V—The Nitrate Method should be thoroughly investigated in comparison with the Dilution Method in order to determine the amount of oxygen available from the nitrate both at 37° C. and at 20° C. It appears possible to develop considerable accuracy and obtain comparable results by this method under proper conditions.

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MOLYBDIC ACID RECOVERY

By C. G. ARMSTRONG

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The large waste of molybdic acid and the difficulty experienced in obtaining the reagent pointed out the great need of a process for its recovery. Numerous methods were tried and cast aside on account of their impracticability or the unnecessary consumption of expensive reagents but finally a method, which is herewith described, was found, which is practical and simple: namely, the precipitation of the acid in HNO_3 by concentration, and its solution in NH_4OH , whereby the molybdic acid is obtained in a condition to be readily used for the preparation of a new stock solution for phosphorus.

PROCESS

On account of the fact that phosphomolybdate precipitates are often added to the waste molybdic acid residues in steel analysis, these should be filtered before the recovery process is commenced. This is most conveniently accomplished by means of an asbestos suction filter.

The filtered solution is then placed in a five-liter German flask and supported inverted over a large evaporating dish on a sand bath, allowing but a small

amount of the solution in the dish. This method allows a large amount of liquid to be evaporated with little attention. The flask may be refilled until the precipitate of MoO_3 , which forms in the bottom of the evaporating dish, becomes too bulky. Remove the flask and evaporate the solution in the dish until it begins to foam considerably and there is just enough solution left to cover the precipitate and keep the iron in solution. Cool, dilute with one-half volume of

cold water, allow to settle and decant. Wash the precipitate thoroughly a couple of times with water by decantation to remove the iron salts and treat with enough 1 : 1 NH_4OH to fill the dish. A dark brown precipitate will form, due to precipitated iron. The whole is then washed into a large flask, warmed slightly and allowed to stand a couple of hours with an occasional shaking to facilitate solution. When all is in solution, or after two hours, the liquid may be filtered off by a siphon, sand and asbestos, suction filter into another flask. Arrange the suction tube so that the lower portion of the solution, containing the precipitate, will be the last to come upon the filter, thus preventing troublesome clogging of the filter by the iron precipitate. Add 5 per cent of the original amount of NH_4OH to the solution to make up for that used in precipitating the iron.

This solution contains the MoO_3 as ammonium molybdate and when the specific gravity of it is taken with a hydrometer at 25° C., by referring to accompanying curve the per cent of MoO_3 present may be found and then the proper amount of fresh MoO_3 added to bring the concentration up to 0.2825 g. per cc., which is the concentration of the precipitating solution for phosphorus.

The solution of $(\text{NH}_4)_2\text{MoO}_4$ may be evaporated to dryness and then roasted at 600° C. to MoO_3 , but this is impractical in most cases.

The specific gravity curve was plotted from data obtained by making up solutions of different concentrations and using a pycnometer at 25° C. Various solutions were made up to test the curve and in each case the specific gravity indicated the per cent of MoO_3 to within 0.003 g. per cc. excepting in concentrations below 0.06 g. per cc., which concentrations are seldom met with in actual practice.

The solution of $(\text{NH}_4)_2\text{MoO}_4$ in 1 : 1 NH_4OH when ready to mix with HNO_3 has a concentration of 0.2825 g. per cc. with a specific gravity of 1.20 (25° C.). This, when mixed with HNO_3 and water, constitutes the regular phosphorus precipitating solution.

The recovery in these tests, which were carried out on large amounts of residues and under actual working conditions, was 93 per cent and the recovered molybdic acid obtained by evaporation and roasting at 600° C. tested chemically pure in all cases (Merck's reagents and their tests).

The cost of recovery is practically nothing except for the gas and time, as no reagents are used which do not go to make up the working solution for phosphorus determinations.

