347. *Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. Part VI.* The Precipitation of Tungsten.*

By R. Belcher and A. J. Nutten.

The tungsten-precipitating properties of benzidine, diphenyline, and certain substituted benzidines, and related compounds have been examined. It was found that 1-amino-4-*p*-aminophenylnaphthalene precipitated tungsten quantitatively from acid solution and gave a complete separation from molybdenum.

The amines described in previous papers in this series have been examined as precipitants for tungsten (in the form of tungstate). Benzidine has been used for this purpose for many years, but does not appear to have achieved wide usage, possibly because of its non-selectivity. Some further tests on benzidine have therefore now been carried out to check the accuracy of the method, and to find to what extent molybdenum (as molybdate) is coprecipitated. To complete the investigation, an examination of diphenyline as a reagent for tungsten has been made. This reagent was proposed by Feigl (*Rec. Trav. chim.*, 1939, **58**, 471) for the detection of tungsten in the presence of molybdenum, since in acid solution up to 10% of molybdenum did not interfere, but no attempt appears to have been made to apply the reaction quantitatively. Unlike benzidine sulphate, diphenyline sulphate is soluble.

Determination of Tungsten (*as Tungstate*), *Benzidine being used as Reagent.*—When tungsten was precipitated from neutral solution, full recovery was obtained under the conditions used. Molybdenum behaved similarly. However, at an acidity of 0·5N. in hydrochloric acid, only about a 90% recovery of tungsten was obtained. Under the same conditions, molybdenum was not appreciably precipitated. When mixtures of tungsten and molybdenum were precipitated at this same acidity, the results obtained indicated appreciable coprecipitation of molybdenum. and this was confirmed by applying the thiocyanate test to the residue obtained on ignition of the precipitate. Hence, it is impossible to separate these elements quantitatively by adjustment of the acidity. The results obtained are summarised below.

Precipitation of tungsten and molybdenum by benzidine from neutral and from acid solutions.

W present (mg.).	Mo present (mg.).	W found (mg.). Final acidity : 0.	W found (mg.). Final acidity : 0·5N.	Mo found (mg.). Final acidity : 0.	Mo found (mg.). Final acidity : 0·5N.
75	—	74·9, 75·1	68·1, 67·5	—	—
—	65	—	—	64·9, 65·0	0·3, 0·1
75	65	—	72·3, 72·9	—	—

It is well known that molybdenum forms strong complexes with oxalic acid, but we were unable to find any reference to similar complex formation with tungsten. Some experiments in which sufficient oxalic acid was added to form the complex with molybdenum showed that tungsten also forms a complex, for recoveries of less than 5% were obtained, as seen from the following results.

Precipitation of tungsten and molybdenum by benzidine from oxalic acid solution.

W present (mg.).	Mo present (mg.).	W found (mg.).	Mo found (mg.).
75	—	3·2, 3·0	—
—	65	—	1·3, 1·0
75	65	4·4, 3·9	—

Precipitation of Tungsten with Diphenyline.—When tungsten was precipitated from neutral solution with diphenyline, full recovery was obtained. When, however, precipitations were effected at acidities of 0·1N., 0·2N., and 0·3N. with respect to hydrochloric acid, the recoveries were less than 80%. When the filtrates from the 0·3N-acid precipitations were evaporated to dryness on the water-bath, redissolved in water, and treated with benzidine, almost all of the unprecipitated tungsten was recovered. Molybdenum was precipitated completely in neutral

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solution, but it was evident that the recovery of tungsten in slightly acid solution was not sufficiently satisfactory to warrant further examination. Results are shown below.

Precipitation of tungsten by diphenyline from neutral and acid solution.

W present (mg.).	Precipitation storage time.	W found (mg.). Final acidity :			
		0.	0·1N.	0·2N.	0·3N.
75	½ hour	74·7, 74·6	—	—	—
75	1 hour	74·9, 74·9	59·9, 58·7	58·8, 58·7	57·8, 57·7
75	2 hours	74·9, 74·9	59·8, 59·9	59·2, 59·4	57·7, 58·2
75	Overnight	—	59·7, 60·0	59·1, 59·4	59·2, 58·8

Precipitation of Tungsten with Various Amines.—The amines described in previous papers were next examined as precipitants for tungsten, since a reagent which would precipitate tungsten from an acid solution is desirable. Hence, in order to test the precipitating properties of our amines, precipitation was effected at a final acidity of 1N. with respect to hydrochloric acid. The results are listed below.

