Microdetermination of Sulfur

The determination of sulfur in organic compounds is based on the combustion of the compound with the subsequent conversion of the sulfur to sulfur trioxide (or sulfate, if alkali or alkaline earth metals are present) and finally to barium sulfate. The organic material can be destroyed by several methods, but the author prefers either the Carius\textsuperscript{37-40,209,214} or the Schöninger.\textsuperscript{198-200,213} The Carius method has been proven reliable, over many years, with practically all types of compounds. There have been, however, a few isolated cases in which low unexplained results were obtained. In spite of these, the Carius method still remains the first method of choice of the author. The period required for each combustion is much longer than that for the other methods, but a number of Carius combustions can be carried out simultaneously in one furnace, overnight, which compensates for the time factor. The second method of choice of the author is the Schöninger and although this was introduced only a comparatively short time ago, it has proven to be reliable with a large variety of types of compounds. The author strongly recommends the use of these two methods and both should be used in cases of controversy. As a third choice, the Pregl catalytic combustion\textsuperscript{11,76,77,161,162,180,186-189,209} should be relied upon since it too has been proven to give good results in the hands of a number of analysts.\textsuperscript{11,165-168}

All of the procedures described in this chapter are applicable to fluorine-containing compounds. Phosphorus-containing compounds must be analyzed by one of the gravimetric procedures since barium phosphate is insoluble in the neutral solution required for the titration using tetrahydroxyquinone as the indicator. With the gravimetric procedures, there is no interference.

CARIUS COMBUSTION

VOLUMETRIC CARIUS METHOD\textsuperscript{209,214}

(Not Applicable to Phosphorus-containing Compounds)

With the Carius method, the organic material is destroyed by heating with nitric acid in the presence of some alkali metal salt as shown by the following:

\begin{itemize}
\end{itemize}
The acid sulfate is converted to sulfate and titrated with standard barium chloride solution to an end point using tetrahydroxyquinone indicator:\textsuperscript{1,3,8,2,169,206,209,213,214,220}

\[
\text{BaCl}_2 + \text{Na}_2\text{SO}_4 \rightarrow 2\text{NaCl} + \text{BaSO}_4
\]

(The sodium, calcium, ammonium, and potassium salts of tetrahydroxyquinone are yellow while the barium salt is red-purple.\textsuperscript{205})

**Reagents**

**FUMING NITRIC ACID, REAGENT GRADE\textsuperscript{209,213,214}**

Reagent grade of fuming nitric acid, sp. gr. 1.49 to 1.50 is used to destroy the organic material. (Caution: This acid must be handled with extreme care.)

**PURE SODIUM OR POTASSIUM SALT\textsuperscript{160,162,209,213,214}**

Any reagent grade of sodium or potassium salt (not containing sulfur), such as oxalate, acid phthalate, chloride, etc., is used for combining with the sulfur trioxide formed during the combustion.

**SODIUM HYDROXIDE, APPROX. 0.1N**

Approximately 0.1N sodium hydroxide (not standardized) is used to convert the acid sulfate to sulfate previous to the titration.

**HYDROCHLORIC ACID, APPROX. 0.01N**

Approximately 0.01N hydrochloric acid (not standardized) is used to back-titrature the excess sodium hydroxide referred to above.

**PHENOLPHTHALEIN INDICATOR**

This solution, prepared as described in Chapter 5, Standard Solutions, is used as an indicator in the titration of the acid sulfate obtained in the combustion.
ETHANOL, 95%
This is used so that the titration with barium chloride can be carried out in approximately 50% alcohol.

TETRAHYDROXYQUINONE INDICATOR (THQ)\(^1\)
(Prepared by W. H. & L. D. Betz.\(^2\)) This material is used as a solid—see Chapter 5 on Standard Solutions.

STANDARD POTASSIUM SULFATE, 0.01N
This solution is prepared according to the directions given in Chapter 5 on Standard Solutions.

STANDARD BARIUM CHLORIDE, 0.01N
This solution is prepared and standardized according to the directions given in Chapter 5 on Standard Solutions.

Apparatus

CARIUS COMBUSTION FURNACE\(^{209,211,225}\)
The combustion furnace used is of the type shown in Fig. 135. It should have at least four wells of approximately 16 mm. inside diameter and 225 mm. long. The wells should be held at a fixed inclined position of approximately 45° or should be adjustable. The furnace should be provided with a device for pushing the combustion tubes from the individual wells.

The furnace must be able to maintain a temperature in the wells of approximately 310° C. and the temperature at any point should not vary more than ± 5° C. from the operating temperature (electrically heated units should be able to perform thusly with voltages as low as 100 volts). The furnace temperature should be adjustable. There should also be a device that shows when the furnace is in operation and a temperature indicator.

The furnace should be equipped with safety devices to confine broken glass in the event of an explosion.

A valuable accessory for the furnace is an automatic time switch (Fig. 136), so that the furnace can be operated at night and be cooled by morning.

CARIUS COMBUSTION TUBES (BOMB TUBES)\(^{211}\)
Two types of tubes (Fig. 137) have been recommended, namely, heavy-walled and thin-walled, although the former is preferred by the author. Regardless of which is used, the conditions listed in Table 21 must be adhered to in order to
Fig. 135. Micro-Carius furnace. Top: Front view. (A) Small adapter tubes for use with undersize Carius tubes. Bottom: Rear view. (B) Push rods for removing Carius tubes.
minimize the danger of explosion. If directions are followed, the incidence of explosion is extremely small.

The specifications are designed for a maximum operating temperature of 300° C. The length of the sealed tube between the bottom and the start

![Automatic time switch.](image1)

![Carius combustion tube.](image2)

WALL THICKNESS MUST BE SAME IN PERFECTLY ROUND BOTTOM AS IN SIDE WALLS.
of the taper at the shoulder should be 150 to 175 mm. for the heavy-walled tubes and 180 to 210 mm. for the thin-walled type.

**TABLE 21**

*RECOMMENDED SPECIFICATIONS*²¹¹ FOR *CARIUS COMBUSTION TUBES*

<table>
<thead>
<tr>
<th>Combustion tube thickness (mm.)</th>
<th>O.D. (mm.)</th>
<th>Length between bottom and start of taper at shoulder (mm.)</th>
<th>Volume of HNO₃ (sp. gr. at 60°F, approximately 1.5)</th>
<th>Temp. (° C.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy-walled</td>
<td>2.3 ± 0.3</td>
<td>13 ± 0.8</td>
<td>210 ± 10</td>
<td>150 to 175</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>250</td>
</tr>
<tr>
<td>Thin-walled</td>
<td>1.2 ± 0.2</td>
<td>13 ± 0.7</td>
<td>240 ± 10</td>
<td>180 to 210</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>300</td>
</tr>
</tbody>
</table>

The glass should have a coefficient of linear expansion not exceeding 0.0000040 cm. per cm. per 1° C., with a softening point of 820° C. (Corning Pyrex 7740 or equal). Tubes at one end should have a closed round bottom of about the same wall thickness as the side walls and at the other end should be open and glazed. Tubes must be well annealed. The thickness of the wall and the length depend upon the volume of nitric acid used.

**BLAST LAMP**

Any small blast lamp as, for example, the type shown in Fig. 138, which gives an intensely hot flame when operated with gas and air or oxygen, may be used for sealing the combustion tubes.*

* With beginners, gas and air is preferred, because the glass does not flow as rapidly and the process is better controlled.
GRINDING WHEEL
A mechanically driven Carborundum grinding wheel of the type shown in Fig. 139 is used for cutting a groove in the combustion tubes previous to their being cracked open with the aid of a hot rod (see below under Procedure).

Fig. 139. Grinding wheel (glass cutter).

ILLUMINATED TITRATION STAND ASSEMBLY
The stand shown in Fig. 71 (Chapter 5—Standard Solutions) is used for the titration of sulfate with barium chloride.