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THE IODIDE METHOD APPLIED TO THE DETERMINATION OF COPPER IN THE PRESENCE OF TIN

By ROBERT W. COLTMAN

Received May 28, 1915

In the determination of copper in a copper-tin alloy, the usual procedures involve a separation of the copper and tin. The most common method is to decompose the alloy with nitric acid, whereby metastannic

acid and copper nitrate are formed. The tin precipitate is filtered off, and the copper determined in the filtrate. This method has the disadvantage that the metastannic acid filters with difficulty; furthermore, the tin precipitate always contains traces of other metals present in the alloy, so that it must undergo further treatment.

Tin and copper may also be separated by sodium sulfide in alkaline solution, whereby the copper separates as sulfide and the tin goes into solution as a sulfosalt. The inconvenience of this method needs no comment.

Having had occasion to investigate the behavior of metallic copper and metallic tin when treated with concentrated sulfuric acid, the writer was struck by the facility with which the tin was held in solution. The fact that tin goes into solution as a stannic salt when treated with concentrated sulfuric acid is made use of in Low's method for antimony in babbitt metal;¹ the hydrochloric acid added after the decomposition of the alloy ensures the tin and antimony remaining in solution after dilution. It was found that the solution of tin in sulfuric acid alone was fairly stable, and with the knowledge that stannic salts do not liberate iodine from a solution of potassium iodide, the question naturally arose as to whether copper might not be determined by the iodide method in a solution containing tin. Further experiments showed that this was quite feasible; by proper treatment of the alloy a solution of stannic and cupric sulfate in sulfuric acid may be obtained that may be titrated for copper with the same accuracy as a copper sulfate solution alone.

Although hydrochloric acid holds tin in solution much more readily than sulfuric, its use was not considered, as copper is not readily soluble in hydrochloric acid and thus would necessitate the use of aqua regia to effect solution of the alloy. The nitric acid would then have to be removed by repeated evaporations with hydrochloric, consuming much time, and making the method much less simple than in its present form.

Preliminary work showed that the best method of preparing the solution was to treat the finely divided alloy with nitric acid until decomposed, and then fume with sulfuric acid over an open flame (using a Jena Erlenmeyer). The metastannic acid dissolves to stannic sulfate, and the copper nitrate is converted into copper sulfate. On taking the cold residue up with water, a clear solution is obtained that may be titrated directly for copper by the iodide method.

The use of sulfuric acid alone to decompose the alloy is not satisfactory, as a small residue of copper remains even after repeated fuming. A large excess of acid must be used, otherwise the pasty mass will spatter. It is practically impossible to control the amount of free sulfuric acid present, and this is important, as in using a mineral acid in the copper iodide method, the acidity must be low.

The allowable amount of tin present under given conditions of acidity was determined as follows:

The volume of the solution to be titrated having been chosen as 75 cc., and the amount of concentrated sulfuric acid as 3 cc., increasing quantities of metallic tin were dissolved in nitric acid, evaporated with 3 cc. of concentrated sulfuric,¹ diluted to 75 cc., and the stabilities of the different solutions compared.

Tin Gram	Vol. Cc.	Conc. H ₂ SO ₄ Cc.	REMARKS
0.05	75	3	No change in one hour
0.1	75	3	Slight turbidity in 15 minutes
0.2	75	3	Would not dissolve to clear solution

It is evident that not more than 0.1 gram of tin may be present, otherwise hydrolysis and precipitation of stannic hydrate take place in a short time.

The weight of copper titrated may be as high as 0.25 gram (=C = 39.3 cc. N/10 Na₂S₂O₃). This weight of copper in the presence of 0.1 gram tin would be equivalent to 71.43 per cent Cu. There would then be 28.57 per cent Sn. As the amount of tin in a bronze is seldom so high as this, there is no danger that the sample taken for analysis will contain more than the allowable weight of tin, provided the amount of copper present is not much over 0.25 gram.

