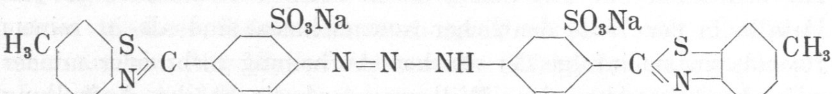
Some Color Reactions for Magnesium.

By I. M. Kolthoff.

(Eingelangt am 7. April 1930.)

In recent years some new color reactions for magnesium have been described in the literature. In this paper some experimental details with regard to the application of these reactions will be discussed.

I. Titan yellow G: Sodium salt of the diazoamino compound of dehydro-thio-p-toluidinsulfonic acid (or the mixed diazoamino compound of dehydro-thio-p-toluidinsulfonic acid and primuline dehydro-thio-p-toluidinsulfonic acid).



(SCHULZ' Farbstofftabellen, 1923, No. 198; F. M. ROWE, Color Index 1924, No. 813.)

Titan yellow G has been proposed by the author[1]) as a reagent for the detection of magnesium. A product marketed by the "British Drug Houses, London, which appeared to have the same properties as „Titangelb A" furnished by Dr. G. GRÜBLER, Leipzig, was used. To 10 cc. of the solution to be tested 0,1 to 0,2 cc. of a 0,1% solution of the indicator in water and about 0,25 to 1 cc. 4 N sodium hydroxide are added. In the absence of magnesium the mixture has a brownish-yellow color; if 5 mg magnesium per liter are present, the solution turns nicely red, with 1 mg. Mg p. l. orange. If a blank without Mg is used for comparison, 0,2 of a mg. Mg p. l. can be detected (sensitivity). Small amounts of calcium intensify the color of the magnesium reaction product, which must

[1]) I. M. KOLTHOFF, Biochem. Z., 185, 344 (1927).

be considered in the application of the reagent to the colorimetric determination of magnesium in presence of calcium salts. In the paper[1]) referred to, it has been shown that the reaction is very suitable for the detection and approximate estimation of traces of magnesium in alkali salts. Similarly it can be used for the detection of this element in calcium salts. In testing calcium carbonate for the presence of magnesium, it was found recently that the most delicate procedure is to dissolve this salt in a small excess of hydrochloric acid then add the indicator and make alkaline with 1 to 2 cc. 4 N sodium hydroxide, a precipitate of calcium carbonate not interfering. 50 mg. of calcium carbonate are treated with 4 drops 4 N HCl, 10 cc. of water and 0,2 cc. 0,1% titan yellow, and 1 to 2 cc. 4 N sodium hydroxide are added. In the presence of 0,1% magnesium in the calcium carbonate a bright red color appears and even 0,01% of magnesium can be detected by comparing with a blank. In the so called "chemically pure" commercial products of calcium carbonate, the presence of magnesium was easily shown.

Previously (lit. ref. 1) it had been found that zinc interferes with the detection of magnesium; it is made harmless by the addition of an excess of sodium sulfide. More advantageous is the use of potassium cyanide. To a solution of 0,5 g. zinc sulfate in 10 cc. of water, 0,8—1 g. potassium cyanide is added; the precipitate formed dissolves on shaking. Then 0,1 to 0,2 cc. of 0,1% indicator solution and 1 to 2 cc. 4 N sodium hydroxide are added. In the absence of magnesium the solution turns brown, in the presence of magnesium, red or orange-red. 0,001% Magnesium in zinc salts can be detected easily; by changing the amount of zinc salt, the sensitivity can be varied ad libitum.

Nickel, cobalt and manganese give the same reaction as magnesium and, therefore, interfere with the detection of the latter element. 10 cc. of a solution containing 10 mg. Ni p. l. gives an orange-red color, sensitivity 3 mg. p. l. Nickel can be made harmless by the addition of an excess of potassium cyanide as has been described under zinc, or by precipitation with ammonium sulfide. In the latter case, however, filtration is necessary; this can be avoided by using potassium cyanide. Cobalt behaves in the same way as nickel; the reaction has the same sensitivity. It can be made inactive by addition of cyanide; however, a yellowish-green color develops and the detection of magnesium is then not as delicate. It is better to remove cobalt as sulfide and to test the filtrate for magnesium. The same holds for manganese, which gives a sensitive reaction with titan yellow (sensitivity about 1 mg. p. l.) On addition of an excess of potassium cyanide, part of the manganese is oxidized by the air to brown higher oxides. Manganese can be removed in ammoniacal medium by boiling with hydrogen peroxide. The manganese dioxide, however, adsorbs a relatively large part of the magnesium. It is better to remove the manganese as sulfide. To a solution of 100 mg. manganous chloride in 10 cc. of water and excess of ammonium sulfide is added, whereupon the mixture is filtered through a dense filter. To the filtrate 0,1 to 0,2 cc. of indicator and an excess of sodium hydroxide are added so that all ammonia from ammonium salts is liberated and an excess of free strong base is present. A red color indicates the presence of magnesium; 0,05% of magnesium could easily be detected in the manganous chloride in the way described. The same procedure can be applied to the detection of magnesium in the presence of nickel and cobalt.