CUVETTE
The cuvette shown in Fig. 72 (Chapter 5—Standard Solutions) is used as a titrating vessel.

ORANGE-BROWN FILTER PLATE
The orange-brown filter plate described in connection with the standardization of barium chloride (Chapter 5—Standard Solutions) is used as a comparator for obtaining the end point of the titration of sulfate with barium chloride.

Procedure
The amount of sample used should be enough to require 3 to 5 ml. of 0.01N barium chloride in the titration. If more or less is required the appearance of the titration mixture at the end point does not match that of the filter plate, adding confusion. If considerably more than 5 ml. of barium chloride is required (Ogg, Willits and Cooper allowed 5 ml. of 0.02 N BaCl₂) the determination is best discarded and the same holds if less than 3 ml. is used. In the former case a smaller sample should be used. In the latter case, a larger sample should be used, or if this is not feasible, enough standard potassium sulfate solution is added, just before titrating with barium chloride, so that the recommended quantity is required.
If the sample is a solid, it should be weighed by difference using a charging tube (Figs. 47-49, Chapter 3). Care should be exercised so as not to have sample on the walls of the Carius tube. This is accomplished by holding the charging tube, containing the sample, upright. The empty Carius combustion tube is brought down over it (closed end upward) as far as possible while still holding the charging tube. The combination is quickly inverted and gently tapped so that the sample drops into the Carius tube and no particles adhere to the charging tube rim. If the sample is a high-boiling liquid, it should be weighed in a porcelain boat (Chapter 3) and the boat inserted in the combustion tube. A low-boiling liquid is weighed in a plain capillary (see Chapter 3), the end of which is broken before insertion in the Carius tube. Methylcellulose capsules also may be used. About 15–20 mg of some pure sodium or potassium salt (such as oxalate, acid phthalate, chloride, etc.) is added to the combustion tube with gentle tapping to dislodge any material adhering to the walls. (If too much salt is added, a fading end point results in the titration. Consequently, if an organic compound is being analyzed which contains an alkali metal, the amount of sodium or potassium salt added should be proportionately reduced.) Next is added 0.5–0.6 (0.7 maximum) ml of fuming nitric acid, sp. gr., 1.49 to 1.50, while rotating the tube so that any adhering material is washed down, and the tube is immediately sealed off as described below. (Caution! As seen from Table 21, this quantity of acid is used only with the heavy-walled tubes. If the other type is employed, the volume should be 0.3 ml or less and the dimensions and temperatures mentioned in the following pages must be so adjusted.) If the sample and acid react at room temperature, the bottom of the tube and the acid should first be cooled in dry ice-acetone mixture. As an alternate procedure, the sample may be weighed in a weighing bottle (Fig. 27, Chapter 3), inserted in the tilted combustion tube after the acid has been added and kept from sliding to the bottom until after the tube has been sealed.)

SEALING THE CARIUS COMBUSTION TUBE

(Note: The beginner will do well to practice both the sealing and cutting—see below—Procedure—using empty tubes before attempting these for actual determinations. It is also good practice to employ a safety glass shield between the operator and the blast lamp.)

The filled Carius tube is held at about a 45° angle to the horizontal. The section near the open end is gently warmed to evaporate off adhering nitric acid which might otherwise cause the tube to crack. The open tip is then strongly heated with a blast lamp and a section of Pyrex tubing about 150–175 mm long is sealed on for use as a handle (Fig. 140a). (A section of an old Carius tube may be used for this purpose. Care should be exercised so that the combustion tube containing the sample and nitric acid is not sealed off by
the addition of the handle.) The tube is held by one hand at the filled closed end and by the sealed-on handle with the other hand. The hot flame of a blast lamp is played on the section of the tube about 160 to 180* mm. from the closed end (Fig. 140a), while it is slowly rotated, using both hands. The soft glass is allowed to flow downward so that the heated section thickeners considerably (Fig. 140b). The tube is slightly drawn out and the side walls of the drawn section again allowed to thicken by the flow of soft glass (Fig. 140c). Finally, when the constricted soft section is attaining capillary dimensions (approximately 0.25 mm. I.D.), the tube is pulled out and the capillary sealed off making a tip of 2–3 cm. in length, about 2–3 mm. O.D. and a very fine inside diameter—a small fraction of a millimeter (Fig. 140d). A well-sealed tube will have the same wall thickness at the constricted portion as it

* These figures apply for the heavy-walled tube only (see Table 21).
does in the main body. This produces one of great strength capable of withstanding the high pressures encountered. Even though very thick-walled capillaries are not needed to withstand the pressures, they are preferred because of less danger of breakage during handling. If there is no means of pulling the tubes out of the furnace, a small hook (Fig. 140e), may be made on the finished capillary by placing in a burner flame and allowing the soft tip to be pulled down by gravity or forcing it with a pair of forceps. A section of wire is then attached to the hook.

The sealed tube is allowed to cool and is then placed in the cold combustion furnace in any desired position, ranging from vertical to about 30° to the horizontal. The furnace is slowly heated to 250°* C. and that temperature maintained for 7–8 hours. (*Caution: High pressure.*) (The author charges the furnace at the close of the day, setting a time switch which shuts off the current during the following early morning hours. The furnace is then back to room temperature at the beginning of the next working day.)

**REMOVAL OF TUBES FROM THE COMBUSTION FURNACE**

Before they can be safely handled, the cooled† Carius combustion tubes must have the residual pressure released. The tube is forced or pulled up part of the way out of the furnace so that the tip is exposed and supported thusly. A small amount of nitric acid condensate will always be present in the capillary tip (Fig. 141a). This is forced back into the main body of the tube by waving a flame near it. The tip is then strongly heated until the internal pressure causes a hole to be blown out of the molten capillary and the gases escape with a hiss (Fig. 141b).

The cutting or grinding wheel (Fig. 139), is adjusted so that it will make a cut of not greater than one-half the depth of the wall thickness of the tube.‡ As soon as the pressure has been released in the tube, it is held at an angle of about 45° to the horizontal against the revolving wheel and a groove cut, all the way around, at a distance of about 75 mm. from the bottom. Distilled water is poured over the groove to remove grindings as well as to wet it. The end of a piece of the soft glass rod is held in a blast lamp flame until it is molten. It is then quickly pressed against the wet groove on the combustion tube and held there for several seconds (Fig. 142). The tube usually cracks either completely around or almost so. Examination against an illuminated area such as a window will reveal the extent of the crack. If it is not complete, the groove should be rewet and the molten tip of a soft glass rod reapplied to whatever portion has not cracked. This should be repeated until

---

* These figures apply for the heavy-walled tube only (see Table 21).
† Caution: Never handle a warm sealed tube.
‡ The tube should not be completely cut through by the wheel or contamination will result.
the crack makes a complete circle and on gently tapping the top of the tube falls off. (If the groove has not been cut deeply enough or the soft glass rod not hot enough, the operation is not successful.) The cut end is then carefully fire polished and the tube set aside to cool. The contents of the tube are then carefully diluted with distilled water and then transferred quantitatively to a small beaker (about 50 ml. capacity). The nitric acid is evaporated off on a steam bath. The dry residue of sodium or potassium acid sulfate is dissolved in a few milliliters of distilled water and the solution transferred quantitatively to the cuvette (Fig. 72), using less than 15 ml. water in all. A few drops of phenolphthalein indicator are added and the solution is made alkaline with approximately 0.1N sodium hydroxide. It is then back-titrated with approximately 0.01N hydrochloric acid, just to expel the color. The contents are then diluted to 15 ml. with distilled water and then 15 ml. of 95% ethanol added, followed by half a scoop of powdered THQ. The vessel is placed on the illuminated titration stand (Fig. 71—Chapter 5 on Standard Solutions) and is titrated with barium chloride, 0.01N, to the end point (identical in appearance to that of the orange filter plate—see Standardization of 0.01N BaCl₂, above-mentioned chapter).

