

[CONTRIBUTION FROM THE HYGIENIC LABORATORY OF THE U. S. PUBLIC HEALTH SERVICE AND FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]¹

THE ESTIMATION OF ARSENIC IN ORGANIC COMPOUNDS.

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The Carius method of preparing organic arsenicals for analysis, while thoroughly dependable, consumes much time, and numerous workers have offered schemes for shortening the labor involved.

Pringsheim² and Little³ use alkaline fusion, but there is danger here of loss by volatilization. Norton and Koch⁴ and Ewins⁵ have imitated the Kjeldahl nitrogen method. They digest the arsenical, mixed with starch, in conc. sulfuric acid, and titrate the resulting arsenious acid. However, the Ewins method was given an extended trial by Myers and DuMez,⁶ who have proved that a considerable loss of arsenic occurs during the digestion. The problem at present is to oxidize the organic matter quickly and without loss; and to use the resulting clear solution in any of the standard procedures for the estimation of arsenic.

Probably the most favored shortcut at the present time is the Lehmann method,⁷ recently modified by Fargher.⁸ In this plan the sample is oxidized with conc. sulfuric acid and potassium permanganate. Rogers⁹ uses ammonium persulfate instead of the permanganate. In either case, the arsenic is obtained as arsenic acid for the actual analysis.

The manganese in the Lehmann analysis restricts the analyst to the Williamson¹⁰ method of estimation, *viz.*, allowing the arsenic acid to react with hydriodic acid and provide free iodine, which is titrated with thio-sulfate. Naturally the manganous salts present will not interfere as they would if any attempt were made to use neutral or alkaline solutions, which are necessary for the best methods of estimating arsenic. Moreover, hydrogen peroxide is used in the process, and this is hard to remove. In any event, the amount of iodine freed for the titration is uncertain in quantity, and a blank must be run to correct the figures obtained.

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² Pringsheim, *Am. Chem. J.*, **31**, 386 (1904).

³ Little, *J. Chem. Soc. (London) Trans.*, **95**, 1477 (1909).

⁴ Norton and Koch, *THIS JOURNAL*, **27**, 1247 (1905).

⁵ Ewins, *J. Chem. Soc. (London) Trans.*, [2] **109**, 1355 (1916).

⁶ Myers and DuMez, *U. S. Public Health Rpt.*, **33**, 1003 (1918).

⁷ Lehmann, *Apoth.-Ztg.*, **27**, 545 (1912).

⁸ Fargher, *J. Chem. Soc. (London) Trans.*, **115**, 992 (1919).

⁹ Rogers, *Can. Chem. J.*, **3**, 398 (1920); also *C. A.*, **14**, 389 (1920).

¹⁰ Williamson, *J. Soc. Dyers Colourists*, **1806**, p. 86.

Gooch and Browning¹ have shown the inferiority of the Williamson method in a series of careful experiments. It has also been found that the Lehmann method of oxidation fails with certain refractory arsenic acids. Accordingly, while the Lehmann method has considerable use in routine work, few investigators trust it in research analysis.

It seems that too little attention has been paid to the excellent method of determining arsenic developed by Gooch, Browning and Morris.² They treat a sample of arsenic acid with dil. sulfuric acid and potassium iodide, boil out the iodine produced in the reaction, neutralize the solution with sodium hydrogen carbonate, and titrate with standard iodine in the presence of starch. This is one of the finest of volumetric processes. In expert hands it is probably equal to the gravimetric procedure, and in less skilled hands decidedly superior.

With the Gooch method in mind, it was the aim in the present work to use an oxidation scheme which would destroy all reducing or iodine-absorbing matter present, and yet leave no excess oxidizing agent capable of destroying hydriodic acid in quantity. The Carius method, properly carried out, answers this requirement, and was used as the standard for comparison in further work.

A method is quoted³ from the "Pharmacopeia Germanica," in which the organic arsenical is oxidized in a mixture of conc. sulfuric and fuming nitric acids, after which the Williamson method of estimation is used. Myers and DuMez⁴ in a series of tests on analytical methods, perform a similar oxidation followed by a gravimetric procedure. By adopting the latter method of estimation they lose time, but do not have to concern themselves over the presence of residual nitric acid. In the Williamson method, nitric acid is not admissible, whence the directions given in various places to take great care to expel the last traces.

For the Gooch-Browning process, however, the writer finds no necessity for removing excess nitric acid, but does find it essential to remove the nitrous acid or oxides which are the natural result of the digestion in the nitric-sulfuric mixture. Briefly, the method proposed is, first, digestion in a nitric-sulfuric mixture at a high temperature; this is followed by the removal of the nitrous compounds by ammonium sulfate, and finally the use of the Gooch-Browning method.

The details of the procedure are as follows. About 0.2 g. of the substance is weighed into a 150-cc. Pyrex Erlenmeyer flask, and 5.5 cc. of conc. sulfuric acid is poured on the substance. After the acid has com-

¹ Gooch, "Methods of Chemical Analysis," Wiley, 1912.

² Gooch, Browning and Morris, *Am. J. Sci.*, [4] 10, 151 (1900); and *Z. anal. Chem.*, 31, 318 (1892).

³ Morgan, "Organic Compounds of Arsenic and Antimony," 1918, p. 349.

