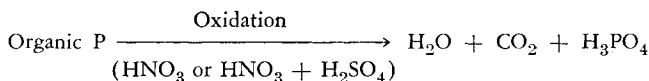
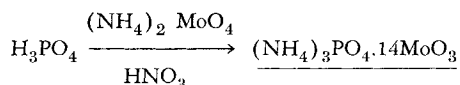


## Microdetermination of Phosphorus

The determination of phosphorus in organic compounds is based on the destruction of organic material, conversion of the phosphorus, in the process to phosphoric acid, and the subsequent conversion of this to ammonium phosphomolybdate according to the following reactions:<sup>66,67,74,89</sup>



and



The formula for the ammonium phosphomolybdate precipitate is empirical, based on the work of Pregl,<sup>74</sup> and is quite different from that accepted in macro-analysis, namely,  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot 2\text{HNO}_3 \cdot \text{H}_2\text{O}$ , which on being heated at 160°–180° C is converted into  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ .<sup>95</sup>

Two procedures of decomposing the sample are given below, namely, one employing a Kjeldahl-like type of digestion and the other employing Carius combustion. The Kjeldahl-like type of digestion is not applicable to fluorine-containing compounds, but is generally proven to be reliable with other substances. This digestion, together with the rest of the procedure described below, was adopted by the Association of Official Agricultural Chemists after being subjected to collaborative study.<sup>69,70</sup> However, this method of destroying organic material is not as vigorous as employing Carius combustion so that it is quite conceivable that certain compounds which resist oxidation might be better treated by the latter. Therefore, it is recommended that both be employed where there is doubt. The Carius procedure described below is applicable to fluorine-containing compounds.<sup>81</sup>

### KJELDAHL GRAVIMETRIC METHOD

(Not Applicable to Fluorine-containing Compounds)\*

#### Reagents

##### CONCENTRATED SULFURIC ACID, SP. GR. 1.84

Reagent grade of concentrated sulfuric acid, sp. gr. 1.84 is used as part of the combustion mixture.

\* A white precipitate is present at the end of the digestion. (Compare Fennel, Roberts, and Webb,<sup>30</sup> and Furman and State.<sup>37</sup>)

**CONCENTRATED NITRIC ACID, SP. GR. 1.42**

Reagent grade of concentrated nitric acid is used along with the sulfuric acid, above, for oxidizing the organic material and converting the phosphorus to phosphoric acid.

**NITRIC-SULFURIC ACID MIXTURE<sup>66,67,89</sup>**

Four hundred and twenty milliliters of concentrated nitric acid, sp. gr. 1.42, is slowly poured into 580 ml. of distilled water. To this is added, slowly, 30 ml. of concentrated sulfuric acid, sp. gr. 1.84.

**AMMONIUM NITRATE SOLUTION, 2%**

A 2% solution of reagent grade of ammonium nitrate in distilled water is prepared and made slightly acid by the addition of two drops of concentrated nitric acid, sp. gr. 1.42, per liter. This solution, which is used as a wash liquid for the precipitate, is stored in a glass-stoppered bottle. This solution must be filtered immediately before being used, as it often develops a flaky precipitate.

**MOLYBDATE REAGENT<sup>66,67,89</sup>**

One hundred and fifty grams of reagent grade of powdered ammonium molybdate is dissolved in 400 ml. of boiling distilled water and the resulting solution, which is usually cloudy, is cooled to room temperature under a tap. Fifty grams of reagent grade of ammonium sulfate is placed in a 1-liter volumetric flask and dissolved in a mixture of 105 ml. of distilled water and 395 ml. of concentrated nitric acid, sp. gr. 1.42. The volumetric flask containing the nitric acid solution of ammonium sulfate is cooled under the tap while the cooled solution of ammonium molybdate (even though cloudy) is added to it, slowly, in a thin stream, and with constant stirring. At no time should the mixture in the volumetric flask be allowed to become warm. The resulting solution which should be almost clear is diluted with distilled water to 1000 ml. and stored in a refrigerator for 3 days. It is then filtered through an ordinary filter paper and stored in a paraffin-lined<sup>\*9,89</sup> glass-stoppered brown reagent bottle in the refrigerator. It is filtered again immediately before being used. Since this reagent is stable for only some months, it should be repeatedly checked by performing a phosphorus determination with it using some known substance. As the reagent ages, low results are obtained even though duplicate determinations will give excellent checks on each other.