Calculation:

1 ml. of 0.01N BaCl₂ is equivalent to 0.1603 mg. of sulfur

\[
\text{ml. of } 0.01N \text{ BaCl}_2 \times 0.1603 \times 100 \quad \text{Wt. sample} = \% \text{ S}
\]

Example:

3.44 ml. of 0.01N BaCl₂ is required to titrate the sulfate resulting from the combustion of a 2.960-mg. sample

\[
\therefore \frac{3.44 \times 0.1603 \times 100}{2.960} = 18.63\% \text{ S}
\]

The allowable error is ±0.3%.
GRAVIMETRIC CARIUS METHOD
(Applicable to Phosphorus-containing Compounds)

Instead of the preferred Carius volumetric method given in the preceding pages, the determination may be done gravimetrically. In the presence of phosphorus, the determination must be done gravimetrically, since barium phosphate is insoluble in the neutral solution of the volumetric procedure and would interfere. Barium chloride (about 15 mg.) is added to the sample (4-9 mg.) plus nitric acid in the Carius tube, no sodium or potas-

![Diagram of Carius Sulfur Crucible](image)

**Fig. 143. (Left) Porcelain sulfur crucible—details of construction.**

**Fig. 144. (Right) Porcelain filter stick—details of construction.**

sium salt being required. The sulfuric acid formed during combustion is immediately converted into barium sulfate:

\[ \text{H}_2\text{SO}_4 + \text{BaCl}_2 \rightarrow \text{BaSO}_4 + 2\text{HCl} \]

The combustion tube is opened and the contents quantitatively washed into a previously weighed porcelain crucible (with black interior) (Fig. 143), containing a porcelain filter stick† (Fig. 144). The nitric acid is removed, by evaporation, on a steam bath and the dry residue is treated with about 3 ml. of 1:300 hydrochloric acid to redissolve the soluble salts. The filter stick is then attached to the vertical tube of the siphon, receiver and inner container shown in Figs. 147 and 148, using a small section of rubber tubing. Vacuum is applied to the side arm of the apparatus and the solution

* The combination should be treated before weighing in exactly the same manner as is done after transfer of the precipitate to it, that is, washing, drying, igniting, etc.

† Transfer is best accomplished by a stream of wash water from a wash bottle (Figs. 145 and 146) into the tilted tube, open end down, the precipitate being carried out with the liquid.
of barium nitrate-chloride sucked from the crucible into the inner container and subsequently discarded. The precipitate remains in the crucible and is washed three times with 1-ml. portions of 1:300 hydrochloric acid, sucking as dry as possible between washings. The crucible plus filter stick is then

Fig. 145. Two views of a graduated wash bottle—details of construction.

Fig. 146. Wash bottle.
heated in an ordinary laboratory oven at 120° C. for 20-30 minutes to thoroughly dry. Crucible and filter stick are then heated in a small muffle furnace of the type shown in Fig. 88, at 700° C. for 5 minutes. The combina-

Fig. 147. (Left) Siphon, receiver, and (right) inner container for barium sulfate filtration—details of construction.

Fig. 148. Siphon, receiver, and inner container for barium sulfate filtration, showing method of use with filter stick and crucible.

tion is then allowed to cool on a metal block or in a metal crucible container with glass dome (desiccator minus the metal cooling block), (Figs. 43, 45, and 46, Chapter 3), rewashed three times with 1-ml. portions of 1:300 hydro-
chloric acid to remove occluded barium nitrate, redried, reignited at 700° C.,
cooled for one hour, and weighed (using a tare flask, Figs. 34–36, Chapter 3,
as a counterpoise weight). The crucible and filter may be cleaned with con­
centrated sulfuric acid or it may be used without cleaning for successive deter­
minations.

Unfortunately, much difficulty has been experienced with these filter sticks
in the past, tiny holes being present between glazed and unglazed portions which
permitted the precipitate to pass through.

Calculation:

\[
\frac{S}{\text{BaSO}_4} = 0.1374
\]

\[
\therefore \frac{\text{Wt. BaSO}_4 \times 0.1374 \times 100}{\text{Wt. sample}} = \% S
\]

Example:

6.231 mg. of \text{BaSO}_4 was obtained from 4.702 mg. of sample

\[
\therefore \frac{6.231 \times 0.1374 \times 100}{4.702} = 18.21\% S
\]

Alternate Gravimetric Carius Procedure
(Applicable to Phosphorus-containing Compounds)

An alternate gravimetric procedure employing the Carius method precipitates
the barium sulfate after removal from the combustion tube. The combus­
tion mixture is the same as given for the THQ titration method, namely,

sample, nitric acid, and sodium salt. After removal from the combustion tube
and evaporation to dryness, the residue is dissolved in 5 ml. of 1:300 hydro­
chloric acid and transferred to the crucible (Fig. 143). (The clean, weighed
filter stick must be kept separated until filtration or soluble sulfate might pass
through the filter and be lost.) The crucible is then heated on a steam bath
and the volume reduced, if necessary, so that there will be no danger of loss of
precipitate (after precipitation) from creeping to the rim. A total volume of less
than 10 ml. is preferred. One milliliter of 10% barium chloride solution is
added and the mixture digested until the total volume has been reduced to 2–3
ml. Regardless of the initial volume, digesting should be done for 30 minutes.
The crucible is removed from the steam bath, cooled at least 15 minutes.
Filtering, washing, etc., of the precipitated barium sulfate is done as de­
scribed above.
SCHÖNIGER COMBUSTION

VOLUMETRIC SCHÖNIGER METHOD
(Not Applicable to Phosphorus-containing Compounds)

With the Schöniger method,\textsuperscript{196,198-200,213} the organic material is destroyed by burning the sample in a special oxygen-filled flask in which the combustion takes place at high temperature, probably around 1200° C. The reaction may be represented by the following:

\[
\text{Organic S} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{SO}_3 + \text{SO}_2
\]

The resulting oxides of sulfur are absorbed and finally converted to sulfuric acid according to the following:\textsuperscript{149}

\[
\text{SO}_3 + \text{SO}_2 + 3\text{H}_2\text{O} + \text{Br}_2 \rightarrow 2\text{H}_2\text{SO}_4 + 2\text{HBr}
\]

or

\[
\text{SO}_3 + \text{SO}_2 \xrightarrow{\text{HNO}_3, \text{H}_2\text{O}} 2\text{H}_2\text{SO}_4
\]

(A number of equations for the conversion of SO\textsubscript{2} into H\textsubscript{2}SO\textsubscript{4} by HNO\textsubscript{3} are given by Mellor.)\textsuperscript{149}

**Reagents**

**SODIUM HYDROXIDE, APPROX. 0.01N**
Approximately 0.01N sodium hydroxide (not standardized) is used for absorbing oxides of sulfur in the combustion flask.

**SODIUM HYDROXIDE, APPROX. 0.1N**

**HYDROCHLORIC ACID, APPROX. 0.01N**
Same as for the Volumetric Carius Method.

**HYDROCHLORIC ACID, APPROX. 0.1N**
Approximately 0.1N hydrochloric acid (not standardized) is used for acidifying purposes in the procedure using bromine water to oxidize sulfur to the hexavalent state.

**BROMINE WATER**
Water saturated with reagent grade of bromine is used in one of the procedures to oxidize sulfur to the hexavalent state.
10. Sulfur

FUMING NITRIC ACID, REAGENT GRADE, SP. GR. 1.49–1.50
This is used to oxidize sulfur to the hexavalent state in one of the procedures.\textsuperscript{213}

\begin{itemize}
  \item PHENOLPHTHALEIN INDICATOR
  \item DISTILLED WATER
  \item ETHANOL, 95\%
  \item TETRAHYDROXYQUINONE INDICATOR (THQ)
  \item STANDARD POTASSIUM SULFATE, 0.01N
  \item STANDARD BARIUM CHLORIDE, 0.01N
\end{itemize}

Same as for the Volumetric Carius Method.