Precipitation of tungsten by certain substituted benzidines and related compounds from acid solution.

Amine.	W present (mg.).	W found (mg.).	Amine.	W present (mg.).	W found (mg.).
2-Methylbenzidine............	15	9·9, 10·3	4-Aminodiphenyl	15	7·7, 6·3
3-Methylbenzidine............	15	2·1, 3·9	1-Amino-4-*p*-aminophenylnaphthalene	15	14·7, 14·8
2 : 2′-Dimethylbenzidine ...	15	4·8, 6·2	2-Aminodiphenylamine ...	15	8·3, 8·1
2 : 3′-Dimethylbenzidine ...	15	6·2, 5·6	4-Aminodiphenylamine ...	15	1·7, 3·5
3 : 3′-Diethylbenzidine ...	15	2·3, 2·6	4 : 4′-Diaminostilbene	15	14·6, 14·5
3 : 3′-Diaminobenzidine ...	15	5·1, 3·9			
2-Aminodiphenyl	15	3·5, 3·7			

The tests were repeated in the presence of sulphuric acid to assist in the formation of more granular precipitates, but similar results were obtained.

Only two amines, 4 : 4′-diaminostilbene and 1-amino-4-*p*-aminophenylnaphthalene, gave results of sufficient promise to warrant further investigation.

Precipitation of Tungsten with 4 : 4′-Diaminostilbene.—In neutral solution both tungsten and molybdenum were precipitated quantitatively. At a final acidity of 0·7N. with regard to hydrochloric acid, tungsten was almost quantitatively precipitated. The amount of tungsten remaining in solution might be disregarded for certain types of industrial analysis, but, unfortunately, occasional inexplicable low results were obtained, even after the precipitates had been kept overnight. Various amounts of tungsten were determined, but in nearly every case the results were slightly, and in some cases considerably, low.

Molybdenum yielded no precipitate at all at an acidity of 0·7N. When tungsten was determined in its presence, there was no coprecipitation at this acidity. The acidity was reduced to 0·5N., but the results for tungsten were still slightly low, and, when molybdenum was present under the same conditions, appreciable coprecipitation occurred. Results are included in the following table.

Precipitation of tungsten and molybdenum by 4 : 4′-diaminostilbene from neutral and from acid solution.

W present (mg.).	Mo present (mg.).	Pptn. storage time, (hrs.).*	W found (mg.). Final acidity.			Mo found (mg.). Final acidity :	
			0.	0·5N.	0·7N.	0.	0·5N.
15	—	2	14·9, 15·1	14·9, 14·9	14·7, 14·4	—	—
15	—	2	14·9, 15·0	14·9, 14·8	13·9, 14·8	—	—
15	—	N	—	—	14·9, 14·5	—	—
15	—	N	—	—	13·6, 14·8	—	—
—	13	2	—	—	—	12·9, 13·0	0, 0
—	13	2	—	—	—	12·8, 12·9	0·1, 0
15	13	N	—	14·9, 15·5	14·8, 13·8	—	—
15	13	N	—	15·5, 15·6	14·7, 14·9	—	—
7·5	—	N	—	—	7·4, 6·9	—	—
7·5	—	N	—	—	7·2, 7·4	—	—
3·8	—	N	—	—	3·5, 3·0	—	—
3·8	—	N	—	—	3·5, 3·4	—	—

* N = Overnight.

Several expedients were tried to overcome the slight loss of tungsten, such as adding paper pulp, reducing the volume of the solution as far as was compatible with that likely to be used in practice, and washing the precipitate both with reagent and with wash solution saturated with precipitate, but no improvement could be observed. The addition of paper pulp, however, gave a more easily filterable precipitate.

Oxidising agents (but not Fe^{3+}) interfered.

