

**249.** *Qualitative Semimicro-analysis with Reference to Noyes and Bray's System: Partial Analysis of the Combined Nickel, Zirconium, and Rare-earth Groups.*

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A scheme of analysis is presented for the detection and approximate determination of 0.25—50 mg. of manganese, cobalt, or nickel, 0.25—10 mg. of titanium, zirconium, indium, or scandium, and a small amount of zinc (minimum 0.25 mg.) in solutions containing a maximum of 50 mg. referred to the metals. These include all the more important elements present in the combined nickel, zirconium, and rare-earth groups of Noyes and Bray's scheme. The maximum amount of any one rare-earth group metal is 10 mg. In separate portions of the solution, manganese, cobalt, nickel, titanium, and zirconium are detected, respectively, by means of potassium periodate, ammonium thiocyanate and extraction with butyl acetate, dimethylglyoxime, chromotropic acid, and *p*-hydroxyphenylarsonic acid. In a sixth portion zinc is separated from cobalt and more than 1 mg. of nickel, and tested for with copper sulphate and ammonium mercury thiocyanate. Finally, in a seventh portion indium and scandium are isolated. Indium is precipitated as indium sulphide and confirmed with alizarin, and scandium detected by means of alizarin-S or morin.

SCHEMES for the analysis on a semimicro-scale of seven groups of Noyes and Bray's system ("A System of Qualitative Analysis for the Rare Elements," 1927) have already been reported by Miller and Lowe (*J.*, 1940, 1258, 1263) and Miller (*J.*, 1941, 72, 786; 1943, 72). This paper describes the further application of semimicro-analytical methods to the detection of manganese, cobalt, nickel, zinc, titanium, zirconium, indium, and scandium in a group containing all the more important metals associated with the nickel, zirconium, and rare-earth groups of Noyes and Bray's scheme.

After removing metals precipitable by hydrogen sulphide in acid solution, Noyes and Bray precipitate those of the ammonium sulphide group in two separate operations. From one precipitate iron, gallium, and components of the aluminium group are eliminated, leaving indium, zirconium, and titanium (zirconium group), some rare-earth group metals, and traces of cobalt, nickel, and zinc. From the other precipitate components of the aluminium group are removed, leaving manganese, cobalt, nickel, and a little zinc (nickel group), and some rare-earth group metals. In the course of analysis of the second precipitate the rare-earth group portion is separated and added to the first precipitate, from which the whole rare-earth group (scandium, thorium, yttrium, lanthanum, cerium, etc.) is extracted before the zirconium group proper is analysed. A variable amount of indium is located in the rare-earth group so that the metal has to be tested for twice.

The method of analysis used here is entirely different. It is supposed that the above precipitates are dissolved in hydrochloric acid and the solutions combined to give a mixture inclusive of all the components of Noyes and Bray's three groups. The mixtures considered here may contain any of *e.g.*, manganese, cobalt, nickel, titanium, zirconium, zinc, indium, scandium, thorium, yttrium, cerium, lanthanum, neodymium, and praseodymium. In portions of them the first five, and sometimes zinc, are tested for directly. Indium and scandium, and zinc in certain circumstances, are detected after they have been freed from interfering elements. In this connection organic solvents as extractants play an important part. As

in earlier papers the experimental conditions described permit the detection of the above metals in accordance with the limits set forth in the summary. Provision is made for the presence of group contaminants, *e.g.*, iron, gallium, and members of the aluminium group. Because of scarcity of material the question of the detection of hafnium, which behaves like zirconium, has not yet been considered, and other rare-earth metals have not been taken into account.

Particulars regarding the isolation of the rare-earth group of metals from one half of the above mixtures, and the subsequent analysis of the group, will, it is hoped, be given later.

#### EXPERIMENTAL.

*Preparation of the Group for Analysis.*—Mixtures containing chlorides or nitrates of the various metals and some hydrochloric acid were evaporated just to dryness and taken up in 1 ml. of 6*N*-hydrochloric acid.

#### *Nickel, Zirconium, and Rare-earth Groups.*

(The figures in parentheses are referred to in "Notes on Methods and Tests.")