Beryllium does not interfere, if enough sodium hydroxide is added to dissolve the beryllium hydroxide. Therefore, magnesium in beryllium salts can be easily detected by means of titan yellow. It should be mentioned, however, that beryllium decreases the sensitivity of the reaction for magnesium, about 0,4% magnesium in beryllium salts can be found without any special separation (Be reacts with 1. 2. 5. 8. oxyanthraquinone: comp. sub 2).

Lanthanium does not react with titan yellow (comp. 1. 2. 5. 8. oxyanthraquinone). With regard to interferences by other elements the reader is referred to the previous papers.

H. D. Barnes[2]) recently proposed the use of Clayton yellow as a dyestuff for the detection of magnesium. In order to learn its behavior experiments have been made with a sample of Clayton yellow prepared by the National-Aniline and Chemical Company New York (N. Y.). Its behavier towards the different elements

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[2]) H. D. Barnes, J. Afr. Chem. Inst. **11**, 67 (1928); Chem. Abstr. **23**, 1838 (1929). This substance is listed in Schulz (Farbstofftabellen) and Rowe (Color index) under the same number as titan yellow.

mentioned is exactly the same as that of the two products of titan yellow. The sensitivity, towards different elements is also the same, with the exception of magnesium, which can be detected down to a concentration of 0,5 mg. p. l., whereas with titan yellow 0,2 mg. Mg p. l. is the limit.

The author has tried to apply the reaction with titan yellow as a spot test on filter paper or on a porcelain spot plate. Titan yellow paper was prepared, a drop of the solution to be tested placed on it and then 1 drop 0,5 N sodium hydroxide. However, it was found with ten different kinds of filter paper that a red color appeared after the application of sodium hydroxide, even though the solution did not contain any magnesium. Even "blueband" paper of SCHLEICHEH and SCHÜLL 589 washed with hydrofluoric acid behaved in the same way. On the other hand a delicate test for magnesium is obtained on a porcelain spot plate. One drop of the solution is mixed with a small drop of 0,1% indicator solution and 1 drop 0,1 N sodium hydroxide. The following behavior is observed.

Drop containing mg Mg p. l.	Absolute amount of Mg present	Appearance mixture
200 mg. p. l.	10 μg.	red color
100 mg. p. l.	5 μg.	red color
40 mg. p. l.	2 μg.	pink-orange (distinctly different from blank)
30 mg. p. l.	1,5 μg.	pink-orange (distinctly diff. from blank)
0 mg. p. l.	0 μg.	Orange

The sensitivity therfore is about 1,5 μg. magnesium in the drop.

It seemed interesting to determine, whether a mixture of a magnesium solution with titan yellow can be used as an indicator for hydroxyl ions. It is well known, that the choice of suitable indicators, which change color in distinetly alkaline medium (p H around 12—13) is very limited. The indicators now available have no pronounced color change, and either have a large salt error (tropaeolin o) or an unstable alkaline form (nitramin). The application of a magnesium-titan yellow mixture is based on the fact that the precipitating magnesium hydroxide is colored red in presence of titan yellow. It is to be expected, that the sensitivity of such a mixture will be dependent upon the magnesium concentration and to a lesser extent on the titan yellow concentration, Hence by varying the magnesium concentration indicators of different sensitivity towards hydroxyl ions can be prepared. The mixture of magnesium chloride and titan yellow has to be freshly made; on standing one or two days a yellow flocculent precipitate, containing magnesium and part of titan yellow is formed. The sensitivity of the following two reagents towards hydroxyl ions has been determined.

Reagent 1 : 0,05% Titan yellow and 0,01% Magnesium (as magnesium chloride).

Reagent 2 : 0,05% Titan yellow and 0,05% Magnesium (as magnesium chloride).

