Some New Applications of Urotropin, Ammonia and Hydrazine as Micro-chemical Reagents.

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The formation of complex or molecular compounds is being widely utilized as means for micro-chemical identification of elements. As is well-known most of these complex or molecular compounds are characterised by well-developed crystal patterns. This can in no small measure be attributed to the nature of the compounds themselves. The crystal-unit of even a simple compound may be favourably compared with the structure of a complex molecule, the constitutent building stones of the unit being arranged in a definite geometrical pattern round one another. This geometrical relationship being one of the prominent factors governing the formation of complex molecular compounds it can reasonably be expected that they would give rise to crystals of highly developed and distinctive character — a property most suitable for micro-chemical identification. This resemblance between the crystal-unit of a simple compound and the structure of a molecular compound may also be regarded as the effect of the close similarity between the forces holding together the building stones of the crystal unit of a simple molecule and the individual members of a molecular compound.

In the present paper some new micro-chemical tests based on the formation of molecular compounds with urotropin, ammonia and hydrazine are described. Some of these may be profitably

uitilized as characteristic tests for the elements in question and the others will be of no small help in individual identification.

Hexamethylene-tetramine has been used by several investigators as a micro-chemical reagent as it readily forms a large number of well-crystalline molecular compounds of a low order of solubility with various simple and complex metallic salts and acids. VIVARIO and WAGENAAR[1]) and to a limited extent, as well as COLE[2]) have described a number of micro-chemical tests with urotropin for the elements Pt, Ir, Pd, Au, Os, Sb, Bi, Mo, W, Sn, Y, Er, Be, Zr, V, Th, Ag, Hg, and with less satisfactory results for Ca, Mg, Fe and Mn. A critical discussion of these works has already been made by MARTINI[3]). So we refrain from making any further observations on the same.

MARTINI (loc. cit.) himself has described certain tests with Urotropin sulfate and urotropin for the elements like Co, Cu, Zn, Fe, V, Mo and In. He employed NH_4SCN and Urotropin sulfate for Co, Cu, Zn, Fe and V and NH_4SCN and Urotropin only in presence of nitric acid for Mo and In. He has suggested that Co, Cu and Zn in these cases form complex compounds with Urotropin of the general formula

$$\left[\begin{matrix} SCN \\ M^{II}\,(SO_4)_2 \\ C_6H_{12}N_4 \end{matrix}\right].$$

Such a composition is extremely improbable even from theoretical considerations as five negative units of affinity of two sulfate and one thicyanate radicals can under no circumstances be satisfied by a bivalent metallic atom. Even if we assume that the urotropin molecule acts as a monovalent base the difficulty is not eliminated. Not only this but we have also found that if sulfuric acid be replaced by any other acid like HCl the same compounds with properties as described by MARTINI are obtained. As a matter of fact, the compounds are simply double or complex thiocyanates of which the cobalt and copper compounds of the

[1]) VIVARIO and WAGENAAR, Pharmac. Weekbl., **54**, 157 (1917); Ztschr. f. analyt. Chem., **58**, 228 (1919), and **67**, 298 (1925).

[2]) COLE, Philippine Journ. of Science, **22**, 631—37 (1923).

[3]) MARTINI, Mikrochemie, **VI**, 28 (1928).

composition $M(SCN)_2$, $2C_6H_{12}N_4$, HSCN have already been described by CALZOLARI[4]). We have further found that similar compounds are also formed by Mn, Zn, and Cd; the properties of the zinc compound are identical with those described by MARTINI. Even without the addition of any acid, Urotropin forms beautifully crystalline compounds with the thiocyanates of ferrous iron, cobalt, nickel, manganese and cadmium of the composition $M^{II}(SCN)_2$, $2\,C_6H_{12}N_4$, $4\,H_2O$ (BARBIERI and CALZOLARI[5]). The crystalline properties of these compounds which are all birefringent and are isomorphous have been studied by EDOARDO BILLOWS[6]). We have found that these latter compounds are more suitable for micro-chemical purpose than the previous acid-compounds as very careful adjustement of the acid concentration and the quantity of ammonium thiocyanate accompanied by frequent scratching is necessary in inducing the crystal formation. Though as a rule however, the acid-compounds are much less soluble than the simple molecular compounds of Urotropin and the metallic thiocyanates. As an illustration the crystalline form of the cobalt thiocyanates-urotropine-compound is shown in the table.