EXPERIMENTAL DATA

STANDARDIZATION OF THIOSULFATE SOLUTION AGAINST COPPER FOIL—The sample was dissolved in nitric, fumed with 3 cc. conc. H₂SO₄, allowed to cool, 25 cc. water added, and evaporated again to fuming. The solution was allowed to cool, diluted to 75 cc., 10 cc. of 40 per cent KI solution added, and titrated with the thiosulfate solution.

No.	Grams copper	Cc. Na ₂ S ₂ O ₃	1 cc. = Grams Cu
1.....	0.2655	42.37	0.006266
2.....	0.2648	42.24	0.006269
3.....	0.2684	42.83	0.006267
AVERAGE VALUE 1 cc. Na ₂ S ₂ O ₃ 0.006267			

TITRATION OF COPPER IN PRESENCE OF TIN—The solution was prepared as before, but metallic tin was added to the copper samples:

No.	Weight—Grams		Per cent		Cc. Na ₂ S ₂ O ₃	Gram	CU FOUND Per cent	DIFFERENCE Per cent
	Cu	Sn	Cu	Sn				
1	0.2526	0.0311	89.04	10.96	40.31	0.2526	89.04	
2	0.2507	0.0504	83.26	16.74	40.02	0.2508	83.30	+0.04
3	0.2455	0.0799	75.45	24.55	39.15	0.2454	75.41	-0.04

These differences lie entirely within the limits of error.

ANALYTICAL PROCEDURE

Weigh out a sample containing not over 0.25 gram copper and boil with 15 cc. of 2 : 1 nitric in a 500 cc. Jena Erlenmeyer provided with a small funnel to prevent loss. When the alloy is thoroughly decomposed, add dilute sulfuric acid equivalent to 3 cc. of concentrated acid, remove and rinse the funnel, and evaporate over an open flame. As the evaporation progresses, the solution becomes more and more clear. After the nitric acid is all driven off, and the sulfuric begins to fume, the stannic and cupric sulfates suddenly separate out, forming a very characteristic crystalline mass of pearly scales somewhat resembling manganese ammonium phosphate. The flask must be removed from the flame immediately after this

¹ Three cubic centimeters of concentrated sulfuric acid is the maximum amount which may be present in the copper iodide method, according to Gooch and Heath, *Z. anorg. Chem.*, **55** (1907), 129.

¹ *J. Am. Chem. Soc.*, **29** (1907), 66.

crystallization takes place or the mass will spatter. After cooling, take up with about 25 cc. water, shake until dissolved, and again evaporate just to fuming in order to remove the last traces of lower oxides of nitrogen. Allow to cool, take up with 50 cc. cold water (the stannic sulfate dissolves more quickly by using less water at first) and when all is in solution, add 25 cc. more water, 10 cc. of 40 per cent KI, and titrate immediately with the $N/10$ thiosulfate. If the alloy contains a small amount of lead, some lead sulfate remains undissolved, and the solution at the end point is yellowish (owing to the lead iodide) instead of the creamy white of cuprous iodide, but the presence of lead has no effect upon the titration, at least in moderate amounts.

A copper-tin alloy containing about 10 per cent of tin and 8 per cent lead analyzed as follows:

No.	Sample Gram	Cc. $\text{Na}_2\text{S}_2\text{O}_3$	Cu Found Gram	Per cent	Average Per cent Cu
1.....	0.3127	39.49	0.2474 (8)	79.14	79.16
2.....	0.3227	40.79	0.2556 (3)	79.22	
3.....	0.3303	41.70	0.2613 (4)	79.12	79.11
4.....	0.3108	39.21	0.2457 (4)	79.06	
5.....	0.3327	42.02	0.2633 (4)	79.15	

In the analyses indicated as 4 and 5 above, the alloy was decomposed with nitric, the metastannic acid filtered off, and the copper determined in the filtrate after evaporation with sulfuric.