**ETHANOL, 95%**

Ethanol, 95%, is used as a wash liquid for the precipitate.

\* The paraffin-lined bottle is prepared by adding molten paraffin (melted on a steam bath) to the dry bottle and rotating until the wax has completely solidified.

## ACETONE

Pure acetone is used as a wash liquid for the precipitate.

## Apparatus

### KJELDAHL DIGESTION FLASK, 30 ML.

The regular straight type of Kjeldahl flask, 30 ml. (Fig. 105, Chapter 8) is used for both oxidation of the organic material and the precipitation of the ammonium phosphomolybdate.

### DIGESTION RACK AND MANIFOLD

The Kjeldahl flasks are held during digestion of the sample in the Kjeldahl digestion rack and manifold described in connection with the Kjeldahl determination of nitrogen (Figs. 107–110, Chapter 8).

### FILTER TUBE<sup>41,42,66,67,74,77–80,89,91</sup>

The filter tubes described in the chapter on the halogen determination are used for collecting the precipitate (see Figs. 158 and 159, Chapter 11). They should be tested to make certain that the filter will retain the phosphomolybdate precipitate. The filter tubes may be used without cleaning for successive determinations done the same day but not at longer periods. The filter tubes are cleaned between determinations by treatment with 0.1N NaOH to dissolve the precipitate followed immediately by water, dilute nitric acid, ammonium nitrate, ethanol, and acetone exactly as done during a determination (see below).

### FILTRATION ASSEMBLY<sup>89,91</sup>

The filtration assembly described in the above-mentioned chapter is used in transferring the precipitate from the Kjeldahl flask to the filter tube (see Fig. 160, Chapter 11).

### WASH BOTTLES

Two wash bottles of the type shown in Figs. 145 or 146, Chapter 10 (one each for the ammonium nitrate and the ethanol) are used in transferring the precipitate from the Kjeldahl flask to the filter tube.

### RUBBER OR NEOPRENE STOPPERS

Two or three small *solid* rubber or neoprene stoppers are used in removing the precipitate from the walls of the Kjeldahl flask during its transfer to the filter tube. These are dropped into the bulb of the flask and shaken around in the presence of a small amount of the wash liquids. They strike the walls

of the flask and act in the same manner as does the ordinary rubber policeman, generally used in macroanalysis. The smaller ends of the universal solid stopper<sup>1,88,89</sup> shown in Fig. 165, serve the purpose very well.

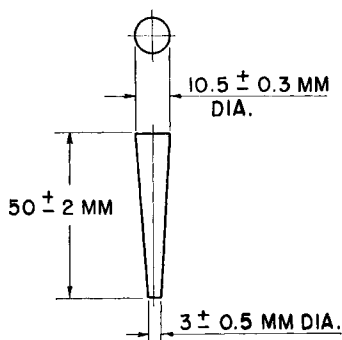


FIG. 165. Solid rubber (or neoprene) stopper—details of construction.

#### VACUUM DESICCATOR

An ordinary vacuum desiccator, without desiccant, is used in drying the precipitate.

#### VACUUM PUMP

An ordinary electric motor-driven vacuum pump, capable of producing a pressure of a fraction of a millimeter of mercury, is used in the drying of the precipitate.