*Solution.*—Contains cobalt, manganese, nickel, titanium, zirconium, zinc, indium, scandium, thorium, yttrium, lanthanum, cerium, neodymium, and praseodymium as chlorides in 1 ml. of 6*N* hydrochloric acid. Test separate portions as follows :

(a) Test 1% for Co in a test-tube ( $\frac{3}{8}$ "  $\times$  3"). Add 0.15 ml. of solution, 2*N* in HCl, add 10–20 mg. of NH<sub>4</sub>F and NH<sub>4</sub>SCN in large excess. Add 0.2 ml. of *n*-butyl acetate and shake briskly. A blue colour in the ester shows **Co**. Increase the ester to a maximum of 2 ml. when much Co is present. Compare with standards. (1.)

(b) Test 1% for Mn in a 5-ml. beaker. Add 0.05 ml. of H<sub>3</sub>PO<sub>4</sub> (88%) and expel HCl by evaporating on the hot-plate. Then add 1 ml. of 2*N*-HNO<sub>3</sub> and 10 mg. of KIO<sub>4</sub>, and keep the solution at the boiling point in the covered beaker for at least 15 mins., keeping the volume constant by additions of water. A purple colour shows **Mn**. Centrifuge if necessary and compare with standards. (2.)

(c) Test 1% for Ni in a 0.5-ml. centrifuge tube. Add 0.1 ml. of 12% aqueous citric acid and 0.05 ml. of ammonia (*d* 0.88). Heat to 80°, add 0.05 ml. of 5% aqueous dimethylglyoxime (Na salt)—allow more for Co (0.1 ml. per 0.5 mg.)—stir thoroughly, and heat further for 1 min. If a red precipitate due to **Ni** appears, ensure complete precipitation, then centrifuge without cooling, separate the precipitate, dissolve it in 2*N*-HCl, and reprecipitate as before. Compare with standards. (3.)

(d) Test 0.25–1% for Ti on a spotting tile. Add 0.04 ml. of 0.2*M*-SnCl<sub>2</sub> in *n*-HCl and 0.05 ml. of 1% chromotropic acid in concentrated H<sub>2</sub>SO<sub>4</sub>. Compare a violet colour, which shows **Ti**, with standards. (4.)

(e) Test 5% for Zr in a 1-ml. centrifuge tube. Make 0.25 ml. of solution, 4*N* in HCl, add 0.05 ml. of perhydrol if Ti is present, heat, and add 0.1 ml. of 4% aqueous *p*-hydroxyphenylarsonic acid. Heat in boiling water for 2 mins. and centrifuge. If a precipitate is present, separate it and add 0.05 ml. of perhydrol and 0.1 ml. of 2*N*-NaOH. Stir up, centrifuge, separate Zr(OH)<sub>2</sub> and dissolve it in 0.1 ml. of 10*N*-HCl and 0.1 ml. of water. Treat with *p*-hydroxyphenylarsonic acid as before. A white precipitate shows **Zr**. Centrifuge and compare with standards. (5.)

(f) Test 10% for Zn. (i) Co absent, Ni < 100 μg. Make 0.25 ml., *N* in HCl, in a 0.5-ml. centrifuge tube, add 0.01 ml. of 0.01*M*-CuSO<sub>4</sub> and 0.1 ml. of ammonium mercury thiocyanate reagent (30 g. of HgCl<sub>2</sub> and 33 g. of NH<sub>4</sub>SCN in 100 ml. of water). Stir briskly and centrifuge. A black or violet precipitate shows **Zn** which should be compared with standards. (6.)

(ii) Ni > 100 μg., and/or Co present. Make 0.5 ml., 2*N* in HCl, in a "Pyrex" test-tube ( $\frac{3}{8}$ "  $\times$  3"), add a large excess of NH<sub>4</sub>SCN and 100 mg. of NH<sub>4</sub>F, and extract twice with 1 ml. of *n*-butyl acetate. Evaporate the combined extracts, with the aid of an air current, in a "Pyrex" test-tube placed in boiling water. Next cautiously decompose the thiocyanates with concentrated HNO<sub>3</sub>, and finally heat in a flame (air current still flowing) until all volatile products are expelled.

If Co is absent, dissolve the residue in 0.25 ml. of *N*-HNO<sub>3</sub> and test for Zn as in (i). If < 500 μg. of Co is present, add 0.2 ml. of water, 0.2 ml. of 2*N*-NaOH, and a drop of 3% H<sub>2</sub>O<sub>2</sub>, boil, centrifuge, remove the solution, and add to it 0.04 ml. of concentrated HNO<sub>3</sub>. Test for Zn as in (i).