The iron and Vanadium compounds described by MARTINI also appear to be double or complex thiocyanates corresponding to the Cobalt, copper and Zinc compounds and in these cases also sulfuric acid can conveniently be replaced by hydrochloric acid.

KORENMAN[7]) has also described a number of micro-chemical tests with Urotropin for the heavy metals like Ag, Pb, Hg^{II}, Hg^{I}, Cd, Bi, Sb, Cu and Sn. He, further, found that by the addition of KY, KBr, or NH_4SCN, the sensitiveness of the reaction in some cases can be considerably enhanced. But as most of these reactions have already been described by VIVARIO and WAGENAAR as well as by COLE it is necessary here to make any more than a bare mention of the same. In the present paper we have, howerver, described a certain entirely new micro-chemical tests with Urotropin for the elements Mg, Ca and Li using the complex ferro-, ferricyanide,

[4]) CALZOLARI, Ber., **43**, 2217 (1910).

[5]) BARBIERI and CALZOLARI, Atti R. Accad. Lincei, **V**, 20, i, 119—125 (1911).

[6]) EDOARDO BILLOWS, Riv. Min. Cryst. Ital., **39**, 3—20 (1909).

[7]) KORENMAN, Pharm. Zentr., **70**, 709—14 (1929).

nitroprusside and thiosulfato-cobalti-penta-cyanide of these metals. The reactions are highly sensitive and the compounds formed in presence of excess of urotropin are almost insoluble and in some cases the crystals formed are exceptionally beautiful. The compounds formed may be regarded as associated complex of the second order. The exact composition and nature of these compounds could not be studied in details at present.

Another entirely new test for Mo with Urotropin in presence of sulfuric acid has also been described. Further a number of micro-chemical tests with urotropin for Mg, Mn, Co, Ni and Ag in presence of sodium dithionate have been studied. Of these Mg, Mn, Co and Ni compounds which are isomorphous have been described by CALZOLARI[8]). The silver compound has not yet been described in the literature. These compounds are all very sparingly soluble in presence of Urotropin and hence serve as useful means for micro-chemical identification. Along with this is described a micro-chemical test for Hg with Urotropin which depends upon the formation of compound of mercuri-iodic acid with latter. This compound has already been described by as RÂY and SARKAR[9]).

A beautiful micro-chemical test for Cu depending on the formation of fine blue needles of ammoniacal cupric thiocyanate is described.

Finally, two more test for Zn and Cd with NH_4SCN and N_2H_4 have been added.

Magnesium.

1. With K_3FeCy_6 and Urotropin: Into a drop of urotropin solution containing about 15 per cent urotropin placed on an object glass, a tiny droplet of a magnesium salt solution (1 : 100) at the end of a small platinum loop introduced. Then a minute drop of a dilute K_3FeCy_6 solution also at the end of a platinum loop was brought into contact with the mixed solution. A yellow precipitate at once formed which under the microscope showed as then transparent yellow plates clustered together in

[8]) CALZOLARI, Atti, R. Accad. Lincei, **V**, 22, i, 787—792.

[9]) RÂY and SARKAR, J. C. S., 390 (1921).

different planes. Examined under the crossed nicols the crystals exhibited oblique extinction.