**Apparatus**

**SCHÖNIGER COMBUSTION FLASK\textsuperscript{146,198–200,225}**

The combustion flask (Fig. 149) consists of a heavy wall, conical flask of borosilicate glass, with a deep bell-shaped flaring lip and elongated inter-changeable ground-glass stopper into which has been sealed a heavy platinum wire gauze sample carrier. Both 300- and 500-ml. flasks are commercially available, but the author prefers the use of the larger size because of the extra available oxygen. Organic solvents should not be used for cleaning, and stopcock grease should never be used on the ground joints because of the possible fire and explosion hazards from so doing. Flasks in constant use need not be dried between determinations. (Figure 150 shows a modification of the Schöniger flask which permits electrical ignition and provides shielding.\textsuperscript{56a,146})
Fig. 150. Modification of Schöniger combustion flask permitting electrical ignition and shielding.
FILTER PAPER CARRIERS

Flag-shaped strips of filter paper are used to hold the sample. They are folded over several times to completely wrap the sample, leaving the small tail sticking out for use as a fuse or ignition point.

METHYLCELLULOSE CAPSULES

These are used for liquid samples (see Chapter 3). The sealed capsule, containing the sample, is wrapped in the filter paper carrier and placed in the platinum gauze basket.

ILLUMINATED TITRATION STAND ASSEMBLY

CUVETTE

ORANGE-BROWN FILTER PLATE

Same as for the Volumetric Carius Method.

Procedure

Enough sample is weighed by difference, using a charging tube (Figs. 47–49) onto the filter paper carrier (Fig. 149) to require 3–5 ml. of 0.01N barium chloride in the final titration (0.48–0.8 mg. S). (Liquid samples are weighed in methylcellulose capsules (Chapter 3) and then placed on the paper carrier.) The paper is folded so as to seal in the sample, but the small tail is left extending for use as the point of ignition (see Fig. 149). The paper is then inserted into the platinum gauze basket attached to the stopper. Ten milliliters of approximately 0.01N sodium hydroxide are added to the combustion flask which is then flushed with oxygen from a cylinder for a few minutes with the tube extending almost to the bottom of the flask. (Caution: No grease should be used on the ground joint.) The exposed tail is ignited by means of a burner and the stopper is inserted immediately into the oxygen filled flask. The stoppered flask is held by the stopper in the inverted position (see Fig. 149), preferably with the open end of the basket upward to prevent the dropping of unburned particles, until the combustion is completed, which takes place at temperatures around 1200° C. and requires a fraction of a minute. By holding the flask in the inverted position, the sodium hydroxide forms a seal around the stopper. (NOTE: As a safety measure, the flask should be held behind a safety glass shield, in a hood, while the operator is protected by means of gloves and goggles.) The flask is allowed to cool for about one minute in the inverted position and the contents are shaken vigorously until cloudiness disappears, after which a few ml. of water is placed in the cup surrounding the stopper and the flask is allowed to remain undisturbed for about 15 minutes to insure complete absorption of the oxidation products. The flask is now under a slightly reduced pressure, due to the consumption
of some of the oxygen originally present, which makes removal of the stopper sometimes slightly difficult. Gentle manipulation loosens the stopper and the water, which was in the cup surrounding the stopper, is sucked in, washing the ground joint. (In case the stopper cannot be loosened easily, the flask is placed, momentarily, on the steam bath in order to increase its internal pressure more nearly to that of atmospheric, but not above it.) The stopper is removed and washed, collecting the washings in the flask. The contents of the flask are then transferred to a 100 ml. beaker and treated according to either (a) or (b), the former being preferred by the author:

(a) One milliliter of fuming nitric acid, sp. gr., 1.49–1.50 is added and the solution evaporated to dryness on a steam bath. The residue is dissolved in water, transferred to a cuvette, neutralized, etc., and titrated with 0.01N barium chloride solution using THQ as the indicator as described under the Volumetric Carius Method.

(b) Bromine water is added dropwise until the color of bromine persists. About 1.1 ml. of approximately 0.1N hydrochloric acid is added (to acidify) and the solution evaporated down on a steam bath to expel the bromine. (Although evaporation to dryness is not necessary, it has the advantage of volume control in the cuvette.) The residue (or small volume) is dissolved in water, transferred to a cuvette, etc., and titrated as described above under (a).

**Calculation:**

Same as for Volumetric Carius Method.

**PREGL CATALYTIC COMBUSTION**

It has been stated previously that the destruction of organic material may be accomplished by other means. During the first few years of the operation of his laboratory, the author used the Pregl catalytic combustion extensively with good results. It is not the method of choice of the author, but its reliability has been definitely proven through collaborative studies.

The sample is burned in an atmosphere of oxygen at red heat in the presence of platinum. The resulting oxides of sulfur are absorbed either by hydrogen peroxide or by bromine and converted into sulfuric acid according to the following:

\[
\Delta \quad \text{Organic } S \xrightarrow{O_2 (Pt)} SO_2 + SO_3 + CO_2 + H_2O
\]

or

\[
SO_2 + SO_3 + H_2O_2 + H_2O \rightarrow 2H_2SO_4
\]

or

\[
SO_2 + SO_3 + Br_2 + 3H_2O \rightarrow 2H_2SO_4 + 2HBr
\]
In the absence of nitrogen, halogens, and phosphorus, the sulfuric acid may be titrated with standard alkali using methyl red as the indicator:

\[ H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O \]

In the presence of nitrogen and halogens, but in the absence of phosphorus, the volumetric procedure, using barium chloride with THQ as the indicator, may be used provided that bromine is used in the spiral to absorb the oxides. The use of hydrogen peroxide eliminates the possibility of using THQ indicator, because a fading end point results regardless of attempts to destroy the peroxide and the sulfuric acid must be determined gravimetrically:

\[ H_2SO_4 + BaCl_2 \rightarrow BaSO_4 + 2HCl \]

In the presence of phosphorus, the gravimetric procedure must be used as explained under the Carius method.

**Reagents**

*For Gravimetric Procedure*

**HYDROGEN PEROXIDE, 30% (SUPEROXOL)**

Reagent grade of 30% hydrogen peroxide (Superoxol) is used as the oxidizing agent to convert sulfur dioxide into sulfur trioxide. However, for this purpose it is diluted as described below. *(Caution: This material must be handled with extreme care. It is stored in a refrigerator.)*

**DILUTE HYDROGEN PEROXIDE**

Twenty ml. of 30% hydrogen peroxide is added to 80 ml. of distilled water.

**DILUTE HYDROCHLORIC ACID**

(One part by volume of reagent grade concentrated acid to 300 parts by volume of water.) This is used for the gravimetric procedure only.

**BARIUM CHLORIDE SOLUTION**

A 10% solution of reagent grade of barium chloride in distilled water is used in the gravimetric procedure.

*For Acidimetric (Direct Neutralization) Procedure*

**DILUTED HYDROGEN PEROXIDE**

See above under Gravimetric Procedure.
STANDARD SODIUM HYDROXIDE, 0.01N
This is prepared and standardized according to the directions given in Chapter 5. It is used only in the absence of nitrogen, halogens, and phosphorus.

METHYL RED INDICATOR
For preparation, see Chapter 5. This is used only in the absence of nitrogen, halogens, and phosphorus.

