue
50	pale blue	bright blue
60	pale blue	bright blue

Discussion of Results. Table 1 shows that the maximum color is developed when the solution is at least 0.8 normal in acid and that increase of acid concentration up to 1.5 normal is without effect. Weakening or disappearance of the blue color at acid concentrations above 3 normal is to be expected if the blue compound is a complex anion. By forming little ionized HSCN high concentration of hydrogen ion should tend to decompose the blue complex and this decomposition should be proportional to the concentration of mineral acid.

Table 2 shows that the thiocyanate concentration should be at least 1 normal and that concentrations above this do not increase the sensitiveness of the test.

Table 3 shows that when the aqueous layer contains only 4 per cent ethyl alcohol the solubility of the blue compound in ether reaches a maximum and that increase of alcohol concentration up to the point where an ether layer no longer separates does not cause any increase of sensitiveness.

Table 4 shows that in acid solution the three alkali thiocyanates used are equally effective as would be expected. Under the optimum conditions of concentration 0.001 mg. of cobalt is detectable in 5 cc. of solution. In neutral solution, however, as appears from table 5, the ammonium complex salt is distinctly more soluble in ether than the sodium or potassium salts. That addition of a little mineral acid to the blue aqueous layer drives all the blue compound into the ether layer is evidence that the ether-soluble compound is a complex acid and not a salt, such as $\text{Co}(\text{SCN})_2$ or $\text{Na}_2\text{Co}(\text{SCN})_4$. Additional evidence upon this point will be presented in another paper.

Table 6, which compares the effectiveness of amyl alcohol-ether, 1:1, used with neutral aqueous solution of ammonium thiocyanate, with 1:4 ethyl alcohol-ether, used with aqueous solution of any alkali thiocyanate 1 normal in mineral acid, shows that the greater solubility in ether of the free complex acid as compared with that of the ammonium salt makes the test slightly more delicate when performed in acid solution. In presence of large quantities of nickel salts this advantage becomes still more marked. In acid solution the interference of ferric iron is considerably greater but this is quickly and easily reduced by shaking with a few crystals of sodium thiosulfate which does not affect at all the reaction with cobalt.

Table 7 shows that in water-alcohol mixtures fairly high in alcohol quite small amounts of cobalt are able to give a distinct color. As the solutions here were neutral, the sodium complex salt must be assumed present. Under these conditions, however, the green color of nickel salts would interfere with the detection of small amounts of cobalt.

SUMMARY.

1. Treadwell's method of carrying out the Vogel test for cobalt in neutral solution using equal parts of ether and amyl alcohol was studied by varying the components of the reaction mixture one by one while keeping the others constant. The optimum conditions were found to be high concentration of thiocyanate, small aqueous volume and small

volume of the ether-alcohol mixture. As little as 0.001 mg. of cobalt in 8 cc. can be detected under these conditions. If only traces of iron are present, it causes less interference when NaSCN is used than when the ammonium salt prescribed by Treadwell is used. The interference of larger quantities of iron is not very satisfactorily overcome by ammonium acetate and tartaric acid.

2. In acid solution and using a small amount of ethyl instead of amyl alcohol the test is at least equally delicate. The optimum conditions were found to be concentrations of thiocyanate and of H_2SO_4 or HCl about 1 normal each and addition of ethyl alcohol equal to about 5 per cent by volume of the aqueous layer and no more ether than required to form a separate layer. In acid solution ferric iron is readily and quickly reduced by shaking with a few crystals of sodium thiosulfate. Even moderately large amounts of iron cause no interference with the test for cobalt. The easy removal of interference by iron, the more general availability of ethyl as compared with amyl alcohol, and that any one of the alkali thiocyanates may be used are features which recommend the test in acid solution as a preferable modification.