### Procedure<sup>66,67,89</sup>

About 5 mg. of sample is weighed and transferred into a Kjeldahl flask, 30 ml., by one of the methods described in Chapter 3, that of using the charging tube (Figs. 47–49, Chapter 3) being preferred to the others for this purpose, since a precipitation also is done in this flask. (In the event that a porcelain boat must be used, it is removed after the digestion and washed with the nitric-sulfuric acid mixture and with the water required to dilute the digest. If the sample must be weighed in a glass capillary, this too must be removed before precipitation either by the use of a platinum wire or by filtration.) The size of the sample should be governed by the percentage of phosphorus present so that a precipitate of not more than 40–50 mg. is obtained. (The weight of the precipitate is roughly sixty-nine times that of the phosphorus present.<sup>74</sup>) One-half milliliter of concentrated sulfuric acid is added to the sample in the Kjeldahl flask followed by four to five drops of concentrated nitric acid. The flask is placed on the digestion rack and the mixture heated, cautiously at first and then strongly, until no more brown fumes of oxides of nitrogen

escape and only white ones of sulfur trioxide are in the neck of the flask. The flask is then cooled under the tap and four to five drops of concentrated nitric acid again added and the above-described heating repeated, cooled, four to five drops of nitric acid added, and the contents heated a third time until white fumes of sulfur trioxide appear. It is then cooled and 2 ml. of the nitric-sulfuric acid mixture added, followed by 12.5 ml. of distilled water. The contents of the Kjeldahl flask are then heated on a steam bath for 15 minutes to insure complete conversion of the phosphorus to orthophosphoric acid. The Kjeldahl flask is then removed from the steam bath, held vertically, and 15 ml. of freshly filtered molybdate reagent added immediately by means of a pipette. The reagent should be added so that it drops into the center of the liquid in the Kjeldahl flask and none flows down the sides. (Note: The mixture should not be heated after the addition of the molybdate reagent.) The resulting yellow solution soon becomes cloudy and after 2–3 minutes the flask is swirled gently to thoroughly mix the contents but not violently enough to cause splashing on the sides. It is then covered so as to prevent contamination with dust and set aside in the dark overnight.

The next morning the precipitate is filtered into a previously weighed filter tube with the aid of the filtration assembly using the technique described for the halogen determination (Chapter 11). After the bulk of the precipitate and the supernatant liquor is transferred, a small amount of precipitate clings to the inner walls of the Kjeldahl flask. Small amounts of ammonium nitrate and ethanol, respectively, are alternately used to complete the transfer of the ammonium phosphomolybdate. If after a few alternate washings, some precipitate still clings to the inner walls, two or three clean tiny solid rubber stoppers are dropped into the flask, followed by a little wash liquid and the stoppers made to bounce around by shaking. This removes the last traces of precipitate from the walls and after several more washings alternately with ammonium nitrate and ethanol, respectively, the transfer is quantitative. (The rubber stoppers are kept in the flask during the transfer and if they have been selected small enough, do not interfere with the siphon tube.) The siphon tube is then disconnected from the filter tube, the stopper which had joined them washed with ammonium nitrate and then with ethanol, catching the washings in the filter tube. The precipitate is then washed with a little more ammonium nitrate, then with ethanol, and finally with acetone and sucked dry. The filter tube is then wiped with a chamois skin (see Chapter 3)\* and placed in a vertical position in a vacuum desiccator which contains no desiccant. The desiccator is then evacuated to a pressure of about one mm. Hg for a period of 30 minutes, the pump being kept in continuous operation. The vacuum is then released and the filter tube *immediately* weighed to the nearest

\* Ground tube after wiping.

0.1 mg. The precipitate is extremely hygroscopic so that it is impossible to attempt to weigh in the normal manner. Unless there is undue delay in weighing the absorbed moisture does not affect the results since the factor is so low.

As explained above, the filter may be used for successive determinations on the same day but not for longer periods.

*Calculation:*

*Factor:* 0.014524\*36,42,74,77-79,89

$$\therefore \frac{\text{Wt. of precipitate} \times 0.014524 \times 100}{\text{Wt. sample}} = \% \text{ P}$$

*Example:*

33.1 mg. of ammonium phosphomolybdate is obtained from a 5.316-mg. sample

$$\therefore \frac{33.1 \times 0.014524 \times 100}{5.316} = 9.04\% \text{ P}$$

The accuracy of the determination is about  $\pm 0.3\%$ .