For Volumetric Procedure

SODIUM HYDROXIDE, APPROX. 0.1N
HYDROCHLORIC ACID, APPROX. 0.07N
PHENOLPHTHALEIN INDICATOR
DISTILLED WATER
ETHANOL, 95%
TETRAHYDROXYQUINONE (THQ) INDICATOR
STANDARD POTASSIUM SULFATE, 0.01N
STANDARD BARIUM CHLORIDE, 0.01N

BROMINE WATER
Saturated solution of bromine in water. This should be stored in a glass-stoppered bottle.

Apparatus

OXYGEN CYLINDER AND REDUCING VALVE
These are the same as used for the carbon-hydrogen determination (Chapter 9).

PRESSURE REGULATOR
This is the same as used for the carbon-hydrogen determination (Figs. 118 and 119, Chapter 9).

BUBBLE COUNTER-U-TUBE
This is the same as used for the carbon-hydrogen determination (Fig. 120, Chapter 9).

COMBUSTION TUBE WITH INNER SPIRAL
The combustion tube (Fig. 151) is prepared from quartz or Vycor (96% silica glass No. 790). In reality, it serves two purposes, namely, combustion tube and absorber of the combustion product. The plain portion is placed in
10. Sulfur

the combustion furnace. The part containing the spiral is moistened with the absorbent and not heated.

**PLATINUM CONTACT STARS**187,188,209,212

Two platinum contact stars (Fig. 152) are used in the combustion tube.

**COMBUSTION APPARATUS**

The apparatus* is the same as used in the Dumas determination of nitrogen [Fig. 89, Chapter 7 or Figs. 123–125 (minus the heating mortar), Chapter 9].

**TEST TUBE**

A standard 8-inch Pyrex test tube is used as a cover for the tip of the combustion tube and for collecting washings.

**ADDITIONAL APPARATUS REQUIRED**

For the gravimetric procedure, the crucible (Fig. 143), filter stick (Fig. 144), wash bottles (Figs. 145 and 146) and siphon, receiver, and inner container (Figs. 147 and 148) are also required.

For the acidimétric (direct neutralization) procedure, an automatic burette (Figs. 69 or 70) is required instead of the crucible assembly, above.

For the volumetric procedure, the illuminated titration stand assembly (Fig. 71), cuvette (Fig. 72) and orange-brown filter plate (Chapter 5) are required instead of the crucible assembly, above.

---

**Assembly and Gravimetric Procedure**

(Applicable to Phosphorus-containing Compounds)

The oxygen cylinder, pressure regulator and bubble counter-U-tube are connected in the order named by means of thin-walled rubber tubing (see Chapter 9). The pressure is then regulated so that approximately 12–15 ml. of oxygen flows through the bubble counter-U-tube per minute. (This is accomplished with the aid of a Mariotte bottle—Fig. 129, Chapter 9—see Pressure Regulation, carbon-hydrogen determination, Chapter 9. The pressure regulation is done without the combustion tube being attached as it offers little added resistance.) The free end of the bubble counter-U-tube is then connected by means of a section of rubber tubing several centimeters in length to a small glass tip inserted in a one-hole rubber stopper† that fits the open end of the combustion tube.

* See footnote, p. 154, Chapter 7.
† Universal stopper9,210 cut to size (see Fig. 153).
Fig. 151. (Top) Combustion tube with inner spiral—details of construction.

Fig. 152. (Center) Platinum contact star. (Bottom) Platinum contact star—details of construction. Tolerances on platinum (unless otherwise shown):

- Height, mm. ± 0.5
- Outside-inside diameter, mm. ± 0.5
- Thickness, mm. ± 0.01
- Weight, gram ± 0.5

---

Prek Catalytic Combustion
The combustion tube is securely held vertically in a suitable clamp and stand with the spiral portion downward. The tip is immersed in 4–5 ml. dilute hydrogen peroxide solution contained in the test tube. Gentle suction is applied to the open end of the combustion tube, protecting it from contamination with a cotton-filled air filter of the type shown in Fig. 154, so that the liquid is drawn up covering the entire spiral and a few millimeters beyond. The suction is then removed and the hydrogen peroxide allowed to drain back into the test tube leaving the spiral wet. The liquid is poured from the test tube, leaving the latter moist.

The combustion tube is then placed in the combustion apparatus, the entire spiral portion extending beyond the long furnace so that it receives no heat.

The test tube, still moist with hydrogen peroxide, is placed over the tip of the combustion tube for protection. A clean platinum contact star is placed in the open end of the combustion tube and pushed with the aid of a platinum wire (Fig. 53, Chapter 3) into the section surrounded by the long furnace and adjacent to the spiral. The end or wire loop of the star should be about 2 cm. from the end of the long furnace (see Fig. 155). The second platinum contact star is then inserted and put into place so that its one wire loop is within a few centimeters of the other contact star and its other loop is about 2 cm. from the end of the long furnace adjacent to the short movable sample furnace (Fig. 155).

The sample (4–9 mg.), previously weighed in a platinum boat or capillary (if the latter, protected with a platinum sleeve, Fig. 84, Chapter 6, or large platinum boat, Fig. 25, Chapter 4) is placed, with the aid of a platinum wire, in the combustion tube at a position about 5 cm. from the end of the long
FIG. 155. Diagram of catalytic combustion setup.
furnace. The rubber stopper which connects the oxygen supply via the bubble counter-U-tube, is inserted into the open end of the combustion tube and the oxygen allowed to flow through at the rate of 12 to 15 ml. per minute.

The long furnace is heated to 800° C. (at least 750°). The short furnace is then heated to 800° C. (at least 750°) and moved up towards the sample cautiously. After combustion has started the short movable sample furnace is slowly moved across the sample and up against the long furnace. Too rapid combustion is liable to allow unburned material to pass through into the spiral. Consequently, it is preferred to operate the movable furnace by hand, at least in the early stages of the combustion. After the first combustion is over, it is best to follow with a rapid second to make certain that nothing remains unburned.

The furnaces are then shut off and the tube allowed to cool while oxygen is swept through. When cool, the tube is removed from the furnaces and the test tube removed from the tip. The combustion tube is then mounted vertically, with spiral at the bottom, in the clamp and stand used at the beginning of the determination. A previously weighed porcelain crucible with black interior (Fig. 143) (see above under gravimetric Carius determination) is placed immediately under the tip to prevent loss upon dripping. (If nitrogen, phosphorus, and halogens are absent, the titrimetric procedure described later may be used.) About 4 ml. of 1:300 hydrochloric acid is added to the crucible, the tip of the tube immersed and the liquid sucked up (see above) until it is about 2 cm. above the spiral. The suction is removed, the tube raised about 2 cm. and the acid allowed to drain into the crucible. Several small portions of dilute acid are added from the top and the wash liquid allowed to drain into the crucible. The test tube previously used is also rinsed with a small amount of acid and this is added to the contents of the crucible. The test tube is then returned to the position under the spiral for further washing later. One milliliter of 10% barium chloride solution is added to the contents of the crucible to convert the sulfuric acid into barium sulfate. (Caution: The crucible should not be nearly full or the precipitate might creep up to the rim.) The crucible is then placed on a steam bath and the contents evaporated down to a few milliliters. In the meantime, the spiral is washed with several small portions of 1:300 hydrochloric acid, catching the washings in the test tube. These are eventually added to the contents of the crucible and the total liquid concentrated to a volume of 2 to 3 ml. The crucible is then allowed to cool. A previously weighed clean filter stick* (Fig. 144—see preceding pages) is attached to siphon, receiver, and inner container (Figs. 147 and 148), inserted into the crucible and the liquid sucked off as described above. The

* Platinum filter sticks (Fig. 156), having platinum sponge as the filter medium have been used successfully for this particular procedure.
precipitate is then treated identically to that described for the gravimetric Carius determination (see preceding pages), that is, washing, drying, igniting, rewashing, redrying, reigniting, and weighing. The crucible and filter stick must be cleaned between determinations for this procedure (see preceding pages).