Too much stress cannot be laid upon the fact that a second fuming of the solution is necessary: 0.05 gram of metallic tin, treated with nitric, fumed *once* with sulfuric, and diluted to 75 cc., gave a blue color with KI and starch requiring 0.55 cc. to discharge it. When this same amount of tin was fumed *twice*, potassium iodide and starch gave no color in the diluted solution.

As regards the time necessary, determinations 1, 2 and 3, cited above, were run in one hour. The filtering, washing and evaporating necessary when the ordinary method was used, made the time about five hours. (In this, no correction was made for any copper remaining with the metastannic acid.)

The method proposed is simple, accurate, and rapid; the advantages of carrying out the analysis in the same container are obvious.

In conclusion, it must be remembered that no metals which separate iodine from potassium iodide may be present, such as antimonious or ferric salts; the method has naturally the limitations of the iodide method in this respect. It is simply the desire of the writer to show an extended use of this excellent method, thus making it available under apparently adverse conditions.

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TITRATION OF NITRATES WITH FERROUS SULFATE

By FRED C. BOWMAN AND W. W. SCOTT

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The great variety of methods of determining nitrates found in chemical literature shows the need felt by chemists for simpler ways of making this important analysis. Most methods now in use involve distillation or evaporation or the use of special appara-

tus, all of which take a good deal of time and attention.

The method proposed by the authors is as easy and quick as any ordinary titration, has a wide range of usefulness and is accurate enough for most purposes.

BIBLIOGRAPHY

The first mention of the method was made by Grossart¹ in 1847. He titrated nitrates in boiling 60 per cent sulfuric acid with a ferrous sulfate solution, using ferricyanide as an outside indicator. He gives no details or test analyses. No doubt his results were less accurate than he thought.

Mohr² announced the discovery of the method in 1861. He dissolved the sample in sulfuric acid (diluted 1 to 9) and titrated at 70° to 80° C. with a ferrous sulfate solution containing 200 grams of the salt per liter, using as the end point the appearance of a brownish color. He declared that it was a good technical method, but Fresenius³ and Eder,⁴ who examined it later, condemned it strongly.

In 1899 van Deventer⁵ carried out the reaction over mercury in a Crum tube with exclusion of air, using fairly strong sulfuric acid as a medium and a weak ferrous sulfate solution as reagent. The process was awkward to handle.

No comment on these methods was found in the journals, and evidently they failed of acceptance. They were all based on the reduction of the nitrate to NO and not to N_2O_3 , as in the method given below, for estimations in presence of sulfuric acid. No mention of acids other than sulfuric was found in the literature.

ESTIMATION OF NITRIC ACID IN PRESENCE OF ARSENIC ACID

The writers devised the method given below, originally, for the purpose of estimating nitric acid in arsenic acid. The original form of the method was as follows:

Dilute the sample to be tested to 100 cc. with nitre-free arsenic acid of such strength that there is not more than 20 per cent water in the mixture. Then titrate with a ferrous sulfate solution, containing 264.7 grams $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 50 cc. strong sulfuric acid per liter (1 cc. = 0.02 g. HNO_3). Standardize the solution on a known amount of nitric acid.

The following reaction occurs:

The ferrous sulfate forms a dark brown color, which disappears on stirring as long as any nitric acid remains. The end point is the first permanent brown and is readable to 0.03 cc. During the first two-thirds of the titration, the ferrous sulfate is taken up very quickly; then a lively evolution of NO commences and continues to the end. It would be thought that the oxygen of the air might reoxidize the NO

¹ "Sur un nouveau dosage de l'acide azotique et des azotates," Grossart, *Compt. rend.*, **1** (1847), 21.

² Dingler's *Polytechnisches Journal*, **160** (1861), 219.

³ *Zeitschrift fuer anal. Chemie*, **1** (1862), 32.

⁴ *Ibid.*, **16** (1877), 267.

⁵ *Zeitschrift fuer physik. Chemie*, **31** (1899), 50.