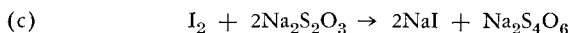
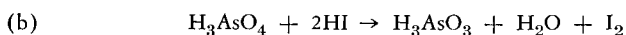
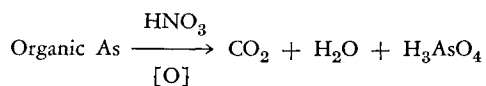


Microdetermination of Arsenic

CARIUS VOLUMETRIC METHOD

The determination of arsenic in organic compounds is based on the oxidation of the organic material to carbon dioxide and water and the arsenic to arsenic acid, simultaneously.^{22-24,43-46,50-53,57,61,65} The oxidation may be effected by several means as well as the subsequent determination of the arsenic acid.^{5,6,11-14,22-24,43-46,50-53,57,61,65} For these, the author prefers the Carius method^{11-14,57} of oxidation (compare Chapters 10 and 11) and the iodometric procedure^{45,50-53,57,65} for the arsenic acid. Although other methods^{23,24,45,46,50-53} have been used in the author's laboratory for both stages, best results were obtained with these. The reactions are as follows^{22,45,50-53,57,65}:

(a) Oxidation:



With this procedure, there is no interference from halogens (bromine, chlorine, fluorine, or iodine), sulfur, or phosphorus. With other procedures, interference has been reported.²²

Reagents

FUMING NITRIC ACID, SP. GR., 1.49-1.50

Reagent grade of fuming nitric acid, sp. gr. 1.49-1.50, is used to oxidize the organic material to carbon dioxide and water and the arsenic to arsenic acid. (*Caution:* see Chapter 10.)

CONCENTRATED HYDROCHLORIC ACID, SP. GR., 1.190

Reagent grade of concentrated hydrochloric acid, sp. gr. 1.190, is treated just before being used, as follows^{45,53,57,65}: About 20-25 ml. of acid is placed in a 125-ml. ground glass-stoppered flask with the stopper removed. The acid is boiled gently for 2-3 minutes to drive out any free chlorine present. The flame

is removed, the ground glass stopper loosely inserted, and the contents of the flask cooled under the tap. (Note: If the stopper cannot be removed after cooling, the closed flask is placed under a warm water faucet for a few seconds, after which the stopper can be removed.)

POTASSIUM IODIDE SOLUTION, 4%^{45,50-53,57}

This solution is prepared immediately before being used and must be colorless. It is converted into hydriodic acid during the determination of the arsenic acid.

STANDARD SODIUM THIOSULFATE, 0.01N

This solution is prepared and standardized according to the directions given in Chapter 5. It is used to titrate the iodine liberated by the reaction between the hydriodic acid (from the KI) and the arsenic acid.

STARCH INDICATOR

This is prepared according to the directions given in Chapter 5.

DISTILLED WATER

This is freshly boiled before the determination.

Apparatus

CARIUS COMBUSTION TUBE⁵⁸

The combustion tube described in Chapter 10 (see Fig. 137) is used in the oxidation.

CARIUS COMBUSTION FURNACE^{30,58,60}

The furnace described in Chapter 10 (see Fig. 135) is used for heating the Carius tube.

BLAST LAMP

The blast lamp described in Chapter 10 (see Fig. 138) is used for sealing the Carius tubes.

GRINDING OR CUTTING WHEEL

The motor-driven Carborundum grinding wheel described in Chapter 10 (see Fig. 139) is used for cutting a groove around the Carius tubes after combustion.

BURETTE

An automatic microburette of the types described in Chapter 5 (Figs. 69, and 70) is used in the titration of the liberated iodine (resulting from the reaction between the HI and H_3AsO_4).

