

## 25. *Qualitative Semimicro-analysis with Reference to Noyes and Bray's System : The Aluminium Group.*

By CHRISTINA C. MILLER.

A scheme of analysis for the metals composing the aluminium group of Noyes and Bray's system is presented for the detection and approximate estimation of 0.25—50 mg. of aluminium, chromium, or zinc, and 0.25—10 mg. of beryllium, tungsten, uranium, or vanadium, in mixtures containing phosphate and a maximum of 50 mg. referred to the metals. In separate portions of the solution zinc is precipitated as zinc (copper) mercury thiocyanate; beryllium, tungsten, and vanadium are detected, respectively, by means of morin, toluene-3 : 4-dithiol, and tannin; chromium (VI), after its separation from vanadium and tungsten, is tested for with diphenylcarbazide; and, finally, aluminium and zinc are separated from the bulk of the other metals. Aluminium is precipitated as caesium alum, and uranium, after further separations, as uranyl ferrocyanide.

SEMIMICRO-ANALYTICAL methods have already been applied by Miller and Lowe (J., 1940, 1258, 1263) and Miller (J., 1941, 72, 786) to six groups of Noyes and Bray's system ("A System of Qualitative Analysis for the Rare Elements," 1927). This paper describes their extension to the aluminium group. Benedetti-Pichler and Spikes (*Mikrochem.*, Molisch-Festschrift, 1936, 3, 36) have analysed the group on the micro-scale, and Fischer, Dietz, Brünger, and Grieneisen (*Angew. Chem.*, 1936, 49, 719) on a scale only a little smaller than Noyes and Bray's.

In Noyes and Bray's scheme the solution remaining after removal of the copper and the tellurium group is successively treated with ammonium acetate and ferric nitrate, and ammonium hydroxide and hydrogen sulphide, whereby two groups of metals are precipitated. When the acid solutions of these are treated with

sodium hydroxide and sodium peroxide, two alkaline extracts result, which are combined to form the aluminium group. It contains aluminium, beryllium, chromium, tungsten, uranium, vanadium, zinc, and phosphate, with perhaps a little contaminating titanium, and iron and gallium, if these have not been satisfactorily eliminated earlier. Phosphate is not tested for, but its influence on other tests must be known. Provision has therefore been made for the detection and estimation of the above seven metals, in mixtures containing phosphate, within the limits set forth in the summary.

The scheme presented differs considerably from those cited. For instance, beryllium, tungsten, vanadium, zinc, and chromium are tested for in separate portions of the group solution, the first four in a very direct manner. The importance of the toluene-3 : 4-dithiol test for tungsten (Hamence, *Analyst*, 1940, **65**, 152) is stressed. Benedetti-Pichler and Spikes stated that they "could not recommend any chemical method for the detection of *small* quantities of tungsten in the presence of large quantities of chromium, uranium, vanadium and phosphate ion." This test admirably fulfils the purpose (see Note 2).

#### EXPERIMENTAL.

*Preparation of the Group for Analysis.*—Mixtures containing the chlorides of aluminium, beryllium, uranium, and zinc, and sodium or potassium chromate, tungstate, vanadate, and phosphate were treated in Pyrex tubes with 0.6 g. of sodium peroxide and a little sodium hydroxide to ensure complete solution. They were heated to decompose the excess of peroxide and analysed according to the following tabulated scheme.

#### Aluminium Group.

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

*Solution.*—Contains sodium aluminate, beryllate, chromate, tungstate, peruranate, vanadate, zincate, and phosphate, with traces of peroxide. Make a definite volume, *e.g.*, 10 ml., and test separate portions as follows:

- (a) Test 0.05—0.2% for Be. Boil with 0.05 ml. of 2*N*-HCl and a few mg. of NaHSO<sub>3</sub>. Add 1 ml. of 2*N*-NaOH, remove any precipitate that forms, then dilute with 5 ml. of water and add 0.1 ml. of morin (0.02% in acetone). A green fluorescence shows **Be**. Compare with standards. (1).
- (b) Test 0.1—1% for W. Acidify with HCl, add a little NaHSO<sub>3</sub>, and evaporate to dryness in a test-tube. To the residue add 0.5 ml. of 1*N*-HCl, 0.5 ml. of *n*-butyl acetate, and solid toluene-3 : 4-dithiol. Heat at 70° for 10—15 mins., add a little more dithiol, and dilute with 0.5 ml. of water. If the ester layer is coloured blue-green, showing **W**, compare with standards. (2).
- (c) Test 0.1—1% for V. Add one drop of 0.05*M*-KH<sub>2</sub>PO<sub>4</sub>, a few mg. of NaHSO<sub>3</sub>, 0.2 ml. of 10% aqueous tartaric acid, and water to make 1 ml., followed by 0.05 ml. of 10% aqueous tannin and solid sodium acetate in large excess. A blue colour attaining its maximum intensity in a few mins. shows **V**. If a white precipitate (Al) or a brown colour (U) appears add 0.05 ml. of 20% aqueous NH<sub>4</sub>F and compare at once with standards. (3).
- (d) Test 10% for Zn. Add a few mg. of NaHSO<sub>3</sub>, acidify with HNO<sub>3</sub>, evaporate to dryness, and dissolve the residue in 0.5 ml. of *N*-HNO<sub>3</sub>. To the solution add 0.05 ml. of 20% aqueous NH<sub>4</sub>F, 0.05 ml. of 0.01*M*-CuSO<sub>4</sub>, and 0.2 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). Shake briskly. A violet or black precipitate shows **Zn**. If the colour of the precipitate is unsatisfactory (V present) dissolve it in a drop of concentrated HNO<sub>3</sub>, dilute with water, and add ammonium mercury thiocyanate. Compare with standards. (4).
- (e) Test 0.1—1% for Cr. Add a few mg. of NaHSO<sub>3</sub>, acidify with 2*N*-H<sub>2</sub>SO<sub>4</sub>, and expel SO<sub>2</sub>. Add one drop of 0.1*M*-FeCl<sub>3</sub>, and an excess of 2*N*-NaOH. Boil and separate Fe(OH)<sub>3</sub>, Cr(OH)<sub>3</sub>, and perhaps Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>. Dissolve the precipitate in 0.05 ml. of 2*N*-H<sub>2</sub>SO<sub>4</sub>, add 0.05 ml. of saturated aqueous Br<sub>2</sub>, and gradually make alkaline with 0.5*N*-NaOH. Set aside for several mins. in order to form Cr<sup>VI</sup>, then heat gently, add a few mg. of phenol to destroy excess Br<sub>2</sub>, and separate and reject the precipitate of Fe(OH)<sub>3</sub> and perhaps Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>. Acidify the centrifugate with 2*N*-H<sub>2</sub>SO<sub>4</sub> making about 1 ml. of solution 0.2—0.3*N* in acid. Add diphenylcarbazide (0.25% in 50% aqueous acetone) until an excess is present. A pink or red colour shows **Cr**. If tribromophenol has separated centrifuge it down or extract it with chloroform. Compare with standards prepared directly from chromate. (5).
- (f) Test 10% for Al and U. Pass CO<sub>2</sub> into the hot solution, diluted to 1.5 ml. After 5 mins., cool the solution and continue the passage of CO<sub>2</sub> for 15 mins. Centrifuge and wash the precipitate with 0.5*M*-NaHCO<sub>3</sub>. (6).

*Precipitate.* Al(OH)<sub>3</sub>, BeCO<sub>3</sub> (part), ZnCO<sub>3</sub>. Dissolve in >0.1 ml. of 4*N*-H<sub>2</sub>SO<sub>4</sub>, add solid Cs<sub>2</sub>SO<sub>4</sub> and stir thoroughly. A white crystalline precipitate of caesium alum shows **Al**, which is compared with standards. To confirm a small precipitate, separate and wash it, dissolve it in a minimum amount of *N*-HCl, and test with alizarin or morin. (7).