If > 500 μg. of Co is present, add to the residue 0.1 ml. of water and just enough 10% aqueous KCN to convert Co into a soluble complex. Add 1 drop of perhydrol and boil for a few mins. to form cobalticyanide. Then add glacial acetic acid in 20% excess by volume, and 0.05 ml. of 10% aqueous potassium cobalticyanide, and heat. If a turbidity appears heat further to coagulate. Separate and wash the precipitate, which may be zinc cobalticyanide, without stirring it up, in 2*N*-acetic acid. To confirm Zn add to the precipitate 0.05 ml. of 4*N*-H<sub>2</sub>SO<sub>4</sub>, heat until fumes of H<sub>2</sub>SO<sub>4</sub> appear and the precipitate is dissolved, and proceed with the removal of Co and the final test for Zn as above. (7.)

(g) Test 10% for In and Sc in a test-tube ( $\frac{3}{8}$ "  $\times$  3"). Add 0.05 ml. of 10*N*-HCl, 0.05 ml. of water, and 0.3 ml. of 10% aqueous cupferron. Extract thrice with 1 ml. of chloroform. To the residual aqueous layer add a large excess of NH<sub>4</sub>SCN and extract twice with 1 ml. of *n*-butyl acetate. Wash the combined extracts with 0.05 ml. of 2*N*-HCl, saturated with NH<sub>4</sub>SCN. Expel the ester, destroy thiocyanates, and remove volatile products as described under (f, ii). Dissolve the residue in 0.15 ml. of water, make approximately neutral, and add sufficient 10% aqueous KCN to convert Co and Zn into soluble complexes. Add a drop of perhydrol, boil, add a few drops of 2*N*-NaOH, and reboil for a short time. If a precipitate [In(OH)<sub>3</sub> and Sc(OH)<sub>3</sub>] appears, separate it, wash it with hot water, and dissolve it in 0.5 ml. of 2*N*-acetic acid. (8.)

(i) Test for In. Into the hot solution pass H<sub>2</sub>S for 10 mins. A yellow precipitate shows **In**. Centrifuge and determine it. If desired, confirm a small precipitate, after washing it, with alizarin. (9.)

(ii) Test for Sc in the centrifugate from In<sub>2</sub>S<sub>3</sub>. H<sub>2</sub>S must be absent for test (β).

(a) To 0.25 ml. of 2*N*-acetic acid add 0.01 ml. of 1% aqueous alizarin-S and 0.05 ml. of the test

solution, and set aside for 5 mins. If no pink colour is observed add more test solution gradually up to a maximum of 0.25 ml., and more reagent if necessary. If a pink colour due to **Sc** appears readily, add additional reagent gradually. Should the colour become too deep a red, repeat the experiment with less of the test solution. Compare with standards. Allow 20 mins. for full colour development. (10.)

(β) To 0.25 ml. of 2*N*-acetic acid add 0.01 ml. of morin (0.02% in acetone) with which **Sc** shows a green fluorescence in ultra-violet light. Gradually add the test solution, up to a maximum of 0.25 ml. if necessary, until a match is obtained with a standard containing between 1 and 50 μg. of **Sc**. (11.)

(h) Reserve 50% for the isolation of the rare-earth group.

*Notes on Methods and Tests.*—The experimental technique has been described in earlier papers of the series.

*Note 1.* The amount of ammonium thiocyanate was such that some remained undissolved throughout the extraction process. The ammonium fluoride masked titanium (0.5 mg.) and group contaminants, *e.g.*, iron, vanadium, and uranium. 0.5 μG. of cobalt was detectable in 0.2 ml. of ester. The extraction of cobalt was highly efficient, and 2 ml. of ester were used merely when the colour was otherwise too dark for matching purposes. The detection of 1 μg. of cobalt was not affected by the presence of at least 1 mg. of any of its associates, or of any member of the aluminium group (Al, Be, Cr<sup>VI</sup>, W<sup>VI</sup>, U<sup>VI</sup>, V<sup>V</sup>), or of iron or gallium. Cobalt was not retained by the precipitated fluorides of the rare-earth metals.

*Note 2.* The limit of identification of manganese was 0.5 μg., and 50 μg. was the maximum desirable for the comparison of colours. The solution could be further diluted with water. 2 μG. of manganese were found in association with 1 mg. of any of the elements mentioned in Note 1, except chromium (VI), of which only 100 μg. were permissible without the preparation of a blank experiment. Phosphate precipitates deposited by titanium, zirconium, and cerium, especially the last, tended to retain a little manganese.