⁴ *Loc. cit.*

pletely wetted or dissolved the substance, one cc. of fuming nitric acid is added, and the flask set on a hot plate in the hood. The temperature of the plate is such that water in a similar flask boils actively but not excessively, and the actual temperature of the mixture undergoing oxidation is approximately 250°. Despite the fuming of the acid at this temperature, there is no apparent loss of arsenic.

In about half an hour arsphenamine or any of its intermediates are likely to be completely oxidized, while such refractory substances as tolyl-arsonic acid are partly oxidized and partly charred. In general, it is safe after one hour to remove the flask, cool it slightly, and add to it 10 or 15 drops more of fuming nitric acid. The flask is replaced on the hot plate, and in 5 minutes more the oxidation is complete. Cautiously add a gram of solid ammonium sulfate, shake the vessel a few moments until the nitrogen has escaped, and set the mixture aside to cool. When the temperature has fallen below 100°, the mixture is clear and colorless. After cooling the flask under the faucet, add water cautiously until the solution reaches a volume of 60 to 70 cc.

Without any concern as to the amount of nitric acid which still persists, the Gooch-Browning procedure is now followed. This can be finished in a half hour if desired. One g. of potassium iodide is added to the mixture with a few grains of porous clay plate. A simple bulb trap, such as an inverted 25-cc. flask with a side vent, is placed in the mouth of the Erlenmeyer flask. The outfit is now heated on the same hot-plate until the liquid has been reduced by boiling to 40 cc. (mark on flask). If the work must be done in haste, the iodine may be boiled out and the liquid reduced to the proper volume by heating on a wire gauze over the lamp. The bulb trap is now rinsed into the flask. A solution of 0.01 *N* thiosulfate is added dropwise until the tint of iodine disappears, and the solution is instantly diluted with cold water to 100 or 120 cc. It is now transferred to a 500-cc. Erlenmeyer flask containing 50 cc. of 4 *N* sodium carbonate solution, and the residual acid neutralized with sodium hydrogen carbonate. A small excess of the latter is included. Starch solution is added, and the arsenite present is titrated with standard iodine solution. A standard solution, one cc. = 0.002 g. of arsenic, is convenient. No blank is necessary.

If a high degree of refinement is desired, the plan of E. W. Washburn¹ may be used, whereby a buffer solution of phosphates is used instead of sodium hydrogen carbonate for keeping the solution exactly neutral during titration.

A solution of sodium carbonate is used instead of the more convenient caustic alkali specified by Gooch, because of the iodine-consuming impurities often to be found in present-day "C. P." alkali. So much of

¹ Washburn, *THIS JOURNAL*, 30, 31 (1918).

the reagent is used in one determination that one must look out for even traces of hypochlorite, particularly.

Many would no doubt prefer to use Kjeldahl flasks for the digestion instead of Erlenmeyers, in case a convenient Kjeldahl outfit is at hand.

In the analytical data below, the purpose is to show whether the digestion method is worthy of confidence as a means of preparing the sample. Accordingly the Carius method, followed by the same Gooch-Browning estimation, is adopted as the standard. In this scheme the sample is sealed in the usual bomb-tube with 2 cc. of fuming nitric acid, oxidized completely, and the contents evaporated to dryness on the water-bath to remove nitric and nitrous acids. The usual reduction with hydriodic acid, and titration, follows.

Substance.	Formula.	Calc. %.	Found.	
			Carius %.	Digestion method. %.
<i>p</i> -Tolyl-arsonic acid....	$\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{AsO}_3\text{H}_2$	34.72	34.52	34.60, 34.44
Phenyl-arsonic acid.....	$\text{C}_6\text{H}_5\text{AsO}_3\text{H}_2$	37.10	37.00	37.04, 36.91
"Salvarsan"-Metz (Ar- sphenamine, 1918).....	31.78	31.58
Neo-arsphenamine.....	{ 18.30 18.18	{ 18.36 18.27
Phenylacetic- <i>p</i> -arsonic acid.....	$\text{COOH}\cdot\text{CH}_2\text{C}_6\text{H}_4\text{AsO}_3\text{H}_2$	28.83	28.58	28.50
Nitro-oxyphenyl-arsonic acid.....	$\text{NO}_2\text{OH}\cdot\text{C}_6\text{H}_3\text{AsO}_3\text{H}_2$	28.50	28.34
Arsanilic acid (from Schamberg, Phila.)...	$\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsO}_3\text{H}_2$	34.55	34.57, 34.40
Hexamethyl-triamino- triphenyl-arsine.....	$(\text{CH}_3)_6\text{N}_3(\text{C}_6\text{H}_4)_3\text{As}$	17.21	17.24, 17.42

Resublimed arsenious oxide: samples of the same material used to standardize the iodine solution were mixed with about 0.2 g. of organic matter, and treated as though they were of an unknown organic arsenical.

Arsenic taken: 0.06794 g., 0.07815 g. Found: 0.0678 g., 0.0783 g.

Summary.

1. A brief review is given of the more convenient methods of analysis of organic arsenicals, with the conclusion that none of these deserves the confidence in research work that can be placed in the tedious but accurate Carius method.

2. A method is proposed, whereby the time of analysis is shortened to 2 hours, during one of which the attention of the worker is not needed. The sample is oxidized with a mixture of nitric and sulfuric acids, freed from nitrous compounds by use of ammonia sulfate, reduced with hydriodic acid, and titrated with standard iodine. Numerical data are given for analyses, made with ordinary rapid technique, to show correspondence with figures obtained in a standard manner.