The minimum quantity of magnesium that can be definitely recognised by this means has been found to be 0,0005 μg. Mg (Erfassungsgrenze). If the magnesium solution be extremely dilute a comparison should be made side by side with the blank reagents. Large quantities of calcium salts, however, interfere with the test due to the formation of corresponding calcium compound, which, however, crystallises in stout prismatic needles. Ba, Sr and Li do not interfere as they give only octahedral crystals. The form of the crystals is shown in Fig. 1 of the table.

2. With K_4FeCy_6 and urotropin: As before, a drop of the urotropin solution (1 : 6) was placed on an object glass and a platinum loop dipped into a dilute solution (1 : 100) of a magnesium salt was then brought into contact with the urotropin solution. Then a tiny crystal of a finely powdered K_4FeCy_6 at the end of a platinum wire was placed at the edge of the drop on the object glass. The cream-colored precipitate which formed at once showed under the microscope a large number of octahedral crystals which readily lost their sharp contours and edges and degenerated into circular and elliptical shapes (Fig. 2). The limit of sensitivity (Erfassungsgrenze) of the reaction has been found to correspond to 0,002 μg. Magnesium. Large quantities of calcium salts, if present, will interfere with the test due to the formation of the corresponding calcium compound; the quadratic plates of calcium potassium ferrocyanide can easily be distinguished if formed and they never appear in the presence of an excess of urotropin. It can be conducted in the presence of Ba and Sr which only give quadratic plates with K_4FeCy_6. Lithium, too, if not in large quantities does not interfere as it forms only stars and bushels of needles. The formation of magnesium ferrocyanide crystals (FEIGL)[10]) do not interfere.

3. With Sodium nitroprusside and urotropin: The procedure for this test was identical with that adopted in the previous case with K_4FeCy_6. The light rose-red precipitate obtained showed a large number of crystals in stars, crosses and stout rectangular prisms with pointed ends under the microscope

[10]) FEIGL, Mikrochemie, **II**, 86 (1924).

(Fig. 3). They were found to be optically isotropic when examined under the crossed nicol and hence belong to the regular system. The limit of sensitivity has been determined and corresponds to 0,008 μg. Mg. The test should not be relied upon in presence of Ca which also gives similar crystals. Reagents alone also give similar crystals, at the edges of the drop when the latter is nearly dried up (RÂY and SARKAR, loc. cit.). Crystals formed by the reagents alone are, however, extremely soluble and can be distinguished without much difficulty from those formed with magnesium salts.

4. With potassium thiosulfato-cobalti-pentacyanide, and urotropin: The preparation and properties of the reagent, potassium thiosulfato-pentacyano-cobaltiate

$$K_4\left[Co\begin{matrix}S_2O_3\\(CN)_5\end{matrix}\right]$$

have been described by one of us (RÂY)[11]). This micro-chemical test for magnesium was conducted exactly in the same way as with the two previous reagents under (2) and (3). The yellow precipitate formed at once showed a large number of short bushels of needles under the microscope and when examined under the polarised light were found to be optically isotropic. The limit of sensitivity (Erfassungsgrenze) corresponds to 0,008 μg. Mg. The test can be conducted in presence of Ba, Sr, Li and Ca, though the last named metal also gives certain crystals which, however being of a different shape can be easily eliminated.

5. With dithionate and urotropin: A drop of sodium dithionate solution (1 : 20) was placed on an object glass and a platinum loop after being dipped in a magnesium salt solution (1 : 100) was plunged into the above drop. This was then touched with a tiny crystal of urotropin at the end of a platinum wire. The white precipitate obtained when examined under the microscope showed a large number of colorters, transparent prismatic plates (Fig. 5). When examined under crossed nicols they were found to give an oblique extinction. The limit of sensitivity corresponds to 0,004 μg. Mg. The composition of the compound is given by the formula MgS_2O_6, $2(CH_2)_6N_4$,

[11]) RÂY, Journ. Ind. Chem. Soc., vol. 5, 325 (1927).