## CARIUS GRAVIMETRIC METHOD (Applicable to Fluorine-containing Compounds)

Although the Kjeldahl gravimetric method has been used with reliability in the author's laboratories for more than twenty years, it is not applicable to fluorine-containing compounds. As stated earlier in this chapter, by substituting Carius combustion for the Kjeldahl digestion these compounds yield correct results. The rest of the method, namely, precipitation as ammonium phosphomolybdate, is the same as for the Kjeldahl. The method is not restricted to fluorine-containing compounds, but may be used on all types of substances. The only disadvantage is the time factor in regard to the combustion, but as pointed out in Chapters 10 and 11, this becomes unimportant. In addition, due to the vigorous treatment during the combustion, certain compounds which resist oxidation are better handled by this method.

\* Pregl<sup>74</sup> established the factor empirically as 0.014524 ( $\log = 16209$ ). Roth<sup>77-79</sup> also gave these figures. However, the English translations of Roth-Pregl by Daw<sup>80</sup> and by Grant<sup>41</sup> and also in the first and second editions of the book by Niederl and Niederl,<sup>86,87</sup> the factor has been mistakenly given as 0.01454. Niederl and Niederl, and Daw list the correct logarithm for 0.014524, namely, 16209, but Grant has listed the log as 16249 which is neither correct for 0.014524 nor for 0.01454.

## Reagents

### FUMING NITRIC ACID, REAGENT GRADE

Reagent grade of acid, sp. gr. 1.49–1.50 is used for destroying the organic material and converting the phosphorus to phosphoric acid. (*Caution!* See Chapter 10.)

CONCENTRATED SULFURIC ACID, SP. GR. 1.84

NITRIC-SULFURIC ACID MIXTURE

AMMONIUM NITRATE SOLUTION, 2%

MOLYBDATE REAGENT

ETHANOL, 95%

ACETONE

} Same as for Kjeldahl gravimetric method.

## Apparatus

### CARIUS COMBUSTION FURNACE<sup>90</sup>

See Chapter 10, Fig. 135.

### CARIUS COMBUSTION TUBE<sup>90</sup>

See Chapter 10, Fig. 137.

KJELDAHL DIGESTION FLASK, 30 ML.

FILTER TUBE

FILTRATION ASSEMBLY

WASH BOTTLES

RUBBER STOPPERS

VACUUM DESICCATOR

VACUUM PUMP

} Same as for Kjeldahl gravimetric method.

## Procedure

About 5 mg. of sample is weighed and transferred into a Carius combustion tube by one of the methods described in Chapter 3 (also see Chapter 10). (If a porcelain boat, capillary, or weighing bottle is used, it must be removed previous to precipitation.) The size of the sample should be governed by the percentage of phosphorus present so that not more than 40–50 mg. of ammonium phosphomolybdate precipitate is obtained. (The weight of the precipitate is roughly sixty-nine times that of the phosphorus present.<sup>74</sup>) One-half milliliter of fuming nitric acid is added and the Carius tube sealed. (*Caution!* See Chapter 10 regarding *all* precautions as to quantities of acid, length of sealed tube, temperatures, opening of tubes after combustion, etc.<sup>90</sup>)

The sealed tube is heated at 250° C.\* for 8 hours in the Carius combustion furnace, after which the tubes are cooled, opened, the contents transferred to a 50 ml. beaker and evaporated to *dryness* on a steam bath. To the residue is added 0.5 ml. concentrated sulfuric acid, followed by 2 ml. of the nitric-sulfuric acid mixture. The resulting solution is transferred to a 30 ml. Kjeldahl digestion flask and diluted with 12.5 ml. of distilled water, which is used in the transfer. The contents of the flask are then heated on a steam bath for 15 minutes to insure complete conversion of the phosphorus to orthophosphoric acid. The flask is then removed from the steam bath, held vertically, and 15 ml. of freshly filtered molybdate reagent added immediately, by means of a pipette, *exactly* as described in the early part of this chapter, in connection with the Kjeldahl gravimetric method. From this point on the procedure is *exactly* the same as that of the above, that is, the mixing, allowing to stand overnight, filtering, washing, drying, and weighing.