Reagent 1: To 6 c. c. solution 0,2 c. c. reagent is added:

0,01 N NaOH: red-pink color
0,005 N NaOH: pink-orange
0,0037 N NaOH: brown-orange
0,0025 N NaOH: pure-yellow (as water).

There is a very marked difference in color between 0,005 N NaOH (p OH = 2,3) and 0,0037 N NaOH (p OH = 2,43). Sensitivity in unbuffered solution: 0,003 N NaOH.

Reagent 2: To 6 c. c. solution 0,2 c. c. reagent is added:

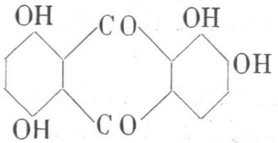
0,01—0,005 N NaOH: brilliant dark red-pink
0,0025 N NaOH: orange red (develops somewhat on standing)
0,0017 N NaOH: after a few seconds orange-pink
0,0012 N NaOH: after a few seconds distinctly orange
0,001 N NaOH: yellow.

Sensitivity in unbuffered solution: 0,001 N NaOH. The entire color change takes place between p OH 3 and 2,5: the color change interval is very short, as can be expected from such a "precipitation-indicator".

Reagent 2 is more sensitive to hydroxyl ions than reagent 1, on account of its higher magnesium concentration. Neutral salts decrease the sensitivity. In 0,05 N to 0,5 N solutions of sodium and potassium chloride the sharp color change takes place at sodium hydroxide concentrations between 0,0025 N (yellow-orange) and 0,005 N (pink-red), if reagent 2 is used. The reagent is not suitable for the sensitive detection of free sodium hydroxide in sodium carbonate, as the carbonate ions react with part of the magnesium.

The reaction described can also be applied as a spot test for hydroxyl ions. Filter paper SCHLEICHER & SCHÜLL 589; extracted with hydrofluoric acid) was moistened with a mixture containing 0,01% titan yellow and 0,05% magnesium (as chloride), and dried in the air. 0,1 N sodium hydroxide causes a red spot; 0,01 N NaOH a distinct red ring, disappearing on standing; 0,005 N NaOH a faint red ring.

II 1·2·5·8. Oxy-anthraquinone. (Alizarincyanin.)



This substance has been recommended by FR. HAHN, WOLFF and JAGER[3]) as a reagent for magnesium, and lately HAHN[4]) developed a method for the micro determination of the element with this dyestuff. In alkaline solution, it has a violet color, in presence of magnesium it is pure blue (corn flower blue); 0,5 mg. Mg p. l. can be detected. It may be mentioned here that 1·2·5·8 oxyanthraquinone is a very sensitive reagent for beryllium[5]) and in weakly acid medium (p H 5,5 to 5,7; acetate buffer) extremely sensitive towards aluminum[6]). It is very suitable for the colorimetric determination of traces of aluminum of the order of 0,01—0,1 mg. Al p. l. It is a less specific reagent for magnesium than titan yellow; besides beryllium, cadmium and lanthanum also react in alkaline medium. Cobalt, nickel and manganese give the same reaction as magnesium.

Cobalt: Sensitivity 1—2 mg. Co p. l., if compared with a blank. Cobalt reacts even at a very low alkalinity; the blue compound is formed in a medium alkaline with borax whereas magne-

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[3]) HAHN, WOLFF and JAGER, Ber., **57**, 1394 (1924).

[4]) FR. HAHN, Mikrochemie, PREGL-FESTSCHRIFT, 127 (1929).

[5]) Comp. H. FISCHER, Wissenschaft. Veröffentl. Siemens Konzern, **5**, 99 (1926); I. M. KOLTSCHOFF, J. Am. Chem. Soc., **50**, 393 (1928).

[6]) I. M. KOLTSCHOFF, J. Amer. Pharmac. Assoc., **17**, 360 (1928).

sium does not react under these conditions. To 10 cc. solution 200 to 300 mg. borax and 0,1 to 0,2 cc. of a 0,1% solution of the anthraquinone in alcohol are added. In absence of cobalt the color is violet, in presence of cobalt, blue to bluish-violet. If compared with a blank, 1 mg. Co p. l. can be detected in this way. Magnesium, however, decreases the sensitivity of this reaction for cobalt. A solution containing 5 mg. Co and 100 mg. Mg p. l. gives a distinct reaction in the way described; with 2,5 g. Mg p. l. no reaction occurs. On long standing the cobalt oxide settles to the bottom in the form of violet flocs, in absence of magnesium as blue flocs.

Nickel: Behaves in the same way as cobalt; if the solution is made alkaline with sodium hydroxide, 1 mg. Ni p. l. can just be detected. In borax solution the reaction is much less sensitive (about 50 mg. Ni p. l.).