$6H_2O$ (CALZOLARI, loc. cit.). The test should not be conducted in presence of Ca which also gives similar crystals though the latter are very soluble. Co, Ni and Mn also give similar crystals as described below.

Of the five tests for magnesium described above which are of extreme sensitive character note I, 2 and 4 can be conveniently employed as distinctive tests for the element either alone or in combination, if necessary. The ferricyanide-urotropin test seems to exceed all the known micro-chemical tests for magnesium in its sensitivity.

Calcium.

With K_3FeCy_6 and urotropin: The same technique was followed as under the corresponding magnesium reaction. The yellow precipitate which appeared at once when examined under the microscope was found to consist of a large number of thick beautiful yellow prismatic needles (Fig. 6). They exhibit oblique extinction under the crossed nicols. The sensitivity (Erfassungsgrenze) was found to correspond to 0,008 μg. Ca. If the solution of calcium be very dilute nearing the limit stated, it should be compared with the blank reagents. Calcium gives crystalline precipitate also with potassium thiosulfato-cobalti-penta-cyanide and urotropin, the crystals resembling the magnesium-ferricyanide-urotropin compounds in appearance. With sodium nitroprusside and urotropin also it gives a crystalline precipitate similar to the corresponding magnesium compound. But they do not possess any special advantage from micro-chemical standpoint and we refrain from giving any detailed account of them.

Lithium.

1. With K_3FeCy_6 and Urotropin: The method of procedure was exactly similar to that employed for the corresponding calcium and magnesium tests. The yellow precipitate formed examined under the microscope appeared to consist of large yellow beautiful octahedral crystals (Fig. 7).

The sensitivity-limit corresponds to 0,065 μg. Li.

Reagents alone also give octahedral crystals (RÂY and SARKAR loc. cit.) when the solution becomes saturated. Hence

when testing for Li in very dilute solution a comparison should always be made with the blank reagents. Ba and Sr also give similar crystals and hence they should be previously removed if present.

2. With K_4FeCy_6 and Urotropin: The method of procedure was identical with that for the corresponding magnesium test. The cream-colored precipitate under the microscope showed a large number of needles and bushels of needles which were found to be optically isotropic when examined in polarised light (Fig. 8). The sensitivity-limit corresponds to 0,065 μg. Li.

Molybdenum.

To a drop of N or N/2 sulfuric acid placed on the middle of an object glass, is added a minute amount of ammonium molybdate solution containing 1 per cent Mo, by means of a platinum loop. The drop is then touched with a tiny crystal of urotropin at the end of a platinum wire. The white precipitate which formed immediately showed a large number of transparent long beautiful needles under the microscope and gave oblique extinction under crossed nicols (Fig. 9). The sensitivity-limit corresponds to 0,065 μg. Mo. The substance seems to be a compound of molybdisulfuric acid with urotropin whose exact composition has not yet been determined.

Silver.

The procedure is identical with that for the corresponding magnesium test described before (No. 5). The white precipitate which formed at once showed under the microscope a large number of rectangular plates readily clustering together into flowery figures (Fig. 10). When examined with polarised light they were found to be feebly birefringent and to give oblique extinction. The sensitivity-limit was found to correspond to 0,065 μg. of Ag. The exact composition of the compound formed is not determined for the present.

Manganese.

With Sodium dithionate and Urotropin: The technique is the same as with silver. The sensitiviy-limit amounts

to 0,02 μg. Mn. The composition of the crystals is identical with that of the corresponding magnesium compound already described. They appear to consist of transparent prisms with oblique extinction (Fig. 11).

Nickel.

With Sodium dithionate and urotropin: The technique is the same as for manganese and the form of the light green crystals and their composition are also similar (Fig. 12).

The sensitivity-limit corresponds to 0,15 μg. Ni.

Cobalt.

1. With sodium dithionate and urotropin: The technique is the same as with Ni and Mn. The form of the light red crystals and the composition of the compound are also similar to those of Ni and Mn. The sensitivity-limit corresponds to 0,02 μg. Co (Fig. 13).