Procedure^{45,50-53,57,65}

Five to 10 mg. of sample (or enough to require about 5 ml. of thiosulfate to titrate the liberated iodine—see below) is weighed* as described in Chapter 3 and placed in a clean, dry Carius combustion tube (refer to Chapter 10). Five to six tenths† (seven tenths *maximum*)⁵⁸ of a ml. of fuming nitric acid, sp. gr. 1.49–1.50, is added to the sample and the combustion tube sealed according to the method described in Chapter 10. The sealed tube is then heated in the Carius combustion furnace at a temperature of 250° C.† for 7–8 hours. The tube is then opened (*refer to method described in Chapter 10*) and the contents quantitatively rinsed into a 30-ml. beaker. The beaker is then placed on a steam bath and the contents evaporated down to dryness. One ml. of the freshly boiled distilled water is then added to dissolve the residue and the resulting solution transferred to a 125-ml. ground glass-stoppered flask. The beaker is then washed with 5 ml. of freshly boiled concentrated hydrochloric acid (in five portions of one ml. each to insure quantitative transfer) and the acid washings added to the water solution of arsenic acid in the ground glass-stoppered flask. To the acid solution is added 2 ml. of 4% potassium iodide (freshly prepared and colorless). The flask is immediately stoppered and the mixture allowed to stand for 10 minutes. The liberated iodine is then titrated with standard 0.01*N* sodium thiosulfate until the solution is light yellow in color. Twenty ml. of recently boiled, cold distilled water is added, followed by three to four drops of starch indicator and the titration with thiosulfate completed (refer to Chapter 5). [Note: A faint pink tint to the solution is considered to be the end point. On standing for several minutes, the blue coloration reappears. In the event that the end point is overstepped, accidentally, a small measured amount of standard iodine solution (see Chapter 5) may be added, followed by thiosulfate to the end point but this should all be accomplished with as little delay as possible or high results will be obtained.]

Calculation:

Factor:

1 ml. of 0.01*N* Na₂S₂O₃ is equivalent to 0.3748 mg. of arsenic

$$\therefore \frac{\text{ml. of 0.01N Na}_2\text{S}_2\text{O}_3 \times 0.3748 \times 100}{\text{Wt. sample}} = \% \text{ As}$$

Example:

4.75 ml. of 0.01*N* thiosulfate is required to titrate the iodine liberated in the analysis of a 6.319-mg. sample.

$$\therefore \frac{4.75 \times 0.3748 \times 100}{6.319} = 28.17\% \text{ As}$$

The accuracy of the method is ± 0.2 – 0.3% .

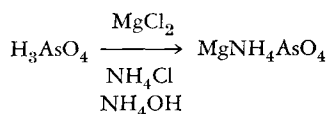
* If the sample is weighed into a porcelain boat, the boat is put into the Carius tube.

† See Table 21, Chapter 10.

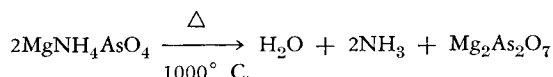
CARIUS GRAVIMETRIC METHOD

Instead of the preferred iodometric method described previously, the determination may be carried out gravimetrically.^{22-24,45,46,50-53,57} The author used this latter method for approximately nine years before changing to the iodometric. Although the gravimetric procedure gives good results there are considerably more manipulations involved besides the necessity of using the small porcelain filter crucible^{23,45,46,50-53,57,59} (Neubauer) (Fig. 166) with the attending danger of loss of precipitate during filtration in the hands of a beginner.

The organic material is destroyed by Carius combustion as described for the iodometric method. The resulting arsenic acid is treated with magnesia mixture yielding magnesium ammonium arsenate which in turn is converted into magnesium pyroarsenate according to the following reactions^{22,57,61}:



then



Reagents

FUMING NITRIC ACID, SP. GR. 1.49–1.50

AMMONIUM HYDROXIDE^{45,46,57}

A 2*N* solution of ammonium hydroxide is prepared by diluting reagent grade of concentrated material (sp. gr. 0.90, 28%²⁹ NH₃, 15*N*²⁹) with water.

MAGNESIA MIXTURE^{22,23,45,46,50-53,57}

Five and one-half grams of crystalline magnesium chloride and 10.5 grams of ammonium chloride, both reagent grade, are dissolved in 100 ml. of distilled water.

ETHANOL, 95%

Apparatus

CARIUS COMBUSTION TUBE	} See above.
CARIUS COMBUSTION FURNACE	
BLAST LAMP	
GRINDING OR CUTTING WHEEL	

PORCELAIN FILTER CRUCIBLE AND COVER^{57,59}

The porcelain filter crucible and cover shown in Fig. 166, are used for collecting and igniting the precipitate. There is an unglazed porous porcelain bottom, which is the filter medium. The crucible is attached to the filter assembly (see below) and cleaned with dilute hydrochloric acid, rinsed with water,

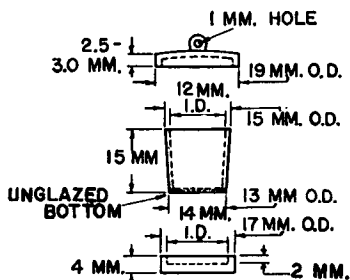


Fig. 166. Porcelain filter crucible and cover (Neubauer)—details of construction.

