

ON METHODS OF SEPARATION IN THE ALUMINUM- CHROMIUM GROUP.

By

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The Separation of Beryllium, Zinc, and Uranium.

The procedure for the separation of zinc and beryllium described in the preceding article was adopted only after several other possibilities were postulated and investigated. In the first scheme tried, beryllium and zinc were separated in an acetate buffer solution by means of 8-hydroxyquinoline. This method works splendidly if uranium is absent, but if uranium is present, it precipitates along with the zinc. The destruction of the reagent in the subsequent treatment of solution and precipitate is quite cumbersome.

In the second scheme investigated, the zinc and beryllium were separated by precipitating the zinc in acetate buffer solution with H_2S . This method permits the detection of small amounts of zinc. However, some beryllium (usually around 1 $\mu g.$) precipitates during the treatment, probably due to hydrolysis, thus making the procedure unsuitable for the detection of small amounts of beryllium.

In the third scheme investigated, the attempt was made to separate the beryllium from the zinc according to A. A. NOYES and W. C. BRAY² by making the solution strongly alkaline with ammonia, centrifuging, and separating solution and precipitate. Theoretically, the zinc should go into solution leaving the beryllium behind in a pure state. However, ammonia does not take the

¹ Abstracted from the thesis submitted by W. F. SPIKES to the faculty of the Graduate School of New York University in partial fulfillment of the requirements for the degree of doctor of philosophy, April 1, 1936.

² Qualitative Analysis for the Rare Elements, New York 1927.

zinc into solution quantitatively. Some will remain behind with the beryllium hydroxide. Of course, the eventual treatment of the precipitate thus obtained either by sublimation or extraction with chloroform will separate the zinc and the beryllium, and thus prevent the former's interference with the qualizarine test.

Separation of the Chromium Group.

To obtain preliminary information, analyses on complex mixtures containing nearly all of the ions of the "third group" according to A. A. NOYES and W. C. BRAY were carried out. The results of two of these analyses are given in table I. It can be seen that phosphate, tungsten, vanadium, beryllium, titanium, zirconium always escaped detection. Accordingly, trouble was to be expected in the chromium (phosphate, tungsten, vanadium, chromium and uranium) and the zirconium (titanium, zirconium, rare-earth elements, and indium) groups³.

The latter group has not been investigated yet; however, the above assumption was found to be confirmed in a careful study of the chromium group.

Table I.

No. of Sample	304		301	
	ADDED	RECOVERED	ADDED	RECOVERED
W	30 μ g	0 μ g	30 μ g	0 μ g
Fe	30 "	8 "	30 "	48 "
PO ₄	30 "	0 "	—	—
Cr	30 "	60 "	—	—
U	30 "	38 "	30 "	low
V	30 "	0 "	—	—
Zn	30 "	25 "	30 "	27 μ g
Al	30 "	45 "	30 "	20 "
Be	30 "	0 "	30 "	0 "
Mn	30 "	3 "	30 "	25 "
Co	30 "	17 "	30 "	8 "
Ni	30 "	30 "	30 "	40 "
Ti	30 "	4 "	30 "	3-4 "
Zr	30 "	0 "	30 "	0 "
RE	30 "	30 "	30 "	0 "

³ All of our experiments have been carried out on a microscale. Therefore, the reported experiences do not necessarily apply to the original scheme of NOYES and BRAY which has been devised for the analysis of 1 g. solid samples.

When mixtures containing 100 $\mu\text{g.}$ of chromium, uranium, vanadium, and tungsten (as phosphotungstate) were analyzed according to the scheme of NOYES and BRAY, it was found that the recovery of the chromium and uranium was quite satisfactory, while only 70 to 80% of the vanadium and none of the tungsten were found. Thirty different schemes for the separation of these four elements were postulated and investigated. A short report of this work will be given here in chronological order.

The first improvement attempted was in the method of separating uranium and vanadium. NOYES and BRAY carry this out by precipitating the uranyl-ammonium phosphate from an acetic acid solution. At times some of the vanadium comes down with the uranium. It was first attempted to extract the uranium nitrate from the vanadium by extraction with isoamyl alcohol. Seventy percent of the uranium was found in the first extract. With small amounts of uranium, it was possible to effect a complete separation of the uranium. No vanadium was found in the alcoholic extract. However, difficulty was experienced in the extraction of large amounts of uranium, since the solubility of uranium is unfortunately rather low; hence, many repetitions of the extraction and large volumes of the solvent are required. For these reasons, the procedure is unwieldy. Consequently, a more convenient solvent was sought. W. W. SCOTT⁴ suggested the use of a mixture of glacial acetic and nitric acids (100:5). The solution containing the vanadium and uranium is treated with dilute nitric acid (1:1), and then evaporated to dryness on a steam bath, thus resulting in the formation of vanadium pentoxide. The acetic, nitric acid solvent is then added to the residue, the mixture stirred, heated on a water bath, and the solution and solid separated. The solution will contain about 5% of the vanadium, and most of the uranium. On careful investigation, it was found that the extraction, even when repeated, did not give better results than the procedure of NOYES and BRAY.

C. A. PIERLE⁵ used anhydrous ether to extract the uranium from residues obtained on evaporating uranium-vanadium solutions

⁴ J. Ind. Eng. Chem. **14**, 531 (1922).

⁵ PIERLE, C. A., J. Ind. Eng. Chem. **12** (1), 60—63 (1920).

with nitric acid. The method did not yield quantitative separations, some of the uranium always remaining in the residue after three or four extractions with ether.