2. With ammonium thiocyanate and urotropin: A saturated solution of urotropin was mixed with an equal volume of a 2 per cent NH_4SCN solution. A drop of this was placed on the middle of an object glass. The drop was then touched with a platinum loop previously dipped into a cobalt solution (1 : 100). A large number of square tablets appeared under the microscope. The properties of the crystals exhibiting oblique extinction under crossed nicol have been already described by EDOARDO BILLOWS (loc. cit.) (Fig. 14). The sensitivity-limit corresponds to 0,15 μg. Co. Identical crystals with similar composition are also given by Ni, Cd and Mn.

Mercury.

Concentraded HCl was mixed with thrice ils volume of KY solution (1 : 20). A drop of this solution was placed on the middle of an object glass. A platinum loop soaked in $HgCl_2$ solution (1% Hg) was then dipped into it. The light yellow precipitate which formed at once appeared under the microscope to consist of a large number of prismatic crystals which showed weak birefringence under crossed nicol (Fig. 15). The sensitivity-limit corresponds to 0,035 μg. Hg. The composition of the crystals

which has been already described by us (RÂY and SARKAR, loc. cit.) is $2HHgJ_3$, $3C_6H_{12}N_4$. COLE has also described a test for mercury with KY and urotropin in neutral solution (loc. cit.).

Copper.

With NH_4SCN and Ammonia. Into a drop of NH_4SCN solution (1 : 20) placed on an object glass, a platinum loop previously soaked in a copper solution (1% Cu) was dipped. The object glass was then inverted over the mouth of a bottle containing liquor ammonia so that the drop was saturated with ammonia. The latter was then examined under the microscope. A large number of long beautiful blue needles appeared shortly (Fig. 16). They were found to exhibit parallel extinction and belonged to the rhombic system.

The composition of the compound is given by the formula $Cu(SCN)_2$, $2NH_3$ (GROSSMANN[12]).

The sensitivity-limit corresponds to 0,065 μg. Cu.

Zinc.

With NH_4SCN and Hydrazine: Equal volumes of NH_4SCN solution (1 : 20) and hydrazine hydrate solution (1 : 25) were mixed together. Into a drop of this solution on the object glass, a platinum loop previously dipped into a zinc solution (1% Zn) was introduced. A white precipitate appeared which under the microscope showed a large number of characteristic colorless crystals (Fig. 17). They were found to exhibit oblique extinction when examined in the polarised light. The sensitivity-limit corresponds to 0,15 μg. Zn.

The composition of the substance has already been described by us (RÂY and SARKAR)[13]) and is $Zn(SCN)_2$, $2N_2H_4$.

Cadmium.

With the same technique as under Zn, the same type of crystals of similar composition was obtained. (RÂY and SARKAR, loc. cit.) (Fig. 18). The sensitivity-limit for Cd is 0,065 μg.

[12]) GROSSMANN, Anorg. Chem., **58**, 269 (1908).

[13]) RÂY and SARKAR, J. C. S., 321 (1920).

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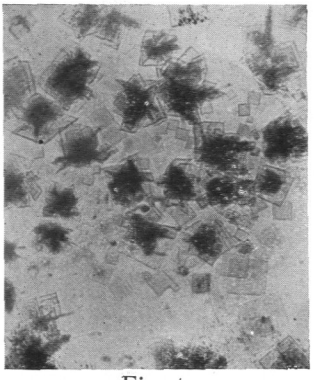

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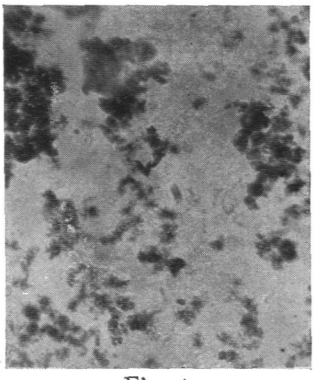

