

ammonium and calcium salts are somewhat more viscous and must therefore be larger, or less symmetrical, than the ordinary complexes of the same salts with water in simple aqueous solutions.

It is not easy to assign a reason why salts of silver, copper and zinc, on the one hand, should show a preference to form compact complexes with ammonia, and, on the other hand, lithium, potassium, ammonium and calcium salts should show a preference to form compact complexes with water. Various analogies suggest themselves, for example, the difference between the sulfo- and the oxy-salts. Thus, tin, arsenic, and antimony show a marked tendency to form well defined sulfo-salts but very poorly defined oxy-salts; on the other hand, chromium and manganese show no tendency to form sulfo-salts, but they do form well defined oxy-salts, as in the chromates and permanganates.

To compare with the viscosity values for ammoniacal aqueous solutions, it seems of great importance to obtain the values for solutions in anhydrous ammonia, both with and without small additions of water. Work in this direction has already been begun in this laboratory.

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TWO NEW AND VERY DELICATE TESTS BY USE OF THE REAGENT, "TETRAMETHYL BASE."

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An acetic acid solution of the organic base, tetramethyldiaminodiphenylmethane, $(\text{CH}_3)_4\text{N}_2(\text{C}_6\text{H}_4)_2\text{CH}_2$, was used by Trillat¹ in 1903 for the detection of traces of lead and manganese. His method is to convert the metals into the form of dry sulfates, then warm and treat with a few drops of a solution of sodium hypochlorite, remove the chlorine by washing and add the reagent and warm. A beautiful blue color develops, which disappears on cooling and reappears on warming. With manganese it is not necessary to add the hypochlorite, but merely to add sodium hydroxide and ignite before adding the reagent. Trillat found that this gave a very delicate test for both lead and manganese.

This base has also been used as a reagent for the detection of ozone in mixtures containing hydrogen peroxide and the oxides of nitrogen. For this purpose the base is dissolved in alcohol, and strips of paper are moistened with the alcoholic solution and held in the gas. Ozone gives a violet color, nitrogen dioxide a straw-yellow and hydrogen peroxide no color whatever. Arnold and Mentzel² were the first to use the reagent for this purpose. They named the reagent "tetra base," but

¹ *Compt. rend.*, 136, 1205-1207; also *J. Chem. Soc. Abstr.*, 1903, 512.

² *Ber.*, 35, 1324.

finding later that *p*-phenylenediamine had long been sold under this name, they changed the name to "tetramethyl base." Fischer and Marx,¹ Fischer and Braehmer,² and Kaiser and McMaster³ have also used this reagent in their work as a test for ozone.

A modification of Trillat's method has been used for some time in this laboratory as a test for manganese, confirming the results obtained by inorganic tests. The base is prepared as follows: Warm on the water bath for one hour a mixture of 30 grams of dimethylaniline, 10 grams of formaldehyde, 200 cc. of water, and 10 cc. of sulfuric acid. After cooling, make alkaline with an excess of sodium hydroxide, drive off the unchanged dimethylaniline with steam. Filter after cooling, wash the brownish product with water, then recrystallize once from alcohol. This gives a pure, yellowish white product.

There are objections to the use of an acetic acid solution of the base, as recommended by Trillat. The acetic acid solution should be heated when used, but when heated the base immediately precipitates and will not dissolve until the solution is cooled. A colorless acetic acid solution of the base is hard to obtain. It is unstable and soon darkens, even though kept away from the light. The use of citric acid as the solvent has been found to be much more satisfactory. The reagent is made up by dissolving 2.5 grams of the organic compound in a solution of ten grams of citric acid in 10 cc. of water. This solution is then diluted to 500 cc. It is perfectly colorless, will not give a precipitate upon heating even to boiling, and is stable, no precautions with regard to keeping out light being necessary.

With any compound of lead or manganese in which the metal has a valence of more than two, a cold solution of the reagent will give a deep reddish purple color due to an oxidation product of the reagent. Cobaltic and nickelic hydroxides also cause the formation of the color, although the reaction takes place perhaps somewhat more slowly and the color is not as deep usually as with manganese or lead. This test finds application in any of the ordinary systems of qualitative analysis. If the metals of the ammonium hydroxide group are separated from each other by the use of sodium peroxide or sodium hydroxide and hydrogen peroxide, the manganese which precipitates in this group will remain with the ferric hydroxide. If no cobalt or nickel is present, the ferric hydroxide precipitate may be tested for manganese by washing it and pouring a small quantity of the reagent over it. The filtrate will have a deep reddish purple color, if manganese is present. The original ammonium hydroxide precipitate may be tested for manganese by washing

¹ *Ber.*, 39, 2555.