Other extraction methods⁶ were found impracticable, too, either because they did not offer clean-cut separations or because they were worthless in the presence of the other ions apt to occur in the chromium group.

H. H. BARKER and H. SCHLUNDT⁷ proposed to separate the vanadium from the uranium by volatilization of the vanadium chlorides and oxychlorides in a stream of dry HCl. Nitric acid is added to the vanadium-uranium solution, and the mixture is evaporated to dryness. Dry HCl is passed over the residue. Brown fumes, characteristic of the vanadium chlorides and oxychlorides appear immediately without external heat. However, the vanadic vanadium residue is partially reduced to the vanadous vanadium, as shown by the disappearance of the yellow color of the vanadium pentoxide. In agreement with W. F. HILLEBRAND⁸, complete removal of the vanadium was never accomplished by this method, even though several evaporations to dryness with subsequent treatments with hydrogen chloride gas were carried out.

Various methods whereby either vanadium or uranium were precipitated were considered. The best of the recommended methods proved to be the one using cupferron, the precipitation being carried out in 10% H₂SO₄ solution⁹. This procedure was adopted in one of the two schemes which have been proposed.

The next problem which demanded attention was the loss of large quantities of tungsten during analysis.

A systematic investigation of the scheme of NOYES and BRAY was carried out; a solution containing 100 μ g. of tungsten only was treated by their procedures 107 and 36¹⁰. Amounts of tungstic

⁶ *E. g.*, C. FRIEDEL and E. CUMENGE (Compt. rend. 128, 532 [1899]; Bull. Soc. Chim. Paris [3] 21, 328) suggested the extraction of uranium with a dilute ammonium nitrate solution. But phosphate must be absent.

⁷ *Met. Chem. Eng.* 14, 18—23 (1916).

⁸ Bulletin No. 70, U. S. Bureau of Mines, 82 (1913).

⁹ HILLEBRAND, W. F., and LUNDELL, G. E. F., *Applied Inorganic Analysis*, p. 357, Wiley 1929.

¹⁰ NOYES and BRAY, *ibid.*, pp. 183 und 92.

acid estimated to be around 100 $\mu\text{g.}$ were recovered. Next a mixture containing 100 $\mu\text{g.}$ of both vanadium and tungsten and then a mixture containing 100 $\mu\text{g.}$ of tungsten, vanadium, and uranium were analyzed. Satisfactory recoveries were obtained in both cases. Finally an analysis was carried out on a mixture containing 100 $\mu\text{g.}$ of tungsten, vanadium, uranium, and *chromium*. Satisfactory recoveries of vanadium (75%), uranium, and chromium were obtained, but the tungsten was no longer found. Hence, it was concluded that the disturbance originated due to the presence of the chromate ion—that is, the loss of the tungsten occurred during the operations necessary to eliminate this ion: namely the precipitation of the lead chromate or the subsequent precipitation of lead sulfide for the removal of the excess of lead. Experiments were then carried out to determine which of these procedures was causing the trouble, and to this end analyses of the lead chromate and lead sulfide precipitates were carried out. In neither of the two could tungsten be found. However, these negative results mean little, since the procedures for the detection of tungsten in the presence of chromium do not seem to be reliable.

It was then attempted to improve the results by avoiding the procedure of NOYES and BRAY for the elimination of chromium.

At first the attempt was made to precipitate CrO_3 from 70% HClO_4 . The solution containing the chromate ion, uranium, vanadium, tungsten, and phosphate was evaporated to dryness. The perchloric acid (25 cmm.) was added to the residue, and the mixture stirred, centrifuged, and solution and precipitate (CrO_3) separated. The CrO_3 was washed with some more HClO_4 , and then dissolved in water, and identified. The filtrate from the CrO_3 was analyzed according to the scheme of NOYES and BRAY. The recovery of chromium and uranium was complete, while most of the vanadium and all but 3 $\mu\text{g.}$ (out of 100 $\mu\text{g.}$) of tungsten were lost. This scheme was given many trials which only confirmed the results of the first analysis. The precipitation of CrO_3 with perchloric acid is excellent as far as the detection of chromium is concerned. However, it seems to cause complications in the detection of tungsten and vanadium. When the precipitate of CrO_3 was dissolved in water, there was always left behind a small

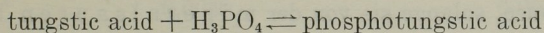
white residue. This residue seems to consist mainly of silicic acid with traces of tungsten.

As another method for the elimination of chromium, the volatilization of the chromyl chloride suggested itself. This method in combination with the analysis of the residue with the use of cupferron proved most useful for the detection of tungsten.

Of the procedures altogether deviating from the scheme of NOYES and BRAY, the following attempts may be mentioned: The treatment of the mixture of chromium, uranium, vanadium, tungsten, and phosphate with metallic tin and concentrated nitric acid which was expected to eliminate the phosphate ion and to precipitate at the same time the tungstic acid. The treatment of the mixture containing the chromium group with sodium hydroxide-sodium sulfide which might cause the precipitation of the uranium and chromium and leave the tungsten and vanadium in solution. The treatment of the chromium group with cesium chloride, thus precipitating the difficultly soluble cesium phosphotungstate at the start of the separation. The separation of the chromium group by electrolysis using the mercury cathode.

All of the attempts and several others, which do not seem worthwhile listing, were unsuccessful. The most promising procedure was the one based on the precipitation of cesium phosphotungstate, which may be used as a test for the detection of tungsten.

At present we cannot 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. Changes in the equilibrium



may be responsible for the difficulties encountered in the attempt to recover the tungsten from such complex mixtures.
