

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY]

NEW QUALITATIVE TESTS FOR COPPER, IRON AND COBALT

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During the course of an investigation in the Cornell Laboratory on the determination of cobalt by dinitroso-resorcinol,¹ it was found that copper and iron were also precipitated by this reagent, which indicated that it might be used for the detection of these metals.

The sensitiveness of the tests for copper, iron and cobalt with the common reagents and with dinitroso-resorcinol was determined, using the procedure of Wagner.² The solution of dinitroso-resorcinol was prepared by adding an excess of the solid to boiling water and then filtering. Under these conditions a clear, brown solution was obtained. The solution was prepared just previous to use and was kept hot while making the tests. The following results were obtained.

TABLE I
SENSITIVENESS OF TESTS

Metal	Reagent	Solvent	Concn.	Limit of	Method of
				detection	
				Mg. per cc.	
Copper	NH ₄ OH	..	0.90	0.0310	blue color
	K ₄ Fe(CN) ₆	..	solid	.0081	red-brown color
	C ₆ H ₄ N ₂ O ₄	H ₂ O	satd.	.0040	brown color
Iron	KCNS	H ₂ O	satd.	.0021	red color
	K ₄ Fe(CN) ₆	..	solid	.0026	blue color
	C ₆ H ₄ N ₂ O ₄	H ₂ O	satd.	.0035	olive-green color
Cobalt	nitroso-β-naphthol	50% acetic	satd.	.0012	orange-red ppts.
	nitroso-β-naphthol	50% acetic	satd.	.0003	orange color
	C ₆ H ₄ N ₂ O ₄	H ₂ O	satd.	.0033	orange-brown color

Similar tests were made using 50% acetic acid and 50% alcoholic solutions of dinitroso-resorcinol but the tests were not as sensitive as when the aqueous solution of dinitroso-resorcinol was used.

After determining the limiting concentration of acid which might be present in making the tests, and that sodium acetate coagulates the precipitate and in large amounts also darkens the color, the tests were repeated to determine whether a smaller quantity of the metals could be detected by the addition of a few small crystals of sodium acetate in the presence of the limiting concentration of the acids. The results presented in Table II were obtained.

The addition of an aqueous solution of dinitroso-resorcinol to one of a salt of cadmium or aluminum does not give a precipitate or coloration, but in the case of chromium or nickel a precipitate or coloration is pro-

¹ Orndorff and Nichols, *THIS JOURNAL*, **45**, 1439, 1536 (1923).

² Wagner, *Z. anal. Chem.*, **20**, 349 (1881).

duced, depending upon the amounts of these metals present. This confirmed the previous results of one of us¹ that the presence of a large amount of nickel interferes with the detection of cobalt.

TABLE II

SENSITIVENESS OF TESTS IN THE PRESENCE OF ACID AND SODIUM ACETATE

Acid	Limiting concn. of acid, <i>N</i>			Limit of detection, mg. per cc.		
	Copper	Iron	Cobalt	Copper	Iron	Cobalt
HCl	0.002	0.030	0.015	0.0080	0.0017	0.0016
HNO ₃	.004	.064	.064	.0080	.0026	.0025
H ₂ SO ₄	.008	.062	.062	.0080	.0038	.0012

The use of this reagent for the detection of copper, iron and cobalt was found to be satisfactory by modifying the usual scheme of analysis in the following manner.

Copper.—Neutralize with sulfuric acid the excess of ammonium hydroxide in the solution containing copper and cadmium and add a little in excess. Add 2 to 4 cc. of dinitroso-resorcinol solution and a few small crystals of sodium acetate to a portion of the solution. The presence of copper³ is shown by a brown precipitate or a dark brown color.

Iron.—Dissolve the ferric hydroxide obtained by the usual method, in the least possible amount of hydrochloric acid and nearly neutralize with sodium hydroxide. Add 2 to 4 cc. of dinitroso-resorcinol solution and a few small crystals of sodium acetate. The presence of iron⁴ is shown by the formation of a green precipitate or color.