Precipitation of Tungsten with 1-*Amino*-4-p-*aminophenylnaphthalene*.—Both tungsten and molybdenum were precipitated quantitatively from neutral solution. At an acidity 0·7N. with respect to hydrochloric acid, tungsten was precipitated almost quantitatively but molybdenum gave no precipitate. When tungsten was precipitated in the presence of molybdenum at an acidity of 0·7N., no coprecipitation occurred. At an acidity of 0·5N., however, there was a slight coprecipitation of molybdenum. High results were obtained and molybdenum was detected in the precipitate by the thiocyanate test. At an acidity of 1N., the results for tungsten were similar to those obtained in 0·7N-solution, but, when the volume was increased at this acidity to 150 ml. and 200 ml., low results were obtained. It is recommended, then, that a volume of 100 ml. or less and an acid concentration of 0·7N. be used to obtain virtually complete precipitation.

When hydrochloric acid alone was used as the wash liquid the results were always slightly lower than when it was saturated with the precipitate.

The effect of varying the storage time at an acidity of 1N. was examined. After 4 hours the results were always low, but after storage overnight, precipitation was virtually complete. The results are always slightly low but the slight error involved may possibly be ignored for most types of analysis, especially when it is considered that a complete separation from molybdenum is obtained. Results are included in the following table.

Precipitation of tungsten and molybdenum by 1-*amino*-4-p-*aminophenylnaphthalene from neutral and from acid solution.*

W present (mg.).	Mo present (mg.).	Pptn. storage time (hrs.).*	Final vol. (ml.).	W found (mg.). Final acidity :			
				0.	0·5N.	0·7N.	1N.
15	—	½	70	14·8, 14·9	—	—	11·4
				14·8, 14·8	—	—	10·8, 10·5
15	—	1	70	14·9, 15·0	—	—	11·1, 11·6
				15·0, 14·9	—	—	11·7
15	—	2	70	—	—	—	12·6, 12·9
				—	—	—	13·0
15	—	4	70	—	—	—	13·2, 13·7
				—	—	—	13·4
15	—	N	70	—	—	—	14·9, 14·8
				—	—	—	14·9
7·5	—	N	70	—	—	7·4, 7·5	7·3, 7·4
				—	—	7·4, 7·4	7·4, 7·3
3·8	—	N	70	—	—	3·6, 3·6	3·5, 3·4
				—	—	3·5, 3·7	3·7, 3·6
—	13 †	1 (for neutral)	70	13·0, 12·9	0, 0	0, 0	
		N (for acid)		12·9, 13·0	0 0	0 . 0	
15	13	N	70	—	—	14·8, 14·8	14·8, 14·9
				—	15·3, 15·2	14·9, 15·0	14·9, 14·8
				—	15·6, 15·6	14·9, 14·8	14·9, 15·0
				—	—	14·9, 14·9	14·9, 14·8
15	—	N	100	—	—	—	14·8, 14·8
				—	—	—	14·7, 14·8
15	—	N	150	—	—	—	14·6, 14·7
				—	—	—	14·7, 14·6
15	—	N	200	—	—	—	14·6, 14·6
				—	—	—	14·5, 14·7

* N = Overnight.

† Results in cols. 5, 6 and 7 are for Mo (mg.).

Under the conditions employed in the precipitation, oxidising agents and Fe^{3+}, which gave a blue-green precipitate with the reagent, interfered; Fe^{2+} did not interfere, nor did the following ions, which were selected from the various analytical groups : Cu^{2+}, Cd^{2+}, Al^{3+}, Cr^{3+}, Ni^{2+}, Zn^{2+}, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}.

EXPERIMENTAL.*

Solutions required.—Tungsten solution. Prepared by fusing pure tungstic oxide with sodium carbonate at 800°, dissolving the melt in distilled water, and neutralising to methyl-red with hydrochloric acid.

Molybdate solution. Prepared by dissolving recrystallised sodium molybdate in distilled water.

Reagents. These were prepared by dissolving the stated quantity of the corresponding hydrochloride in 100 ml. of distilled water: benzidine, 1 g.; diphenyline, 1 g.; amines, 0·5 g.; 4 : 4′-diaminostilbene, 0·5 g.; 1-amino-4-*p*-aminophenylnaphthalene, 1 g.

I. *Precipitation with Benzidine.*—(1) *Neutral solution* (see table, p. 1516). (i) Tungsten. 20 Ml. of benzidine reagent were added to 50 ml. of neutral tungstate solution. After 2 hours, the precipitate was filtered through a pulp pad, washed with a 5% solution of the reagent, and ignited in a platinum crucible at 750°; the residue was weighed as WO_3.