Manganese: In strongly alkaline medium sensitivity about 4 mg. p. l. Soon after addition of sodium hydroxide the blue color is spoiled by the air oxidation of the manganous hydroxide to brown higher oxides. Manganese does not react in borax medium.

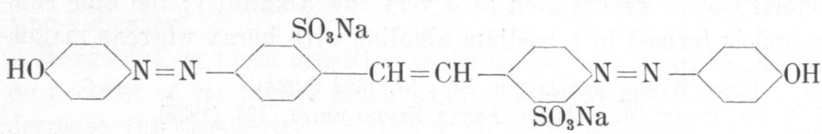
Zinc: Does not react, but interferes with the detection of magnesium. For the detection of the latter element in presence of cobalt, nickel, zinc and manganese, comp. under “titan yellow”.

Lanthanum: Sensitivity 1 mg. La p. l., if compared with blank. In borax medium the color is not pure blue, but bluish-violet. Sensitivity if compared with blank, 1 mg. La p. l. Lanthanum even gives a distinct color in weakly acid medium just as aluminium does. Sensitivity at p H of about 5,5 1 mg. La p. l.

Cadmium: Gives in strongly alkaline medium a blue precipitate. Sensitivity about 50 mg. Cd p. l.

Copper does not react.

III. Brilliant yellow: (Schulz, No. 303; Rowe 364). Diaminostilbene-diphenylsulfonic acid:



Brilliant yellow behaves in about the same way as titan yellow though it gives a less sensitive reaction. Besides, the blank (with excess of sodium hydroxyde) is more orange than with titan-yellow. The procedure is the same as described for titan yellow:

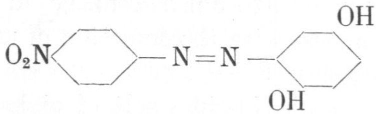
Magnesium: Sensitivity 4 mg. Mg p. l.

Cobalt: Sensitivity 2 mg. Co p. l.

Nickel: Sensitivity 2 mg. Ni p. l.

Manganese does not give a distinct reaction, but interferes on account of the air oxidation. With regard to the behavior of other elements, the reader is referred to what has been said for titan yellow.

IV. o. p-dihydroxy—azo-p-nitrobenzene.



This diazo compound has been recommended by K. SUITSU and K. OKUMA[7]) as reagent for magnesium. The Japanese authors recommend working with 0,5% solution of the dye in 1% sodium hydroxide, adding 1 drop to 10 cc. of the solution to be tested and making alkaline with sodium hydroxide. However, it will be shown that the sensitivity is much greater if a more dilute solution of the diazo compound is used as a reagent.

It may be mentioned that this diazo compound (prepared according to the directions of SUITSU and OKUMA) is a suitable indicator for hydroxyl ions. In 0,005 N sodium hydroxide the color is brownish, in 0,1 N sodium hydroxide, violet; color change interval between p H 10,8 to 13,0.

Magnesium: Reagent 1: 0,5% diazo compound (according to SUITSU and OKUMA).

Procedure: To 10 cc. solution 1 drop reagent and 1 cc. 4 N NaOH are added. With 100 mg. Mg p. l. a sky-blue color is formed; on standing the lake settles in blue flocs; with 20 mg. Mg p. l. a blue-violet color develops — about the limit of sensitivity.

Reagent 2: 0,1% diazo compound in 50% alcohol.

Procedure: 100 cc. solution, 0,1 cc. reagent, and 1 cc. 4 N NaOH.

Sensitivity: 2 mg. Mg p. l.

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[7]) K. SUITSU and OKUMA, J. Soc. Chem. Ind., Japan, **29**, 132 (1926); Chem. Abstr., **20**, 3000 (1926); Comp. also W. L. RUIGH, J. Am. Chem. Soc. **51**, 1456 (1929).

If only 0,02 cc. reagent is used, the sensitivity extends to 1 mg. Mg p. l. if compared with blank (red-violet).

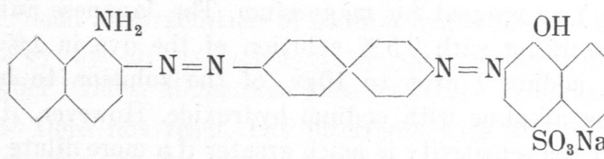
Cobalt: With the strong indicator solution (0,5%) the sensitivity is very small; the color cannot be sharply distinguished between violet and blue. With 0,02 cc. of 0,1% indicator to 10 cc. solution 10 mg. Co p. l. can just be detected.