*Note 3.* Ammonium citrate held all the metals in solution. 0.5 μG. of nickel was detectable. Excess of dimethylglyoxime commonly separated out from cold solutions without seriously affecting estimations. Nickel was detectable in association with at least a 1000-fold excess of the metals cited in Note 1, including cobalt, if sufficient reagent was present. Iron and cobalt together may form a brown precipitate with dimethylglyoxime. 25 μG. of iron, which is much more than one would expect to have here, did not upset the detection of 1 μg. of nickel in the presence of 1 mg. of cobalt, if prolonged boiling was avoided. Reprecipitation of the nickel complex corrected for a marked diminution in the bulk of the precipitate, caused by other metals and especially cobalt.

*Note 4.* The final concentration of 50% sulphuric acid was chosen because, at lower concentrations, the sensitivity of the test was reduced, and, at much higher concentrations, the chromotropic acid itself gave too pronounced a colour, probably because of impurity. Stannous chloride prevented or reduced the interference of iron, vanadium, tungsten, and uranium. 0.5 μG. was just detectable, and 25 μg. were set as a maximum for determinations and for the amount of reagent recommended. Colours did not deteriorate within two hours. 2 μG. of titanium were detectable in the presence of at least a 1000-fold excess of any component of the group, or of aluminium, beryllium, gallium, or zinc; and 5 μg., with a 100-fold excess of chromium, iron, uranium, or vanadium, or a 10-fold excess of tungsten.

*Note 5.* This test was used for the detection of zirconium in the tantalum group. Precipitation was best effected in a solution 2–5*N* in hydrochloric acid, and 1 μg. of zirconium was just detectable. The maximum amount of titanium under consideration was held adequately in solution by perhydrol, provided that heating was not prolonged. The titanium complex, if inadvertently deposited, was readily soluble in a drop of hydrochloric acid and a drop of perhydrol, whereas even a small precipitate of the zirconium complex remained undissolved. Other metals in the solution might reduce the bulk of the complex. The reprecipitation process prevented under-estimation, and at the same time eliminated any titanium that might have been carried down. 5–10 μG. of zirconium were found in association with 100 times the amount of titanium. 2 μG. were detectable in the presence of at least a 1000-fold excess of any other group component, and also of iron, gallium, aluminium, beryllium, chromium, uranium, or vanadium.

*Note 6.* Zinc was detected in the aluminium group by this method. Nitric acid solutions are said to give superior results, but tests made in hydrochloric acid solution were very satisfactory also, 2 μg. of zinc being found. 10 μG. of zinc were detectable in association with at least a 100-fold excess of scandium, and a 500-fold excess of manganese, indium, zirconium, gallium, iron (more reagent needed), or rare-earth group metals. Only a 100-fold excess of titanium, which hindered the deposition, was permissible. Nickel greatly hindered the precipitation and a 5-fold excess only could be tolerated. Cobalt reacted with ammonium mercury thiocyanate and, in the presence of copper sulphate, violet and black precipitates like those for zinc might be obtained. Consequently cobalt had to be completely removed before zinc was tested for.

*Note 7.* The extraction of cobalt and zinc from thiocyanate-fluoride solutions by means of *n*-butyl acetate was essentially complete, and practically nothing except a little indium accompanied them, even when the maximum amounts of other metals were present. After the destruction of thiocyanates, and when cobalt was absent, the direct test for zinc was applicable. Experiments made with 25 μg. of zinc in association with varying amounts of cobalt showed that the separation of 0.5 mg. of the latter by means of sodium hydroxide involved the loss of 40% of the zinc. When, therefore, more than 0.5 mg. of cobalt was present it was converted into cobalticyanide, and zinc precipitated as zinc cobalticyanide. As a precipitate might be produced by traces of other metals, it was essential to dissolve it, separate cobalt, and test for zinc as above. In mixtures containing in addition to 25 μg. of zinc, 5 mg. of cobalt, nickel, manganese, or rare-earth group metals, or 1 mg. of each of titanium, zirconium, indium, and scandium, the amounts of zinc retrieved were 12, 10, 10, 20, and 25 μg., respectively. The low results were attributed to difficulty in recovering all the zinc cobalticyanide, which was very finely divided and separated extremely slowly.