(ii) Molybdenum. 20 Ml. of benzidine reagent were added to 50 ml. of neutral molybdate solution; after the same procedure as in (i), ignition in a platinum crucible at 500° afforded MoO_3.

(2) *Acid solution* (see table, p. 1516). (i) Tungsten. 20 Ml. of benzidine reagent were added to 50 ml. of acid tungstate solution, the final acidity of the solution being 0·5N. to hydrochloric acid. The liquor was kept overnight and the procedure was then as in (1)(i).

(ii) Molybdenum. 20 Ml. of benzidine reagent were added to 50 ml. of acid molybdate solution, the final acidity of the solution being 0·5N. to hydrochloric acid. The solution was kept overnight, and then treated as in (1)(ii).

(iii) Tungsten + molybdenum. 20 Ml. of benzidine reagent were added to 50 ml. of acid tungstate + molybdate solution, the final acidity of the solution being 0·5N. Next morning, the precipitate was treated as in (1)(ii), the residue being weighed as WO_3.

(3) *Oxalic acid solution* (see table, p. 1516). These experiments were carried out as for I(2) but in neutral solution to which 1 g. of oxalic acid had been added.

II. *Precipitation with Diphenyline* (see table, p. 1517).—(1) *Neutral solution.* (i) Tungsten. As for I(1), but with 20 ml. of diphenyline reagent as precipitant and various times.

(2) *Acid solution.* (i) Tungsten. As for I(2), but with 20 ml. of diphenyline reagent as precipitant, and with final acidities 0·1N., 0·2N., and 0·3N. with respect to hydrochloric acid.

III. *Precipitation with Substituted Benzidines and Related Compounds* (see table, p. 1517).—20 Ml. of amine reagent were added to 50 ml. of acid tungstate solution, the final acidity of the solution being 1N. with regard to hydrochloric acid. A small amount of paper pulp was added, and after being kept overnight, the precipitate was filtered through a pulp pad, washed with a 5% solution of the reagent, ignited in a platinum crucible at 750°, and weighed as WO_3.

IV. *Precipitation with 4 : 4′-Diaminostilbene* (see table, p. 1517).—(1) *Neutral solution.* (i) Tungsten. Procedure was as for I(1), but with 20 ml. of 4 : 4′-diaminostilbene reagent as precipitant.

(ii) Molybdenum. As for I(1), but with 20 ml. of 4 : 4′-diaminostilbene reagent as precipitant.

(2) *Acid solution.* (i) Tungsten. As for I(2), but with 20 ml. of 4 : 4′-diaminostilbene reagent as precipitant. The final acidities were 0·5N. and 0·7N. with respect to hydrochloric acid.

(ii) Molybdenum. As for I(2), but with 20 ml. of 4 : 4′-diaminostilbene reagent. The final acidity was 0·5N. with regard to hydrochloric acid.

(iii) Tungsten + molybdenum. As for I(2), but with 20 ml. of 4 : 4′-diaminostilbene reagent. The final acidities were 0·5N. and 0·7N. with respect to hydrochloric acid.

V. *Precipitation with 1-Amino-4-p-aminophenylnaphthalene* (see table, p. 1518).—(1) *Neutral solution.* (i) Tungsten. Procedure as for I(1), but with 20 ml. of the reagent as precipitant. Paper pulp was added to the solution, and to the solutions referred to in the following paragraphs, to give a more easily filterable precipitate. The precipitate was kept for ½ or for 1 hour.

(ii) Molybdenum. The procedure was similar to that in I(i). The precipitate was set aside for 1 hour.

(2) *Acid solution.* (i) Tungsten. Procedure as for I(2), with 20 ml. of reagent. The tungstate solution contained varying amounts of tungsten. Times, final acidities, and final volumes at an acidity of 1N. to hydrochloric acid were varied.

(ii) Molybdenum. Procedure was similar to that in I(2).

(iii) Tungsten + molybdenum. Procedure was as for I(2), 20 ml. of reagent solution being used.

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CHEMISTRY DEPARTMENT, THE UNIVERSITY, BIRMINGHAM, 15. [*Received, December 13th,* 1950.]

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* The weights of tungsten and molybdenum in each test solution are given in the corresponding tables.