*Calculation:*

Same as for the Kjeldahl Gravimetric Method.

## SIMULTANEOUS DETERMINATION OF BARIUM AND PHOSPHORUS

Barium and phosphorus may be determined simultaneously. After Carius combustion, the contents of the tube are washed with distilled water into a previously weighed porcelain sulfur crucible (Fig. 143, Chapter 10), and the contents evaporated to dryness on a steam bath. The residue is treated with 2–3 ml. of distilled water and about one ml. of 10% sulfuric acid, and the contents digested on a steam bath to coagulate the precipitate. (If Kjeldahl digestion<sup>79,80</sup> has been used instead of Carius combustion, the contents of the Kjeldahl flask are washed into the porcelain sulfur crucible. In this case, no additional sulfuric acid should be added. However, since barium phosphate is *soluble* in dilute acid solution, the Carius procedure is to be preferred, because, with the Kjeldahl procedure, the precipitated barium sulfate is difficult to transfer to the porcelain sulfur crucible.) The filtrate is sucked off *and the washings* added to the main filtrate, keeping the volume to about 12 ml. The precipitate ( $\text{BaSO}_4$ ) is dried, ignited, and weighed (see Chapter 10). The filtrate and washings are transferred to a 30 ml. Kjeldahl flask and *if* Carius combustion was used, 0.4 ml. of concentrated sulfuric acid is added. (However, if Kjeldahl digestion was used *no additional concentrated sulfuric acid should be added.*) Then, 2 ml. of the nitric acid-sulfuric acid mixture is added,

\* See Table 21, Chapter 10.



followed by heating on the steam bath for 15 minutes, addition of 15 ml. of molybdate reagent, standing overnight, filtration, drying, and weighing of the ammonium phosphomolybdate as described previously in this chapter.

TABLE 24

## ADDITIONAL INFORMATION ON REFERENCES\* RELATED TO CHAPTER 12

As with the previous chapters, the author wishes to call to the attention of the reader additional material in regard to the determination of phosphorus. This is shown in Table 24. (See statement at top of Table 4 of Chapter 1, regarding completeness of this material.)

**Books**

Association of Official Agricultural Chemists, 2  
Belcher and Godbert, 6, 7  
Clark, E. P., 19  
Clark, S. J., 20  
Furman, 36  
Grant, 41, 42  
Milton and Waters, 63  
Niederl and Niederl, 66, 67  
Niederl and Sozzi, 68  
Pregl, 74  
Roth, 77-80  
Steiermark, 89

**Collaborative studies**

Association of Official Agricultural Chemists, 2  
Ogg, 69, 70

**Ultramicro-, submicro-methods**

Harvey, 43  
Kirsten, 51, 52  
Lindner and Kirk, 59  
Nakamura, 64  
Schaffer, Fong, and Kirk, 84  
Welch and West, 99

**Simultaneous determination of phosphorus and other elements**

Bartels and Hoyme, 4  
Eger and Lipke, 28  
Klimova, Korshun, and Terent'eva, 54  
Korshun and Terent'eva, 55  
Merz, 62  
Roth, 79, 80

**Fluoro-compounds**

Belcher and Macdonald, 8  
Fennell, Roberts, and Webb, 30  
Fennell and Webb, 31  
Furman and State, 37  
Rush, Cruikshank, and Rhodes, 81

**General, miscellaneous**

Bachofer and Wagner, 3  
Bartels and Hoyme, 4  
Chen, Toribarb, and Warner, 18  
Fennell and Webb, 32  
Harvey, 43  
Kirsten and Carlsson, 53  
Ma and McKinley, 61  
Tunncliffe, 97