2*N* ammonium hydroxide, ethanol, and again with 2*N* ammonium hydroxide, in the order named. It is then dried in an oven for 20 minutes at 120° C., after which it and the cover are heated to 1000° C. for 10 minutes in a muffle furnace, cooled for one hour on a metal block in a desiccator (Figs. 43–46), Chapter 3), and weighed.

CRUCIBLE FILTER ASSEMBLY^{57,59}

A suction flask assembly similar to that used in Chapter 11 (Fig. 160) is required. The tube shown in Fig. 167, which fits into the suction flask, takes the place of that used with the above mentioned assembly. The crucible is held securely on top of this tube by means of a rubber sleeve made of thin-walled rubber tubing. This simple assembly is recommended in preference to the more complicated Wintersteiner assembly^{57,59,64} which is difficult to control and seems to be very little used at present.

OVEN

An ordinary laboratory type oven (Chapter 4) is used to dry the precipitate.

MUFFLE FURNACE⁶⁰

A small muffle furnace of the type shown in Fig. 88, capable of attaining a temperature of 1000° C., is used to convert the magnesium ammonium arsenate to magnesium pyroarsenate.

Procedure^{22,23,45,46,50-53,57}

Five to 10 mg. of sample is decomposed in a Carius tube and the resulting nitric-arsenic acid solution evaporated to dryness in a 30-ml. beaker exactly as described for the iodometric method in the preceding pages.

The residue is then dissolved in 4 ml. of 2*N* ammonium hydroxide. To the resulting solution is added 1 ml. of magnesia mixture and the beaker is then placed in the freezing compartment of a refrigerator overnight. The precipitate which is at first amorphous becomes crystalline. The next morning

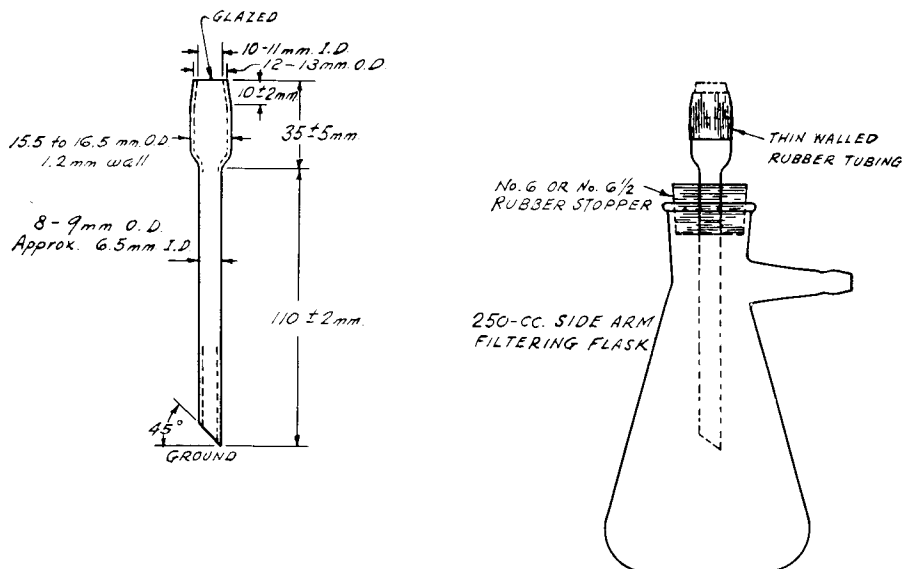


FIG. 167. Crucible filter assembly—details of construction.

the contents are allowed to melt and the precipitate transferred to the porcelain filter crucible with the aid of a medicine dropper.^{45,46,54,57} The precipitate and supernatant liquid are sucked up into the dropper and slowly deposited onto the filter while mild suction is applied to the flask. (Or, if preferred, a conventional glass rod covered by a rubber sleeve or policeman may be used.) After the main bulk of the precipitate has been transferred to the filter, the remaining precipitate in the beaker is transferred with the aid of small portions of, alternately, 2*N* ammonium hydroxide and ethanol. The precipitate is then washed with 3 ml. of 2*N* ammonium hydroxide and the crucible placed in an oven at 120° C. for 20 minutes. The crucible cover is then put in place, the covered crucible removed to a muffle furnace, and heated at 1000° C. for 10 minutes after which it is allowed to cool for one hour on a metal block in a desiccator (Figs. 43-46, Chapter 3) and weighed.

