[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

THE DETERMINATION OF ARSENIC PENTOXIDE AS MAGNESIUM AMMONIUM ARSENATE

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The author has applied the methods of Brookman[1] and Schmitz[2] to the estimation of phosphorus pentoxide and the results of this investigation appeared recently.[3] The present investigation details the results of an attempt to apply the principles of these methods to the estimation of arsenic pentoxide as magnesium ammonium arsenate. It was found that precipitation was complete in a short time without the use of ammonium acetate, and sufficiently accurate results were obtained for the quantitative estimation of arsenic by filtering on a Gooch crucible and igniting to constant weight.

Probably the method most frequently employed for this determination is that described according to Treadwell.[4] Two methods are recommended for the conversion of magnesium ammonium arsenate to magnesium pyro-arsenate.

First, the precipitate is dried in a Gooch crucible at 100° and heated in an electric oven quite gradually to a temperature of about 400–500° until no more ammonia is evolved. The temperature is then raised to 800–900° and kept there for about ten minutes. The crucible is then cooled in a desiccator and the precipitate weighed in the form of magnesium pyro-arsenate.

Second, if an electric oven is not available, the crucible with the precipitate is placed in an air-bath so that the bottom of the Gooch crucible comes within about 2–3 mm. of the bottom of the outer crucible. A thin layer of ammonium nitrate is added to the precipitate, which is heated at first gently, gradually increasing the temperature until a light red glow in the outer crucible is obtained, after which the precipitate is allowed to cool in a desiccator and is weighed as magnesium pyro-arsenate.

It has been found that satisfactory results cannot be obtained by igniting the precipitate in the presence of a thin layer of ammonium nitrate, first gently, and then to red heat as stated above. Results ranging from 2–3 mg. high were obtained, and when the ignition was carried out at 800° with a Meker burner there was a continual loss of from 0.4 to 0.5

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[1] Brookman, *Repert. anal. Chem.*, **2**, 297 (1882).

[2] Schmitz, *Z. anal. Chem.*, **65**, 46 (1924).

[3] McNabb, THIS JOURNAL, **49**, 891 (1927).

[4] Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, **1924**, vol. 2, 6th ed., p. 201.

mg. for every 15-minute period of ignition, which was probably due to decomposition of the magnesium pyro-arsenate.

A number of analyses were made from definite quantities of pure, recrystallized monopotassium hydrogen arsenate with variations of time for complete precipitation (see Table I for details of these results).

The salt was dissolved in 25 to 30 cc. of water, after which 5 cc. of concd. hydrochloric acid was added. To this solution were added 10 cc. of magnesia mixture (prepared by dissolving 55 g. of crystallized magnesium chloride and 70 g. of ammonium chloride in 650 cc. of water and diluting to a volume of 1 liter with ammonium hydroxide, d. 0.96) for each 0.1 g. of arsenic present and a drop of phenolphthalein solution. With constant stirring a 10% solution of ammonium hydroxide was added from a buret until the phenolphthalein imparted a permanent red color

TABLE I

ALLOWED TO STAND 20 TO 24 HOURS

KH_2AsO_4, 0.2000 g.; As_2O_5 calcd., 0.1277 g.

	$Mg_2As_2O_7$, g.	As_2O_5, g.	As_2O_5 difference, g.
	0.1728	0.1279	+0.0002
	.1727	.1279	+ .0002
	.1721	.1274	− .0003
	.1727	.1279	+ .0002
Av.	.1726	.1278	+ .0001

Av. % deviation from calcd., +0.08

ALLOWED TO STAND ½ HOUR

KH_2AsO_4, 0.2000 g.; As_2O_5 calcd., 0.1277 g.

	$Mg_2As_2O_7$, g.	As_2O_5, g.	As_2O_5, difference, g.
	0.1728	0.1279	+0.0002
	.1723	.1276	− .0001
	.1723	.1276	− .0001
	.1725	.1277	.0000
Av.	.1725	.1277	.0000

Av. % deviation from calcd., 0.00

ALLOWED TO STAND 12 TO 14 HOURS

KH_2AsO_4, 0.2000 g.; As_2O_5 calcd., 0.1277 g.