Cobalt.—Dissolve the precipitated sulfides of cobalt and nickel in aqua regia and nearly neutralize the solution with ammonium hydroxide. To a portion of the solution add 2 to 4 cc. of dinitroso-resorcinol solution, a few small crystals of sodium acetate and warm the mixture gently. The presence of cobalt⁵ is shown by the formation of an orange-red precipitate or color.

Summary

1. When an aqueous solution of dinitroso-resorcinol is added to a solution of a copper, iron or cobalt salt a precipitate or coloration is produced, depending upon the amount of the salt present.

2. In neutral solution this reagent is capable of detecting 0.0040 mg. of copper, 0.0035 mg. of iron and 0.0033 mg. of cobalt in 1 cc. of solution, which limits compare favorably with those of the tests used at present for the detection of these metals.

³ This test is more sensitive when the solution is compared with a standard.

⁴ The solution must not be strongly acid for the best results.

⁵ If the solution to be tested for cobalt is decidedly green, the amount of nickel must be reduced before the cobalt can be detected. This is accomplished best by treating the solution with dimethylglyoxime, filtering and testing the filtrate for cobalt as directed.

3. In very dilute acid solutions in the presence of sodium acetate the sensitiveness of the tests for cobalt and iron is increased but not for copper.

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ADSORPTION BY ACTIVATED SUGAR CHARCOAL

II.¹ ADSORBABILITY OF HYDROGEN AND HYDROXYL IONS

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Adsorbent charcoals are generally attributed with the power of adsorbing hydrogen and hydroxyl ions equally. In this paper data are presented which show that this assumption is based on erroneous experimental evidence. The data presented also indicate that the hydroxyl ion is last instead of first in the order of decreasing adsorbability of anions by pure charcoal.

Michaelis and Rona² after a study of the adsorbability of the anions of a series of ammonium salts by blood charcoal reported that the hydroxyl ion was adsorbed to a greater extent than any other of the series which included $\text{SO}_4 < \text{Cl} < \text{Br} < \text{I} < \text{CNS} < \text{OH}$.

Rona and Michaelis³ attempted to arrive at the relative adsorbability of hydrogen and hydroxyl ions by determination of the increase in adsorption of hydrochloric, nitric and sulfuric acids and of potassium and sodium hydroxides due to the presence of increasing amounts of neutral salts. They found that while the hydroxides alone were not adsorbed to quite the same extent as the acids alone, the addition of neutral salts to each, nevertheless, caused approximately the same increase in adsorption. On the basis of these findings they concluded that, within the limits of their experiments, the adsorbability of hydrogen and hydroxyl ions by charcoal is the same. These conclusions have been widely accepted and utilized in the explanation of the adsorbent action of charcoal and of adsorption phenomena in general.⁴

From previous work with pure activated sugar charcoal the writer surmised that the results reported by Rona and Michaelis with blood charcoal might conceivably be due to factors other than pure adsorption by the char-

¹ Published by permission of the Director of the Experiment Station.

² Michaelis and Rona, *Biochem. Z.*, **94**, 240 (1919).

³ Rona and Michaelis, *ibid.*, **97**, 85 (1919).

⁴ (a) Bancroft, "Applied Colloid Chemistry," McGraw-Hill Book Co., 1921, p. 233. (b) Freundlich, "Kapillarchemie," third ed., Akademische Verlagsgesellschaft m. b. H., Leipzig, 1923, p. 287. (c) Svedberg, "Colloid Chemistry," Chemical Catalog Co., 1924, p. 177. (d) Gyemant, *Kolloid Z.*, **28**, 103 (1921). (e) Schilow and Lepin, *Z. physik. Chem.*, **94**, 25 (1920). (f) Tanner, *J. Ind. Eng. Chem.*, **14**, 442 (1922). (g) Chaney, Ray and St. John, *Ind. Eng. Chem.*, **15**, 1253 (1923).