*Solution.* Na<sub>2</sub>CrO<sub>4</sub>, Na<sub>3</sub>VO<sub>4</sub>, Na<sub>2</sub>WO<sub>4</sub>, Be (part) and U as complex carbonates. Gradually acidify with 5*N*-HCl and evaporate to dryness. Dissolve the residue in 0.2 ml. of 1*N*-HCl and 0.6 ml. of water. Add an excess of 10% aqueous cupferron and extract the brown V complex and the excess of the reagent with three 1 ml. portions of chloroform. To the aqueous layer add 0.4 g. of KSCN and extract twice with 0.5 ml. of *iso*amyl acetate, rejecting the ester layers. Finally extract uranium thiocyanate with 2 ml. of ethyl acetate. Evaporate the ester layer to dryness (steam-bath), dissolve the residue in 0.1—0.3 ml. of 0.5*N*-HCl, add 0.05—0.15 ml. of 0.25*M*-K<sub>4</sub>Fe(CN)<sub>6</sub>, and stir thoroughly. A dark brown precipitate shows **U**. Compare with standards prepared from U that has been extracted by means of ethyl acetate from 0.5 ml. of *N*-HCl containing 0.1 g. of NaCl and 0.2 g. of KSCN. (8).

*Notes on Methods and Tests.*—The experimental technique was the same as formerly.

*Note 1.* The method prescribed for this excellent test is based on that developed for quantitative purposes by Sandell (*Ind. Eng. Chem. Anal.*, 1940, **12**, 674, 762). The conditions under which the aluminium group is isolated are such that possible interfering metals, *e.g.*, scandium and calcium, are adequately removed. Chromium (VI) and traces of peroxide, which prevented the fluorescence, had to be reduced with sodium bisulphite. For the present purpose the interference of zinc was negligible. In the estimation of beryllium the solutions were examined in vials (1 in. diameter) held against a dark background under a daylight lamp. The amount of beryllium must not exceed 5 μg.; 0.25 μg. was easily detected.

*Note 2.* This method of applying the toluene-3 : 4-dithiol test for tungsten (Miller, J., 1941, 792) permitted the detection of <1 μg. in a mixture containing at least 5 mg. of each of the group components, including phosphate. Sodium

bisulphite was added to reduce chromium(VI) and vanadium(V), which would otherwise have used up much of the expensive reagent.

*Note 3.* The production of a blue colour or precipitate, when sodium acetate was added to a slightly acid solution containing vanadium and tannin, was seriously hindered by tungstate, and might be masked by an excess of aluminium or uranium. Oxidising agents had to be absent. The presence of not less than an equal weight of phosphate ( $\text{PO}_4'''$ ) and an excess of tartaric acid counteracted the influence of tungstate, and the addition of fluoride dissolved the tannin complex of aluminium and almost eliminated the colour due to uranium. A 100-fold excess of tungsten halved the sensitivity of the test. Chromium(III) in excess modified the colour but did not prevent the detection of the minimum amount of vanadium under consideration. Of possible group contaminants iron and titanium did not prevent the detection of the same amount of vanadium, and gallium behaved like aluminium. 1  $\mu\text{G}$ . of vanadium was detectable, and for estimations 10  $\mu\text{g}$ . was the upper limit.

*Note 4.* The precipitation of zinc as white zinc mercury thiocyanate permitted its detection in minimum amount in solutions containing maximum amounts of all the other group components except vanadium which decomposed the reagent. Chromium(III) was preferable to chromium(VI). Cuvelier and Bosch (*Natuurwetensch. Tijds.*, 1936, 18, 9; through A., 1936, 560) have shown that the test should preferably be made in nitrate solution. In the presence of copper, which alone gives a green precipitate, the precipitates from more than twice the weight of zinc are coloured violet, and from an equal weight, black. Consequently, if a constant amount of copper were always added one could utilise the colour of the precipitate to estimate small quantities of zinc. It was then advisable to mask with ammonium fluoride a possible trace of iron that otherwise behaved like copper. The double precipitation effectively eliminated the interference of an excess of vanadium.

*Note 5.* This test for chromium(VI) (Feigl, "Qualitative Analyse mit Hilfe von Tüpfelreaktionen," 1938, 230; Sandell, *Ind. Eng. Chem. Anal.*, 1936, 8, 336), which is applicable in the presence of many metals, had to be done in the absence of vanadate and tungstate which gave a brown and a turbid solution, respectively. The method prescribed for the separation and oxidation of chromium(III) is based on Järvinen's observations (*Z. anal. Chem.*, 1928, 75, 1).