**Carius combustion**

Olivier, 71  
Rush, Cruikshank, and Rhodes, 81

**Kjeldahl-type digestion (sulfuric or perchloric plus nitric acids)**

Association of Official Agricultural Chemists, 2  
Chalmers and Thomson, 17  
Clark, S. J., 20  
Cogbill, White, and Susano, 21  
Kirsten and Carlsson, 53  
Lévy, 56  
Sakamoto and Hayazu, 82  
Sterges, Hardin, and MacIntire, 86  
Steiermark, 89  
Welch and West, 99

\* 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 24 (Continued)

**Bombs and fusion in general**

Batt, 5  
 Burton and Riley, 15  
 Clark, E. P., 19  
 Clark, S. J., 20  
 Niederl and Niederl, 66, 67  
 Parr, 72

**Oxygen flask combustion**

Belcher and Macdonald, 8  
 Bennowitz and Tänzer, 10  
 Cohen and Czech, 22  
 Corner, 23  
 Fleischer, Southworth, Hodecker, and  
 Tuckerman, 34  
 Kirsten and Carlsson, 53  
 Thomas, 94

**Gravimetric procedures**

Clark, E. P., 19  
 Clark, S. J., 20  
 Fennell and Webb, 31  
 Furman, 36  
 Gheorghiu and Radulescu, 39  
 Gottschalk, 40  
 Heller, 45  
 Lorenz, 60  
 Niederl and Niederl, 66, 67  
 Pregl, 74  
 Roth, 77-80  
 Rush, Cruikshank, and Rhodes, 81  
 Schuhecker, 85  
 Steyermark, 89  
 Tsuzuki, Miwa, and Kobayashi, 96  
 Woy, 100

**Volumetric procedures**

Belcher and Macdonald, 8  
 Diemair and Baier, 26  
 Fleischer, Southworth, Hodecker, and  
 Tuckerman, 34  
 Lindner and Kirk, 59  
 Niederl and Niederl, 67  
 Roth, 79, 80  
 Sakamoto and Hayazu, 82

**Quinoline phosphomolybdate****(8-quinolinol phosphomolybdate)**

Belcher and Macdonald, 8  
 Fennell and Webb, 31  
 Gottschalk, 40

**Strychnine phosphomolybdate methods**

Embden and Schmidt, 29  
 Hegedüs and Dvorszky, 44

**Spectrophotometric, colorimetric, optical methods**

Batt, 5  
 Bernhart and Wreath, 11  
 Bruno and Belluco, 14  
 Burton and Riley, 15  
 Carles, 16  
 Chalmers and Thomson, 17  
 Di Bacco, 24  
 Dickman and Bray, 25  
 Fiske and Subbarow, 33  
 Fleischer, Southworth, Hodecker, and  
 Tuckerman, 34  
 Fontaine, 35  
 Furman, 36  
 Gates, 38  
 Harvey, 43  
 Hegedüs and Dvorszky, 44  
 Jureček and Jeník, 47, 48  
 King, 49  
 Kirsten and Carlsson, 53  
 Nakamura, 64  
 Rhodes, 75  
 Roth, 76, 79  
 Sass, Ludemann, Witten, Fischer, Sisti,  
 and Miller, 83  
 Schaffer, Fong, and Kirk, 84  
 Taussky and Shorr, 92  
 Taylor, Miller, and Roth, 93

**X-ray fluorescence**

Natelson, 65  
 Philips Electronics, 73

**Flame photometry**

Brite, 13  
 Dippel, 27

TABLE 24 (Continued)

<b>Amperometric, potentiometric, polarographic methods</b>	<b>Manometric, gasometric methods</b>
Boos and Conn, 12	See Chapter 18
Cogbill, White, and Susano, 21	Hoagland, 46
Lévy, 56-58	Kirk, 50
Stern, 87	Van Slyke, Page, and Kirk, 98
<b>EDTA, complexometric procedures</b>	<b>Cation-exchange, chromatographic methods</b>
Bennewitz and Tänzer, 10	Bruno and Belluco, 14
Fleischer, Southworth, Hodecker, and Tuckerman, 34	Cogbill, White, and Susano, 21
	Eger and Lipke, 28

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