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## Semi-Micro Analysis of Tungsten

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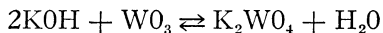
## SEMI-MICRO ANALYSIS OF TUNGSTEN

JACK HINMAN AND W. C. OELKE

The growing use of tungsten in high speed steels and for electrical purposes makes it increasingly desirable to include this element in the scheme of analysis.

Metallic tungsten is seldom if ever found in nature, but occurs in several well-crystallized tungsten minerals of which Scheelite,  $\text{CaWO}_4$ , is typical. From its position in the periodic table, Group VI—Series 6, one should expect tungsten to have amphoteric properties. Although we are more familiar with tungsten in the metallic state, it almost invariably behaves as a non-metal in chemical combination. For this reason in analytical work tungsten naturally falls among the anions.

In the semi-micro scheme of analysis tungsten can best be detected in the form of the tungstate. Solutions for laboratory purposes may be obtained by heating to high temperatures such compounds as ammonium paratungstate,  $(\text{NH}_4)_6\text{W}_7\text{O}_{24} \cdot 6\text{H}_2\text{O}$ . This leaves a residue of  $\text{WO}_2$  which is quickly oxidized in air to  $\text{WO}_3$ . The tungsten trioxide, as well as nearly all other tungsten compounds, is practically insoluble in acids, but is quite soluble in certain alkalies, particularly KOH. From the reaction:

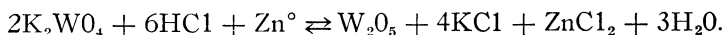


potassium orthotungstate is formed and crystallizes as a dihydrate. In dilute alkaline solutions  $\text{WO}_4^-$  ions are released and respond to tests.

Tungsten may be detected in minerals and alloys by boiling the finely ground material with concentrated HCl until insoluble yellow tungstic acid is formed.<sup>1</sup> The zinc test of Runner and Hartmann can be modified and used on a semi-micro scale as follows:

Three to five drops of the solution in question, or of the yellow solid  $\text{WO}_3$ , are put on a white spot plate. One micro-spatula load of zinc powder is added with two or three drops of concentrated HCl following. If a deep blue coloration and precipitate result, tungsten is present.

Probably the reaction involved in a typical "Zinc Test" is as follows:



<sup>1</sup> Runner, J. J. and Hartmann, M. L., The occurrence, chemistry, metallurgy, and use of tungsten. South Dakota State School of Mines, Bull. 2, 1918.

Undoubtedly the blue precipitate is  $W_2O_5$ , which seems to be quite stable. In the test used by Runner and Hartmann for the detection of tungsten in alloys and minerals, they report that the blue compound formed is unstable, but we have found that the blue compound formed is stable when precipitated under the conditions of the semi-micro "Zinc Test."

#### INTERFERING IONS

The presence of several anions interferes with the above test. These ions are:  $NO_3^-$ ,  $NO_2^-$ ,  $AsO_3^{=}$ ,  $CrO_4^{=}$ ,  $Fe(CN)_6^{=}$ ,  $Fe(CN)_6^{=}$ ,  $CNS^-$ ,  $(C_2H_3O_2^-)$ . However, in every case the interference is easily eliminated and in some cases may even be used to detect other ions.

The nitrate ion,  $NO_3^-$ , interferes by causing a light yellow precipitate (probably  $H_2WO_4$ ) instead of the usual blue.  $NO_3^-$  can be precipitated with Fornitrol reagent (Nitron in formic acid) and removed by centrifuging. The characteristic blue of the "Zinc Test" will then appear if the test is repeated.

The nitrite ion,  $NO_2^-$ , causes the formation of a white precipitate. If acetic acid (not  $HNO_3$  nor  $HCl$  because W compounds will be precipitated) is added and the solution boiled vigorously, the  $NO_2^-$ , will be driven off and the "Zinc Test" will work.

The arsenite ion,  $AsO_3^{=}$ , interferes slightly by making the precipitate blue-black instead of bright blue. If silver nitrate is added to the alkaline solution in question, the  $AsO_3^{=}$  will be removed in the resulting precipitate.

The colored anions,  $CrO_4^{=}$ ,  $Fe(CN)_6^{=}$ , and  $Fe(CN)_6^{=}$  make the blue precipitate of the "Zinc Test" difficult to detect.  $CrO_4^{=}$  can be precipitated by the addition of barium chloride solution. Both  $Fe(CN)_6^{=}$  and  $Fe(CN)_6^{=}$  will come down upon the addition of ferrous sulfate solution.