Calculation:
Same as for Gravimetric Carius Method.

Fig. 156. Platinum filter stick—details of construction. Tolerances on platinum (unless otherwise shown):

- Height, mm. ± 0.5
- Outside-inside diameter, mm. ± 0.5
- Thickness, mm. ± 0.01
- Weight, gram ± 0.5

**Acidimetric (Direct Neutralization) Procedure**
(Not Applicable to Nitrogen-, Halogen-, or Phosphorus-containing Compounds)

In the absence of nitrogen, phosphorus, and halogens, the spiral is washed with water (instead of hydrochloric acid as described above) catching the washings in a 125-ml. Erlenmeyer flask. Two drops of methyl red indicator (Chapter 5) are added, the liquid boiled for 30 seconds to remove carbon dioxide, and the sulfuric acid titrated with 0.01N sodium hydroxide to the end point (canary yellow for 2 minutes).\(^\text{161,162,180}\)

Calculation:

\[
1 \text{ ml. of } 0.01N \text{ NaOH is equivalent to } 0.1603 \text{ mg. of sulfur} \\
\text{ml. of } 0.01N \text{ NaOH } \times 0.1603 \times 100 \quad = \% \text{ S} \\
\text{Wt. sample}
\]

Example:

3.05 ml. of 0.01N NaOH is required to titrate the sulfuric acid formed from a 6.087-mg. sample

\[
\text{ml. of } 0.01N \text{ NaOH } \times 0.1603 \times 100 \quad = 8.03\% \text{ S} \\
6.087
\]
Volumetric Procedure
(Not Applicable to Phosphorus-containing Compounds)

In the absence of phosphorus, the THQ titration procedure may be used, *provided* that bromine (and *not* hydrogen peroxide⁸²,⁸³) is used in the spiral as the absorbent. The rest of the procedure is the same as for the volumetric Carius or Schöninger ones.

*Calculation:*

Same as for the Volumetric Carius Method.

**ADDITIONAL INFORMATION FOR CHAPTER 10**

Instead of the combustion tube with inner spiral, the combustion tube and absorber may be separate and connected by means of a ground joint¹¹ as shown in Fig. 157. With this system, the joint is heated to 350° C. by means of a third furnace or heater.

![Diagram of Association of Official Agricultural Chemists' catalytic combustion setup showing details. (Same setup without the 350° C. furnace used by that Association for determination of bromine and chlorine—see Chapter 11.)](image)

This assembly was used in the procedures (volumetric and gravimetric) adopted¹¹,¹⁶⁵-¹⁶⁸ by the Association of Official Agricultural Chemists following collaborative studies. For the gravimetric, the precipitated barium sulfate was washed with five or six 3-ml portions of 1:300 HCl instead of the rewashing and reigniting before weighing.
The determination of sulfur in organic compounds has been the subject of many investigations due to the tremendous importance of the sulfur compounds, particularly the sulfonamides, and in the first part of this chapter it was emphasized that the use of referee methods is often desirable. Table 22 lists a number of references which the author wishes to call to the attention of the reader. (See statement at top of Table 4 of Chapter 1, regarding completeness of this material.)

* 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 22**

**ADDITIONAL INFORMATION ON REFERENCES* RELATED TO CHAPTER 10**

<table>
<thead>
<tr>
<th>Books</th>
<th>General, miscellaneous (Cont.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Association of Official Agricultural Chemists, 11</td>
<td>Kent and Whitehouse, 104</td>
</tr>
<tr>
<td>Belcher and Godbert, 17, 18</td>
<td>Kirsten, 109, 111, 114</td>
</tr>
<tr>
<td>Clark, E. P., 42</td>
<td>Kono, 121</td>
</tr>
<tr>
<td>Clark, S. J., 43</td>
<td>Kress, 127</td>
</tr>
<tr>
<td>Friedrich, 63</td>
<td>Lees and Folch, 134</td>
</tr>
<tr>
<td>Furman, 67</td>
<td>Lincoln, Carney, and Wagner, 136</td>
</tr>
<tr>
<td>Grant, 76, 77</td>
<td>Malissa, 144</td>
</tr>
<tr>
<td>Milton and Waters, 155, 156</td>
<td>Pepkowitz, 176</td>
</tr>
<tr>
<td>Niederl and Niederl, 161, 162</td>
<td>Pepkowitz and Shirley, 177</td>
</tr>
<tr>
<td>Niederl and Sozzi, 163</td>
<td>Rieman and Hagen, 182</td>
</tr>
<tr>
<td>Pregl, 180</td>
<td>Rodden, 183</td>
</tr>
<tr>
<td>Roth, 186-189</td>
<td>Romyn, 184</td>
</tr>
<tr>
<td>Steyermark, 209</td>
<td>Večerča and Snobl, 233, 234</td>
</tr>
<tr>
<td></td>
<td>Volynskiǐ, 239</td>
</tr>
<tr>
<td></td>
<td>Volynskiǐ and Chudakova, 240</td>
</tr>
<tr>
<td>Reviews</td>
<td></td>
</tr>
<tr>
<td>Alicino, 7</td>
<td></td>
</tr>
<tr>
<td>Hallett, 81</td>
<td></td>
</tr>
<tr>
<td>Horáček, 91</td>
<td></td>
</tr>
<tr>
<td>Kainz, 105</td>
<td></td>
</tr>
<tr>
<td>Lamo and Doadrio, 132</td>
<td></td>
</tr>
<tr>
<td>Thomson, 227</td>
<td></td>
</tr>
<tr>
<td>Willits, 246</td>
<td></td>
</tr>
<tr>
<td>Collaborative studies</td>
<td></td>
</tr>
<tr>
<td>Association of Official Agricultural Chemists, 11</td>
<td></td>
</tr>
<tr>
<td>Ogg, 165-168</td>
<td></td>
</tr>
<tr>
<td>General, miscellaneous</td>
<td></td>
</tr>
<tr>
<td>Batt, 13</td>
<td></td>
</tr>
<tr>
<td>Battles, 14</td>
<td></td>
</tr>
<tr>
<td>Bussmann, 35</td>
<td></td>
</tr>
<tr>
<td>Dixon, 47</td>
<td></td>
</tr>
<tr>
<td>Doležil, 48</td>
<td></td>
</tr>
<tr>
<td>Gorsuch, 73</td>
<td></td>
</tr>
<tr>
<td>Gouverneur and Van Dijk, 74</td>
<td></td>
</tr>
<tr>
<td>Gourevich and Bühlér, 92</td>
<td></td>
</tr>
<tr>
<td>Fluoro-compounds</td>
<td></td>
</tr>
<tr>
<td>Belcher and Macdonald, 20</td>
<td></td>
</tr>
<tr>
<td>Ma, 139</td>
<td></td>
</tr>
<tr>
<td>Neudorffer, 159</td>
<td></td>
</tr>
<tr>
<td>Rush, Cruikshank, and Rhodes, 192</td>
<td></td>
</tr>
<tr>
<td>Steyermark, Bass, Johnston, and Dell, 213</td>
<td></td>
</tr>
<tr>
<td>Nitrogen compounds</td>
<td></td>
</tr>
<tr>
<td>Belcher, Nutten, and Stephen, 21</td>
<td></td>
</tr>
<tr>
<td>Lysyj and Zarembo, 138</td>
<td></td>
</tr>
<tr>
<td>Steyermark, 209</td>
<td></td>
</tr>
<tr>
<td>Phosphorus compounds</td>
<td></td>
</tr>
<tr>
<td>Association of Official Agricultural Chemists, 11</td>
<td></td>
</tr>
<tr>
<td>Fischer and Chen, 59</td>
<td></td>
</tr>
<tr>
<td>Lysyj and Zarembo, 138</td>
<td></td>
</tr>
<tr>
<td>Ogg, 168</td>
<td></td>
</tr>
<tr>
<td>Apparatus</td>
<td></td>
</tr>
<tr>
<td>Beazley, 15</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 22 (Continued)