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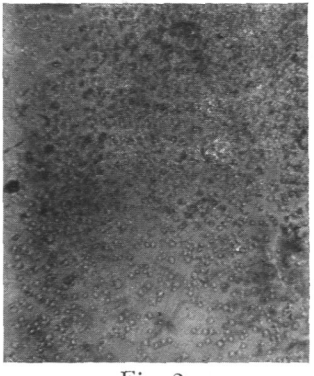

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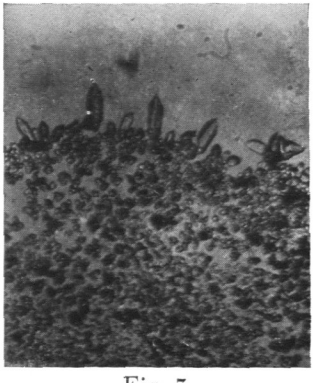

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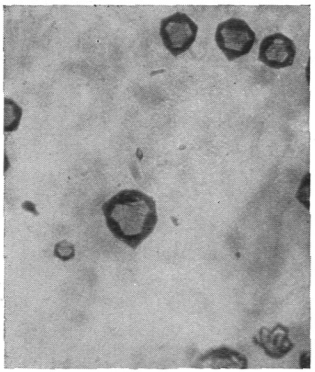

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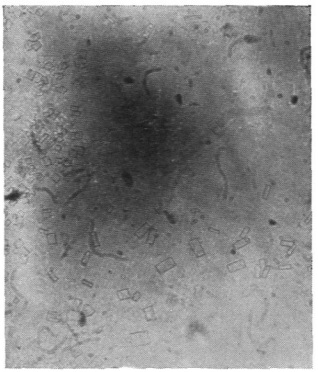

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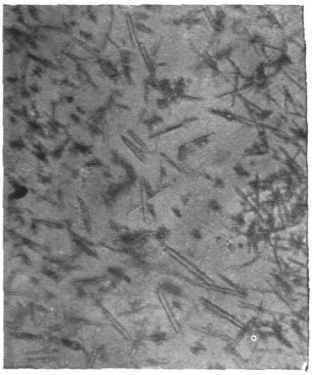

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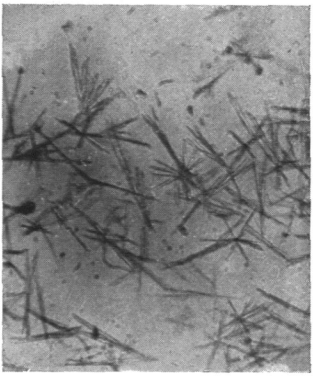

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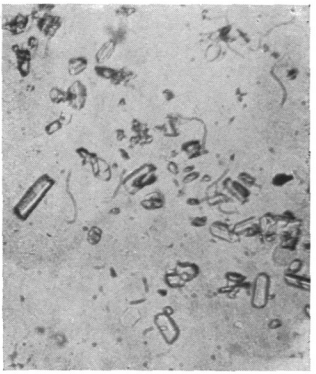

Fig. 12.

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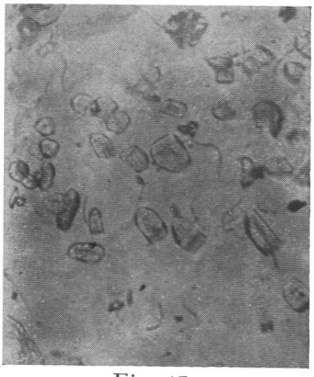

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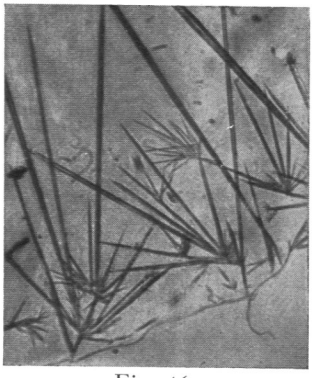