² *Ibid.*, 39, 940-68.

³ *Am. Chem. J.*, 39, 96.

it thoroughly and allowing it to stand with free access of air for several minutes, then adding the reagent to a portion of the precipitate. Cobalt and nickel do not interfere. In the ammonium sulfide group, the manganese sulfide may be dissolved in cold, dilute hydrochloric acid, the hydrogen sulfide boiled out, and manganese separated from zinc by the use of sodium hydroxide and bromine water. The precipitate of manganese dioxide should be thoroughly washed and if cobalt and nickel are absent, the solution of the organic reagent may be poured over it. If cobalt or nickel is present, the precipitate should be dissolved in hydrochloric acid with the addition of peroxide, if desired, and the manganese separated by the action of ammonium hydroxide and hydrogen peroxide. The resulting precipitate is washed and tested with the reagent. Another way of carrying out the test is to boil out the hydrogen sulfide from the hydrochloric acid solution of manganese sulfide, then add sodium hydroxide in excess, filter, wash thoroughly, let stand a few moments and add the reagent. A rapid test for manganese, which may be used upon a solution containing all of the ordinary metals, consists in boiling the acidified solution to remove chlorine or other halogen, then adding sodium hydroxide in excess, filtering the precipitated hydroxides, washing, allowing to stand about ten minutes and then adding the reagent. Lead, cobalt, nickel and other elements give no colorations.

Use of Reagent as a Test for Gold.—No mention has ever been made of the action of this reagent upon salts of gold. With very dilute solutions of gold chloride, the reagent gives a very beautiful purple color, due to the oxidizing action of the gold salt; this soon changes to blue and then becomes colorless. The blue color reappears upon warming. With more concentrated solutions the color is purple by transmitted light and bluish to green by reflected light. It was found by working with very dilute solutions that this reagent affords a very delicate test for gold, not interfered with by platinum, palladium, or other elements. The color is very much more distinct than "purple of Cassius." Free mineral acid interferes with the reaction. Solutions should be neutralized and made slightly acid with acetic or citric acid. To determine the delicacy of the test, a gold solution was made up by dissolving 20 mg. of metallic gold in nitrohydrochloric acid. This was evaporated to remove chlorine, neutralized with sodium carbonate and made slightly acid with acetic acid. The solution was then diluted to one liter. Portions of this solution were diluted to 50 cc. and tested with the reagent. The following table gives the results:

Au solution.			Result.
Cc.	Grams of gold.		
25	0.0005		Very fine purple color.
5	0.0001		Good blue color.
1	0.00002		Plainly visible light blue.
0.5	0.00001		Barely visible light blue.

The delicacy of the test in a solution containing nothing but gold is 0.01 mg. per 50 cc.

Use as a Test for Ammonia.—The test for ammonia makes use of the fact that hydrogen peroxide has no action upon a solution of a manganous salt unless an alkali is present. In the presence of even a trace of alkali the peroxide instantly oxidizes the manganese to a brown higher oxide. The test is carried out by heating the solution supposed to contain the ammonium salt with sodium hydroxide in an Erlenmeyer flask fitted with a rubber stopper through which passes a short glass tube bent at right angles. A piece of filter paper is moistened with a solution made up by dissolving 2 grams of manganous sulfate in 200 cc. of water and adding 5 cc. of the ordinary laboratory hydrogen peroxide solution. This filter paper is held directly in front of the tube through which the steam and ammonia are passing. If ammonia is present in any quantity a brown stain will appear upon the paper. This stain may be moistened with a drop of the organic reagent, and a deep purple color will appear. The excess of hydrogen peroxide present has no effect upon the test. With exceedingly small quantities of ammonia, no brown stain will be formed, but a purple stain will readily be obtained upon adding the reagent. Steam itself has no action if manganous sulfate is used. If manganous acetate is used, very slight purple stains may form even when no ammonia is present. To test the delicacy of this test, a solution of ammonium chloride was made up containing 63 mg. of ammonium chloride per liter, which would be equivalent to 20 mg. of ammonia per liter. The following table gives the results obtained:

NH ₄ Cl solution. Cc.	Grams NH ₃ .	Result.
25	0.0005	Very distinct brown color. Very brilliant purple stain.
5	0.0001	Faint brown color. Very brilliant purple stain.
2.5	0.00005	Faintly visible brown color. Good purple stain.
1	0.00002	No visible brown stain. Distinct purple spot.
0.5	0.00001	Slight bluish spot.
Steam alone		No coloration.

It is possible then by this method to easily detect 0.02 mg. of NH₃ and by carrying out carefully to be able to detect 0.01 mg.