Calculation:

Factor:

$$\frac{2\text{As}}{\text{Mg}_2\text{As}_2\text{O}_7} = 0.4826$$

$$\therefore \frac{\text{Wt. precipitate} \times 0.4826 \times 100}{\text{Wt. sample}} = \% \text{ As}$$

Example:

6.053 mg. of $\text{Mg}_2\text{As}_2\text{O}_7$ is obtained from a 7.801-mg. sample

$$\therefore \frac{6.053 \times 0.4826 \times 100}{7.801} = 37.45\% \text{ As}$$

The method has an accuracy of about $\pm 0.3\%$.

TABLE 25

ADDITIONAL INFORMATION ON REFERENCES* RELATED TO CHAPTER 13

In addition to the methods described in detail in the preceding pages of this chapter, the author wishes to call to the attention of the reader the references listed in Table 25. (See statement at top of Table 4 of Chapter 1, regarding completeness of this material.)

Books

Belcher and Godbert, 5, 6
 Clark, S. J., 17
 Furman, 22
 Grant, 23, 24
 Milton and Waters, 43, 44
 Niederl and Niederl, 45, 46
 Pregl, 48
 Roth, 50-53
 Steyermark, 57

General, miscellaneous, and review material

Heller, 28
 How, 31
 Jacobs and Nagler, 32
 Roth, 49

Ultramicro-, submicro-methods

Kingsley and Schaffert, 35

Simultaneous determination of arsenic and other elements

Grant, 24
 Roth, 52
 Schulek and Wolstadt, 55

Carius combustion

Steyermark, 57

Kjeldahl-type digestion (nitric and sulfuric acid, sulfuric acid and hydrogen peroxide, chloric acid, etc.)

Belcher and Godbert, 5
 Furman, 22
 Lévy, 39, 40
 Niederl and Niederl, 45
 Roth, 51-53
 Tuckerman, Hodecker, Southworth, and Fleischer, 62

Oxygen flask combustion

Corner, 18
 Merz, 42

Bomb methods and fusion in general

Beamish and Collins, 4
 Jureček and Jeník, 33, 34

Volumetric, iodometric methods

Bahr, Bieling, and Thiele, 1, 2
 Furman, 22
 Jureček and Jeník, 33, 34
 Sloviter, McNabb, and Wagner, 56

* The numbers which appear after each entry in this table refer to the literature citations in the reference list at the end of the chapter.

TABLE 25 (Continued)

Ceric sulfate titration	Marsh, Gutzeit,^{21,22,25} arsine, etc., methods
Kolthoff and Amdur, 36	Bodnar, Szep, and Cielezsky, 7
Photometric, colorimetric methods	Bystrov and Parshikov, 10
Bricker and Sweetser, 8	Cassil, 15
Bruno and Belluco, 9	Furman, 22
Chaney and Magnuson, 16	Grant, 23, 24
Crawford, Palmer, and Wood, 19	Haight, 26
Di Bacco, 20	How, 31
Jacobs and Nagler, 32	Jureček and Jeník, 33, 34
Oliver and Funnell, 47	Lachele, 37
Tuckerman, Hodecker, Southworth, and Fleischer, 62	Levy, G. A., 38
Electrolytic, potentiometric, coulometric methods	Milton and Waters, 43
Grant, 23, 24	Yoshimura, 66
Lévy, 39–41	Distillation of trichloride
Tutundžić and Mladenović, 63	Bang, 3
Yoshimura, 66	Milton and Waters, 43
Gravimetric methods	Chromatographic method
Heller, 27	Bruno and Belluco, 9
Saschek, 54	
Wintersteiner, 64	

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