Nickel: As cobalt.

Manganese: No definite color develops on account of the air oxidation of manganous hydroxide.

Beryllium, aluminum, lanthanum, zinc and cadmium do not react with o. p-dihydroxy — azo-p-nitrobenzene in alkaline medium, but interfere more or less with the detection of magnesium. (Comp. under titan yellow.)

V. Congo corinth: Sodium salt of diphenyl-disazo-4-sulfo-α-naphthylamin-α-naphthol-4-sulfonic acid



Reagent: 0,1% solution in water. In alkaline medium the color is red, in presence of magnesium, cobalt, or nickel a brilliant violet color develops.

Magnesium: 10 c. c. solution+0,1 to 0,2 c. c. reagent+1 c. c. 4 N NaOH. Sensitivity: 4 mg Mg p. l.

Cobalt and Nickel: Sensitivity: 0,5 resp. 1 mg. p. l.

Manganese: Does not give a distinct reaction, but interferes by the development of a brown color on account of air oxidation.

Beryllium, aluminium, zinc, lanthanum and cadmium do not react, but interfere more or less with the detection of magnesium.

VI. "La Motte Purple."

Under this name a purple solution is put on the market by "La Motte Chemical Products Company, Baltimore, Maryland", which behaves like an acid-base indicator. The composition is kept secret. This indicator shows a color change between p H 9,6 and 12,2 from purple to red. However, it was found by the author that in presence of magnesium, cobalt or nickel, the color is blue instead of violet in strongly alkaline medium. Therefore, the dyestuff does not work as an acid-base indicator in presence of any of these elements.

M a g n e s i u m: 5 c. c. solution with 0,1 c. c. indicator and 1 c. c. 4 N NaOH.

100 mg. Mg p. l.: blue color; after 30 seconds, blue-violet floc.
10 mg. Mg p. l.: purple-blue.
5 mg. Mg p. l.: violet-purple.
2 mg. Mg p. l.: violet-red.
0 mg. Mg p. l.: red.

Sensitivity (compare with blank): 1 mg. Mg p. l.

C o b a l t and N i c k e l: behave in the same way.

B e r y l l i u m: does not react, but decreases the sensitivity of the megnesium test. In a solution containing 1 g. Be p. l. the presence of 0,5% magnesium (with respect to beryllium) can be detected. By comparing with a blank the sensitivity is still greater.

Some other dyestuffs like curcumin, benzopurpurin, anilin yellow S. („KAHLBAUM“, composition not given) have been examined. Curcumin behaves somewhat like titan yellow, though it is much less sensitive towards magnesium. Anilin yellow reacts with many metals even in neutral or sometimes in weakly acid medium with the formation of a violet colored product. Therefore, this reaction for magnesium is not at all specific. In an acetate buffer of p H 5,0 to 5,2, the following metals give e violet color with anilin yellow (blank is yellow-orange):

L a n t h a n u m: Sensitivity: 1 mg. La p. l.

(Aluminum does not react, but decreases the sensitivity of the lanthanum reaction.)

C o b a l t: Sensitivity: 100 mg. Co p. l.

N i c k e l: Sensitivity: 100 mg. Ni p. l.

C o p p e r: Sensitivity: 0,4 mg. Cu p. l.

Therefore the test is very delicate for lanthanum and copper.

Finally it may be mentioned that E. EEGRIWE[8]) mentions toluylene orange R(S), azoblue (By), diaminereinblue F. F. as sensitive reagents for magnesium. Nickel and cobalt again behave like magnesium.

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[8]) E. EEGRIWE, Z. anal. Chem. **76**, 354 (1929).

Summary.

The application of several dyestuffs for the detection of magnesium in strongly alkaline medium has been examined. In all cases cobalt and nickel give the same test as magnesium and manganese in some. Methods for the sensitive detection of magnesium in presence of other cations have been discussed.

Titan yellow is a very delicate reagent for magnesium and more specific than 1·2·5·8 oxyanthraquinone. The latter reacts also with beryllium, lanthanum and cadmium, whereas these elements do not form a colored compound with titan yellow.

A mixture of titan yellow and magnesium chloride can be used as a reagent for hydroxyl ions; the sensitivity being dependent upon the magnesium concentration. The reaction can also be applied as a spot test on filter paper.

Anilin yellow S (Kahlbaum) reacts very sensitively with lanthanum and copper in weakly acid medium (acetate buffer p H around 5,0).