<table>
<thead>
<tr>
<th>Apparatus (Cont.)</th>
<th>Carius combustion (Cont.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>British Standards Institution, 33</td>
<td>Horeischy and Bühler, 92</td>
</tr>
<tr>
<td>Clark, E. P., 42</td>
<td>Kuck and Griffel, 129</td>
</tr>
<tr>
<td>Ingram, 97</td>
<td>Milton and Waters, 155, 156</td>
</tr>
<tr>
<td>Kuck and Griffel, 129</td>
<td>Niederl, Baum, McCoy, and Kuck, 160</td>
</tr>
<tr>
<td>Ma and Benedetti-Pichler, 140</td>
<td>Niederl and Niederl, 161, 162</td>
</tr>
<tr>
<td>Ma, Kaimowitz, and Benedetti-Pichler, 141</td>
<td>Roth, 186–189</td>
</tr>
<tr>
<td>Martin and Deveraux, 146</td>
<td>Tanaka, 223</td>
</tr>
<tr>
<td>Peters, Rounds, and Agazzi, 178</td>
<td>Yagi and Egami, 251</td>
</tr>
<tr>
<td>Royer, Alber, Hallett, and Kuck, 191</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Submicro-, ultramicro-, microgram-methods</th>
<th>Oxygen flask combustion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Belcher, Bhasin, Shah, and West, 16</td>
<td>Gildenberg, 71</td>
</tr>
<tr>
<td>Dunicz and Rosenqvist, 49</td>
<td>Hempel, 87</td>
</tr>
<tr>
<td>Granatelli, 75</td>
<td>Horáček, 91</td>
</tr>
<tr>
<td>Holton and Linch, 89</td>
<td>Lysyj and Zarembo, 137</td>
</tr>
<tr>
<td>Jacobs, Braverman, and Hochheiser, 100</td>
<td>Mikl and Pech, 152–153</td>
</tr>
<tr>
<td>Jones and Letham, 102</td>
<td>Ottosson and Snellman, 171</td>
</tr>
<tr>
<td>Kirsten, 108, 109, 113</td>
<td>Schöniger, 196, 198–200</td>
</tr>
<tr>
<td>Larsen, Ross, and Ingber, 133</td>
<td>Soep, 206</td>
</tr>
<tr>
<td>Stratmann, 217</td>
<td>Soep and Demoen, 207</td>
</tr>
<tr>
<td>White, 245</td>
<td>Steyermark, Bass, Johnston, and Dell, 213</td>
</tr>
<tr>
<td>Wilson and Straw, 249</td>
<td>Thomas, 226</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Simultaneous determination of sulfur and other elements</th>
<th>Empty tube technique, oxyhydrogen flame, catalytic combustion, etc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agazzi, Fredericks, and Brooks, 2</td>
<td>Beazley, 15</td>
</tr>
<tr>
<td>Belcher and Spooner, 22, 23</td>
<td>Belcher and Ingram, 19</td>
</tr>
<tr>
<td>Boëtius, Gubiani, and Reith, 29</td>
<td>Etienne and Léger, 56</td>
</tr>
<tr>
<td>Etienne and Herrmann, 55</td>
<td>Grant, 76, 77</td>
</tr>
<tr>
<td>Fedoseev and Ivashova, 57</td>
<td>Graue and Zöhler, 79</td>
</tr>
<tr>
<td>Friedrich, 63</td>
<td>Grote and Kreckeler, 80</td>
</tr>
<tr>
<td>Fujimoto, Utsui, and Ose, 66</td>
<td>Hallett and Kuipers, 82</td>
</tr>
<tr>
<td>Klimova and Berezinskaya, 118</td>
<td>Heine, 85</td>
</tr>
<tr>
<td>Korshun and Chumachenko, 124</td>
<td>Hudy and Mair, 93</td>
</tr>
<tr>
<td>Korshun and Terent'eva, 126</td>
<td>Huffman, 94</td>
</tr>
<tr>
<td>Margolis and Egorova, 145</td>
<td>Ingram, 96</td>
</tr>
<tr>
<td>Mizukami, Ieki, and Kondo, 157</td>
<td>Körbl and Pribil, 122</td>
</tr>
<tr>
<td>Oda, Kubo, and Norimasa, 164</td>
<td>Lévy, 135</td>
</tr>
<tr>
<td>Roth, 189</td>
<td>Makovetskii and Kholodkovskaya, 143</td>
</tr>
<tr>
<td>Carius, 37–40</td>
<td>McChesney and Banks, 148</td>
</tr>
<tr>
<td>Clark, E. P., 42</td>
<td>Niederl and Niederl, 161, 162</td>
</tr>
<tr>
<td>Emich and Donau, 53</td>
<td>Pregl, 180</td>
</tr>
<tr>
<td>Grant, 76, 77</td>
<td>Roth, 186–189</td>
</tr>
<tr>
<td>Sakamoto, Hayazu, and Takenaka, 193</td>
<td>Stragand and Safford, 216</td>
</tr>
<tr>
<td>Sundberg and Royer, 219, 220</td>
<td>Večuša, 230–232</td>
</tr>
<tr>
<td>Empty tube technique, oxyhydrogen flame, catalytic combustion, etc. (Cont.)</td>
<td></td>
</tr>
<tr>
<td>Večera and Šnobl, 234, 235</td>
<td></td>
</tr>
<tr>
<td>Večera and Synek, 238</td>
<td></td>
</tr>
<tr>
<td>Wagner, 241</td>
<td></td>
</tr>
<tr>
<td>Walter, 243, 244</td>
<td></td>
</tr>
<tr>
<td>Wilson and Straw, 249</td>
<td></td>
</tr>
<tr>
<td>Zinneke, 259</td>
<td></td>
</tr>
<tr>
<td>Silver gauze absorbent technique</td>
<td></td>
</tr>
<tr>
<td>Bladh, Karrman, and Andersson, 27</td>
<td></td>
</tr>
<tr>
<td>Etienne and Leger, 56</td>
<td></td>
</tr>
<tr>
<td>Kuck and Grim, 130, 131</td>
<td></td>
</tr>
<tr>
<td>Stragand and Safford, 216</td>
<td></td>
</tr>
<tr>
<td>Sudo, Shimoe, Tsuji, and Soeda, 218</td>
<td></td>
</tr>
<tr>
<td>Večera and Šnobl, 234, 235</td>
<td></td>
</tr>
<tr>
<td>Zinneke, 259</td>
<td></td>
</tr>
<tr>
<td>Bombs, fusion</td>
<td></td>
</tr>
<tr>
<td>Agazzi, Parks, and Brooks, 3</td>
<td></td>
</tr>
<tr>
<td>Alicino, 6</td>
<td></td>
</tr>
<tr>
<td>Broekhuysen and Bechet, 34</td>
<td></td>
</tr>
<tr>
<td>Callan and Toennies, 36</td>
<td></td>
</tr>
<tr>
<td>Colson, 44</td>
<td></td>
</tr>
<tr>
<td>Elek and Hill, 52</td>
<td></td>
</tr>
<tr>
<td>Furman, 67</td>
<td></td>
</tr>
<tr>
<td>Inglis, 95</td>
<td></td>
</tr>
<tr>
<td>Kimball and Tufts, 107</td>
<td></td>
</tr>
<tr>
<td>Lincoln, Carney, and Wagner, 136</td>
<td></td>
</tr>
<tr>
<td>Maboney and Michell, 142</td>
<td></td>
</tr>
<tr>
<td>Niederl and Niederl, 161, 162</td>
<td></td>
</tr>
<tr>
<td>Parr, 173</td>
<td></td>
</tr>
<tr>
<td>Peel, Clark, and Wagner, 174</td>
<td></td>
</tr>
<tr>
<td>Siegfried, Wiberley, and Moore, 202</td>
<td></td>
</tr>
<tr>
<td>Steyermark and Biava, 215</td>
<td></td>
</tr>
<tr>
<td>Wurzschmitt, 250</td>
<td></td>
</tr>
<tr>
<td>Potassium, sodium, magnesium, etc., fusion (Cont.)</td>
<td></td>
</tr>
<tr>
<td>Schöniger, 197</td>
<td></td>
</tr>
<tr>
<td>Večera and Špěvák, 236</td>
<td></td>
</tr>
<tr>
<td>Zimmermann, 255–258</td>
<td></td>
</tr>
<tr>
<td>Perchloric acid combustion, wet digestion with dichromate and nitric acid, chloric acid, etc.</td>
<td></td>
</tr>
<tr>
<td>Bethge, 25</td>
<td></td>
</tr>
<tr>
<td>McChesney and Banks, 148</td>
<td></td>
</tr>
<tr>
<td>Rosenthaler, 185</td>
<td></td>
</tr>
<tr>
<td>Szekeres, Főti, and Pályi, 221</td>
<td></td>
</tr>
<tr>
<td>Tanaka, 223</td>
<td></td>
</tr>
<tr>
<td>Zdybek, McCann, and Boyle, 254</td>
<td></td>
</tr>
<tr>
<td>Hydrogenation methods</td>
<td></td>
</tr>
<tr>
<td>Furman, 67</td>
<td></td>
</tr>
<tr>
<td>Gel'man, 69</td>
<td></td>
</tr>
<tr>
<td>Irimescu and Chirnoaga, 98</td>
<td></td>
</tr>
<tr>
<td>Korshun and Gel'man, 125</td>
<td></td>
</tr>
<tr>
<td>Meulen, ter, 150</td>
<td></td>
</tr>
<tr>
<td>Meulen, ter, and Heslinga, 151</td>
<td></td>
</tr>
<tr>
<td>Stratmann, 217</td>
<td></td>
</tr>
<tr>
<td>Yudasina and Vysochina, 253</td>
<td></td>
</tr>
<tr>
<td>Manometric and gasometric procedures</td>
<td></td>
</tr>
<tr>
<td>See Chapter 18</td>
<td></td>
</tr>
<tr>
<td>Hoagland, 88</td>
<td></td>
</tr>
<tr>
<td>Holter and Løvtrup, 90</td>
<td></td>
</tr>
<tr>
<td>Various volumetric procedures</td>
<td></td>
</tr>
<tr>
<td>Bladh, Karrman, and Andersson, 27</td>
<td></td>
</tr>
<tr>
<td>Boos, 31</td>
<td></td>
</tr>
<tr>
<td>Bovee and Robinson, 32</td>
<td></td>
</tr>
<tr>
<td>Callan and Toennies, 36</td>
<td></td>
</tr>
<tr>
<td>Chalmers and Rigby, 41</td>
<td></td>
</tr>
<tr>
<td>Dirscherl, 46</td>
<td></td>
</tr>
<tr>
<td>Erdos, 54</td>
<td></td>
</tr>
<tr>
<td>Fischer and Chen, 59</td>
<td></td>
</tr>
<tr>
<td>Fritz and Freeland, 64</td>
<td></td>
</tr>
<tr>
<td>Fritz and Yamamura, 65</td>
<td></td>
</tr>
<tr>
<td>Geilmann and Bretschneider, 68</td>
<td></td>
</tr>
<tr>
<td>Gildenberg, 71</td>
<td></td>
</tr>
<tr>
<td>Hallett and Kuipers, 83</td>
<td></td>
</tr>
<tr>
<td>Inglis, 95</td>
<td></td>
</tr>
<tr>
<td>Iritani and Tanaka, 99</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 22 (Continued)