*Note 6.* In order to separate aluminium, beryllium, and zinc from the other group components, Noyes and Bray (*op. cit.*, p. 176) neutralised the solution with nitric acid and then added about 1% of sodium bicarbonate, which small amount ensured complete precipitation of beryllium and usually held uranium in solution. Sometimes, however, uranyl vanadate entered the precipitate, and a small amount of uranium was carried down by a large precipitate. The modified process prescribed was utilised solely in order to separate aluminium from phosphotungstate, and uranium from zinc (see Notes 7 and 8). Since it was immaterial whether or not beryllium was precipitated, and greater dilution of the original solution and a higher concentration of sodium bicarbonate favoured the retention of uranium in the solution, the strongly alkaline mixture was made 50% more dilute than usual, and a final concentration of 10% of sodium bicarbonate was assured by saturating it with carbon dioxide. In this way 25  $\mu\text{g}$ . of uranium were adequately separated from a mixture containing 5 mg. of precipitable metals, and 25  $\mu\text{g}$ . of aluminium from a mixture containing 5 mg. of non-precipitable metals and 5 mg. of phosphate ( $\text{PO}_4'''$ ).

*Note 7.* Provided that the metals were present mainly as sulphates in a small volume of dilute sulphuric acid, 25  $\mu\text{g}$ . of aluminium were detectable in the presence of the maximum excesses of zinc, uranium and beryllium under consideration. At least 25-fold excesses of chromium(VI) and vanadium(V) were permissible, but phosphotungstate had to be absent, since its caesium salt is insoluble. The test with morin or alizarin (Feigl, *op. cit.*, pp. 244, 246) served to distinguish it from caesium alum. Gallium which behaves like aluminium must be effectively removed before testing for the latter, and preferably before isolating the aluminium group for analysis (see Noyes and Bray, *op. cit.*, p. 151).

*Note 8.* The test for uranium with potassium ferrocyanide is very distinctive, but it must be made in the absence of other metals that give insoluble ferrocyanides, e.g., vanadium and zinc, and group contaminants such as titanium, iron, and gallium. The concentration of the uranium salt must not be too low. In the bicarbonate treatment zinc, titanium, iron, and part of the gallium were eliminated. The cupferron-chloroform treatment removed all but a minor amount of vanadium, even in the presence of tungstate, and any titanium, iron, or gallium accidentally present. It was found that a small amount of vanadium in association with phosphotungstate gave very slowly with potassium ferrocyanide a brown solution from which a precipitate resembling uranyl ferrocyanide eventually deposited. The addition of an excess of potassium thiocyanate to the solution ( $\sim 2N$  in hydrochloric acid) and extraction with *isoamyl* acetate prevented this interference by removing the tungstate without loss of uranium. The uranium thiocyanate left in the aqueous layer was then readily extracted by means of ethyl acetate, the removal of which permitted the precipitation of uranyl ferrocyanide under the conditions of acidity found most suitable by Noyes and Bray (*op. cit.*, p. 421). As a small amount might coagulate very slowly, it was advisable to re-examine a doubtful test after  $\frac{1}{2}$  hour.

*Analysis of Mixtures.*—As a final check five mixtures of unknown composition were analysed. Each mixture contained 25 mg. of phosphate ( $\text{PO}_4'''$ ). The results shown in the table, which are considered satisfactory, are the estimated weights (in mg.) of the metals found. Where these differed from the actual amounts taken, the latter are shown in parentheses.

Element.	Al.	Be.	Cr.	W.	U.	V.	Zn.
No. 1	0.25	0	0.2 (0.25)	7 (5)	0	6 (7)	10 (12)
2	0.5	3 (4)	0	2	0.25	0.6 (1)	20 (30)
3	10 (12)	1.5 (2)	30 (24)	6 (7)	2	0.15 (0.25)	0.25
4	0	13 (10)	0.5 (1)	0	5 (8)	0	3 (2)
5	20 (25)	0.15 (0.25)	4 (5)	0.25	0.5	7 (10)	0