	$Mg_2As_2O_7$, g.	As_2O_5, g.	As_2O_5 difference, g.
	0.1725	0.1277	0.0000
	.1723	.1276	− .0001
	.1722	.1275	− .0002
	.1727	.1279	+ .0002
Av.	.1724	.1276	− .0001

Av. % deviation from calcd., −0.08

KH_2AsO_4, 0.5000 g.; As_2O_5 calcd., 0.3192 g.

	$Mg_2As_2O_7$, g.	As_2O_5, g.	As_2O_5 difference, g.
	0.4316	0.3195	+0.0005
	.4313	.3193	+ .0001
	.4311	.3191	− .0001
	.4315	.3195	+ .0003
	.4312	.3192	.0000
Av.	.4313	.3193	+ .0001

Av. % deviation from calcd., +0.03

ALLOWED TO STAND 6 TO 8 HOURS

KH_2AsO_4, 0.2000 g.; As_2O_5 calcd., 0.1277 g.

	$Mg_2As_2O_7$, g.	As_2O_5, g.	As_2O_5 difference, g.
	0.1724	0.1276	−0.0001
	.1727	.1279	+ .0002
	.1726	.1278	+ .0001
	.1727	.1279	+ .0002
Av.	.1726	.1278	+ .0001

Av. % deviation from calcd., +0.08

KH_2AsO_4, 1.0000 g.; As_2O_5 calcd., 0.6384 g.

	$Mg_2As_2O_7$, g.	As_2O_5, g.	As_2O_5 difference, g.
	0.8630	0.6389	+0.0005
	.8626	.6386	+ .0002
	.8620	.6381	− .0003
	.8628	.6387	+ .0003
Av.	.8626	.6386	+ .0002

Av. % deviation from calcd., +0.03

ALLOWED TO STAND 1 HOUR

KH_2AsO_4, 0.2000 g.; As_2O_5 calcd., 0.1277 g.

	$Mg_2As_2O_7$, g.	As_2O_5, g.	As_2O_5 difference, g.
	0.1724	0.1276	−0.0001
	.1724	.1276	− .0001
	.1726	.1278	+ .0001
	0.1724	0.1276	−0.0001
	.1726	.1278	+ .0001
Av.	.1725	.1277	− .0000

Av. % deviation from calcd., 0.00

to the solution, and then more of the 10% ammonium hydroxide solution was added to equal one-third the volume of the neutralized solution. After standing for definite intervals, the solution was filtered through a Gooch crucible. The precipitate clinging to the sides of the beaker was transferred to the crucible with small portions of the filtrate, and then washed with 2.5% ammonium hydroxide, until free from chlorides. It was drained as completely as possible by means of suction. The Gooch crucible containing the precipitate was placed in a large porcelain crucible; it rested about 3 mm. from the bottom of the large crucible. After the addition of a very thin layer of ammonium nitrate powder, the outer crucible was at first heated very gently with a Bunsen burner, the temperature being gradually increased to full heat. This gave a temperature of from 500–600° in the Gooch crucible. All ignitions were carried out at half-hour intervals until constant weight was obtained.

Conclusions

1. It is not necessary to allow a solution of monopotassium hydrogen arsenate to stand in the presence of magnesia mixture for 12 to 24 hours, as precipitation is complete in half an hour.
2. In the conversion of magnesium ammonium arsenate to magnesium pyro-arsenate, accurate results cannot be obtained by heating to 800 and 900° for ten minutes. In attempting to ignite to constant weight at this temperature a continual loss took place, varying with the time of ignition.
3. Heating just until a light red glow was obtained in the outer crucible gave high results.
4. Accurate results can be obtained in the conversion of magnesium ammonium arsenate to magnesium pyro-arsenate by finally igniting to constant weight at a temperature of from 500–600°.
5. Results obtained from this method, allowing the precipitate to stand for half an hour, gave an average error of —0.02%.
6. The accuracy obtainable by the method described above would indicate that there would be no advantage in applying the combined method of Brookman and Schmitz to the estimation of arsenic pentoxide as magnesium ammonium arsenate.

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