*Note 8.* For indium and scandium no direct tests applicable in the presence or any or all of the group components were found. The tests for scandium required the absence of a great many elements, and that for indium, a considerable number. The series of simple operations prescribed separated indium and scandium, with comparatively little loss, from all the other members of the group and likely contaminants. For instance, cupferron and chloroform eliminated titanium, zirconium, iron, gallium, vanadium, and some rare-earth metals (Lundell and Hoffman, "Outlines of Methods of Chemical Analysis," 1938, 118). The butyl acetate extract contained indium, scandium, zinc, and cobalt, and contaminants, *e.g.*, aluminium, beryllium, uranium, and tungsten. By means of potassium cyanide and sodium hydroxide all of these except indium and scandium, which were precipitated as hydroxides, were taken into solution.

*Note 9.* The above separation of indium and scandium was so satisfactory that the precipitation of indium sulphide sufficed for the detection of the element, 5  $\mu\text{g}$ . being readily found. For a doubtful test [precipitate too pale (ZnS), or discoloured (CoS)] confirmation by means of alizarin (Wenger, *Helv. Chim. Acta*, 1945, **28**, 539) is recommended. The hydrochloric acid solution of the precipitate is spotted on drop-reaction paper which has been impregnated with alizarin (0.2% in alcohol), and the spot developed over concentrated ammonia. The paper is then momentarily dipped in 10% aqueous potassium cyanide and finally soaked in saturated aqueous boric acid. Indium leaves a violet-pink spot. The cyanide destroys colours initially produced by zinc and cobalt.

*Note 10.* The test with alizarin-S (Beck, *Mikrochim. Acta*, 1937, **2**, 9) must be made in a weakly acid solution. The colour develops slowly and its depth varies with the acid concentration. In 2*N*-acetic acid interference from rare-earth metals is prevented, and that from other metals minimised. Indium did not itself react but, in the presence of scandium, it intensified the colour. The limit of identification of scandium was 2  $\mu\text{g}$ ., and amounts in excess of 25  $\mu\text{g}$ . gave too deep colours for determination. 25  $\mu\text{g}$ . of scandium required fully 0.1 ml. of the reagent. An excess is undesirable because of its own colour.

*Note 11.* This test was described by Beck (*loc. cit.*). Under the prescribed conditions 1  $\mu\text{g}$ . of scandium was detectable. For determinations the upper limit was 50  $\mu\text{g}$ . Many other elements fluoresced, *e.g.*, thorium, zirconium, yttrium, indium, gallium, aluminium, beryllium, and zinc. A few quenched the fluorescence of scandium. The method of isolating scandium was, however, so satisfactory that the brightest fluorescence noted in mixtures containing 5 mg. of other elements, and no scandium, corresponded to <2  $\mu\text{g}$ . of scandium.

*Analysis of Mixtures.*—Eight mixtures were analysed in order to test the validity of the scheme. All contained, in addition to the normal group components, 0.5 mg. of each of iron, gallium, aluminium, and vanadium as contaminants. No. 5 contained 40 mg. of rare-earth group metals (Th, Y, Ce, La, and Pr); No. 7, 8 mg. of thorium and 1 mg. of lanthanum; and No. 8, 1 mg. of yttrium. The results shown in the table are the estimated weights in mg. of the metals found. Where these differed from the weights taken, the latter are shown in parentheses.

	Co.	Ni.	Mn.	Zn.	Ti.	Zr.	In.	Sc.
1	33 (44)	0.2 (0.25)	0	0.1 (0.25)	0.2 (0.25)	0.7 (1)	0	0.1 (0.25)
2	0.25	0.25 (0.5)	34 (28)	1 (2)	0.4 (0.5)	3 (4)	0.4 (0.5)	0.5
3	5 (6)	14 (12)	6 (7)	0	2.5 (4)	8 (9)	7 (6)	3 (4)
4	0.5	0	0.4 (0.5)	0	0	0.5	0.5 (1)	5 (7)
5	1.75 (1)	1.5 (2)	3	0.15 (0.25)	6	0	0.3 (0.5)	0.15 (0.25)
6	0	1.75 (1)	0	0	1	0	7 (10)	0.5 (1)
7	43 (32)	0	0.25	0.5 (1)	0	0	0	0
8	0	27 (36)	0.7 (1)	1 (0.5)	1 (0.5)	0.2 (0.25)	0.2 (0.25)	0

The results were considered satisfactory, and all the tests, except that for zinc in the presence of much cobalt, were expeditiously carried out. It would be a great advantage if one had a sensitive test applicable to the detection of zinc in these circumstances.

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