<table>
<thead>
<tr>
<th>Various volumetric procedures (Cont.)</th>
<th>Gravimetric procedures (Cont.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kirsten, 112, 114</td>
<td>Callan and Toennies, 36</td>
</tr>
<tr>
<td>Koch, Eckhard, and Malissa, 119</td>
<td>Etienne and Léger, 56</td>
</tr>
<tr>
<td>Kondo, 120</td>
<td>Fischer, 58</td>
</tr>
<tr>
<td>Lysyj and Zarembo, 137</td>
<td>Fischer and Sprague, 60</td>
</tr>
<tr>
<td>Makovetskiï and Kholodkovskaya, 143</td>
<td>Fiske, 61</td>
</tr>
<tr>
<td>Massie, 147</td>
<td>Freri, 62</td>
</tr>
<tr>
<td>Milner, 154</td>
<td>Heller, 86</td>
</tr>
<tr>
<td>Ottosson and Snellman, 171</td>
<td>Klein, 116</td>
</tr>
<tr>
<td>Padewetz, 172</td>
<td>Lincoln, Carney, and Wagner, 136</td>
</tr>
<tr>
<td>Padowetz, 172</td>
<td>Lysyj and Zarembo, 137</td>
</tr>
<tr>
<td>Pepkowitz, 175</td>
<td>Ma and Benedetti-Pichler, 140</td>
</tr>
<tr>
<td>Scalamandre and Guerrero, 195</td>
<td>Ma, Kaimowitz, and Benedetti-</td>
</tr>
<tr>
<td>Siegfriedt, Wiberley, and Moore, 202</td>
<td>Pichler, 141</td>
</tr>
<tr>
<td>Sirotenko, 203</td>
<td>Saschek, 194</td>
</tr>
<tr>
<td>Smith and Syme, 204</td>
<td>Schulek, Pungor, and Guba, 201</td>
</tr>
<tr>
<td>Soep and Demeun, 207</td>
<td>Stragand and Safford, 216</td>
</tr>
<tr>
<td>Soibel’man, 208</td>
<td>Wagner and Miles, 242</td>
</tr>
<tr>
<td>Tamaiya, 222</td>
<td></td>
</tr>
<tr>
<td>Tettweiler and Pilz, 224</td>
<td></td>
</tr>
<tr>
<td>Večeřa, 230–232</td>
<td></td>
</tr>
<tr>
<td>Večeřa and Šnobl, 233–235</td>
<td></td>
</tr>
<tr>
<td>Večeřa and Spěvák, 236, 237</td>
<td></td>
</tr>
<tr>
<td>Wagner, 241</td>
<td></td>
</tr>
<tr>
<td>Walter, 243</td>
<td></td>
</tr>
<tr>
<td>White, 245</td>
<td></td>
</tr>
<tr>
<td>Yamaji, 252</td>
<td></td>
</tr>
<tr>
<td>Zinnecke, 259</td>
<td></td>
</tr>
</tbody>
</table>

| EDTA titration                         |                               |
| Bather, 12                            |                               |
| Belcher, Bhasin, Shah, and West, 16   |                               |
| Belcher and Macdonald, 20              |                               |
| Wilson, Pearson, and Fitzgerald, 248   |                               |

| Indicators—THQ, and others            |                               |
| Abrahamzcik and Blümel, 1             |                               |
| Alicino, 5                            |                               |
| Hallett and Kuipers, 82, 83           |                               |
| Ogg, Willits, and Cooper, 169         |                               |
| Smith-New York Company, 205           |                               |
| Sundberg and Royer, 220               |                               |

| Gravimetric procedures                |                               |
| Bladh, Karrman, and Andersson, 27     |                               |
| Bogan, 30                             |                               |
REFERENCES

44. Colson, A. F., _Analyst_, 67, 47 (1942).
69. Gel'man, N. E., _Zavodskaya Lab._, 8, 673 (1939).
10. Sulfur

313 References

244. Walter, R. N., Personal communication. 1951.