The presence of  $CNS^-$  ion with  $WO_4^{=}$  ion causes the formation of a deep purple precipitate when the "Zinc Test" is made. In order to be sure of the presence of the two ions in a solution, concentrated  $HCl$  should be added (without the zinc powder) to cause the precipitation of the yellow tungstic acid mentioned previously. This precipitate in itself is a good indication of the presence of W, but the detection can be confirmed by redissolving the yellow precipitate in  $KOH$  and repeating the "Zinc Test."

If the acetate ion,  $C_2H_3O_2^-$ , is present with  $WO_4^{=}$ , the "Zinc Test" will give a blue precipitate which turns black almost imme-

diately. The acetate ion can be eliminated by adding dilute  $H_2SO_4$  to the hot solution, thus causing the formation of  $CH_3COOH$ .

#### OTHER REAGENTS FOR "ZINC TEST"

Both dilute and concentrated  $H_2SO_4$  may be used in place of  $HCl$  in the "Zinc Test" with equally good results.  $Al$ ,  $Mg$ , or  $Sn$  can be substituted for  $Zn$  as the reducing agent. An interesting result of the use of  $Mg$  powder instead of zinc as the reducing agent in the presence of both  $CNS^-$  and  $WO_4^{=}$  is that the characteristic blue precipitate is formed rather than the purple.

#### OTHER TESTS

Diphenyl carbazide may be used for the detection of the  $WO_4^{=}$  ion. The procedure for the test is as follows:

Place about five drops of the solution to be tested on a white spot plate. Add one drop of diphenyl carbazide reagent (1 per cent alco. solution). A reddish coloration indicates the presence of tungsten as  $WO_4^{=}$ . Add enough concentrated  $HCl$  to bleach the red color and then add one micro-spatula load of magnesium powder. If the solution turns green or blue-green with a precipitate of the same color, the presence of tungsten is confirmed. This test does not work for tungstic acid.

The above mentioned test may be used in place of the "Zinc Test" in anion analysis. The following anions interfere with the formation of the green precipitate and coloration:  $NO_2^-$ ,  $NO_3^-$ ,  $AsO_4^{=}$ ,  $CrO_4^{=}$ ,  $Fe(CN)_6^{=}$ , and  $Fe(CN)_6^{=}$ . In the case of  $CrO_4^{=}$  the solution turns green without the addition of magnesium powder. Since the above mentioned anions also interfere when the "Zinc Test" is used, the same methods for their elimination can also be used.

A fusion test suggested by Prescott and Johnson<sup>2</sup> serves very well under semi-micro conditions. Sodium carbonate is fused with a tungstate, and taken up in  $H_2O$ . A strip of filter paper is soaked with the solution and concentrated  $HCl$  added. If tungsten is present, a yellow coloration is noted as the wet filter paper is heated high over a bunsen flame. If stannous chloride solution is dropped on the filter paper, the color will change from yellow to blue. Spot paper may be substituted for filter paper.

Böttger<sup>3</sup> recommends the so-called "Stannous Chloride Test." The principals of the test are as follows: stannous chloride gives a yellow precipitate with a solution of a tungstate. This becomes

<sup>2</sup> Prescott & Johnson. "Qualitative Chemical Analysis," p. 135, D. Van Nostrand Co., 1905.

<sup>3</sup> Böttger, The Principles of Qualitative Analysis, p. 268, Blakiston Sons, 1911.

blue upon the addition of  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ , and warming. This test is not as dependable as the other two.

Many other tests for tungsten can be found in the literature, but we have found the tests depending upon the formation of  $\text{W}_2\text{O}_5$  the most dependable and practical.

#### PROCEDURE FOR GENERAL UNKNOWN

In a general unknown, such as one used in college laboratories, containing both cations and anions, tungsten may be removed before the Group I metals are precipitated. Except under special conditions, tungsten compounds must exist in the general unknown solution as a flocculent precipitate. If the yellow tungstic acid is used in the general unknown, it can be centrifuged and tested with the "Zinc Test." If an alkaline solution of  $\text{WO}_4^{2-}$  is added to the general unknown, it will, of course, be precipitated. This precipitate may be centrifuged, redissolved in  $\text{KOH}$ , and tested with "Zinc Test" or the test employing diphenyl carbazide. Either tartaric acid or acetic acid can be used to keep the tungsten compounds from precipitating in a general unknown, whenever the presence of one of these organic acids does not interfere with the normal action of the cations in the solution.

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