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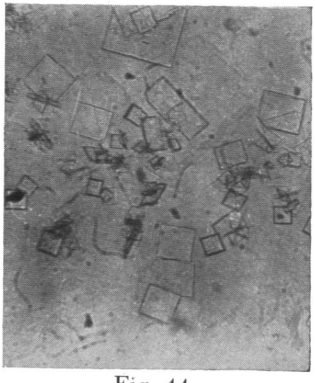

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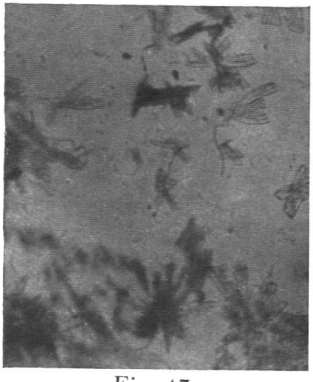

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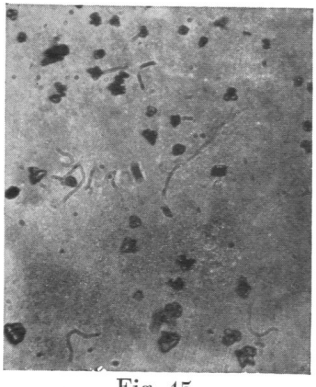

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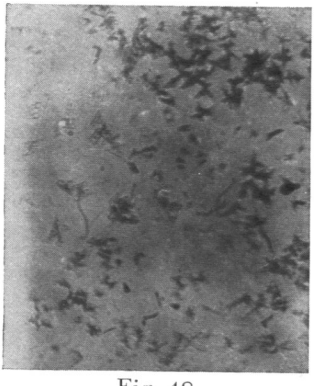

Fig. 18.

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In conclusion a table showing the sensitivity-limit of all the reactions here described is given below:

Name of the Element:	Reagents	Sensitivity-limit	Fig. No. in the plate:
Magnesium . .	$K_3FeCy_6 + (CH_2)_6N_4$	0,0005 μg.	1
Magnesium . .	$K_4FeCy_6 + (CH_2)_6N_4$	0,002 μg.	2
Magnesium . .	$Na_2FeCy_5(NO) + (CH_2)_6N_4$	0,008 μg.	3
Magnesium . .	$K_4Co(S_2O_3)Cy_5 + (CH_2)_6N_4$	0,008 μg.	4
Magnesium . .	$Na_2S_2O_6 + (CH_2)_6N_4$	0,004 μg.	5
Calcium	$K_3FeCy_6 + (CH_2)_6N_4$	0,008 μg.	6
Lithium	$K_3FeCy_6 + (CH_2)_6N_4$	0,065 μg.	7
Lithium	$K_4FeCy_6 + (CH_2)_6N_4$	0,065 μg.	8
Molybdenum . .	$H_2SO_4 + (CH_2)_6N_4$	0,065 μg.	9
Silver	$Na_2S_2O_6 + (CH_2)_6N_4$	0,065 μg.	10
Manganese . . .	$Na_2S_2O_6 + (CH_2)_6N_4$	0,02 μg.	11
Nickel	$Na_2S_2O_6 + (CH_2)_6N_4$	0,15 μg.	12
Cobalt	$Na_2S_2O_6 + (CH_2)_6N_4$	0,02 μg.	13
Cobalt	$NH_4SCN + (CH_2)_6N_4$	0,15 μg.	14
Mercury	$HI + (CH_2)_6N_4$	0,035 μg.	15
Copper	$NH_4SCN + NH_3$	0,065 μg.	16
Zinc	$NH_4SCN + N_2H_4$	0,15 μg.	17
Cadmium . . .	$NH_4SCN + N_2H_4$	0,065 μg.	18