



Designation: E 50 – 00

Standard Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials¹

This standard is issued under the fixed designation E 50; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 These practices cover laboratory apparatus and reagents that are required for the chemical analysis of metals, ores and related materials by standard methods of ASTM. Detailed descriptions of recommended apparatus and detailed instructions for the preparation of standard solutions and certain nonstandardized reagents are included. An identifying number has been assigned each apparatus (see Section 8) and reagent (see Section 25) for convenience of reference in the analytical methods. Included also are general recommendations on the purity of reagents and protective measures for the use of hazardous reagents.

1.2 The aim of these recommendations is to present descriptions of such apparatus and reagents as are common to several ASTM methods, and thus avoid needless repetition. No attempt has been made to provide a description of every apparatus and reagent prescribed in ASTM methods for the chemical analysis of metals. Other apparatus and reagents that are required will be found listed or specified in the individual methods of analysis.

1.3 These recommendations are intended to apply to the ASTM methods of chemical analysis of metals when definite reference is made to these practices, as covered in Section 3.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazards are given in Section 7 and Note 2.

NOTE 1—The use of the verb “shall” (with its obligatory third person meaning) in this standard has been confined to those aspects of laboratory

safety where regulatory requirements are known to exist. Such regulations, however, are beyond the scope of these practices.

2. Referenced Documents

2.1 ASTM Standards:

- D 1193 Specification for Reagent Water²
- E 1 Specification for ASTM Thermometers³
- E 70 Test Method for pH of Aqueous Solutions with the Glass Electrode⁴
- E 77 Test Method for Inspection and Verification of Liquid-in-Glass Thermometers³
- E 100 Specification for ASTM Hydrometers³
- E 126 Test Method for Inspection and Verification of Hydrometers³
- E 128 Test Method for Maximum Pore Diameter and Permeability of Rigid Porous Filters for Laboratory Use⁵
- E 287 Specification for Burets⁵
- E 288 Specification for Volumetric Flasks⁵
- E 438 Specification for Glasses in Laboratory Apparatus⁵
- E 542 Practice for Calibration of Volumetric Ware⁵
- E 694 Specification for Volumetric Ware⁵
- E 969 Specification for Glass Volumetric (Transfer) Pipets⁵
- E 1044 Specification for Glass Serological Pipets (General Purpose and Kahn)⁵
- E 1621 Guide for X-Ray Emission Spectrometric Analysis⁶

3. Significance and Use

3.1 The inclusion of the following paragraph, or a suitable equivalent, in any standard (preferably after the section on Scope) is due notification that the apparatus and reagents required in that standard are subject to the recommendations set forth in these practices.

¹These practices are under the jurisdiction of ASTM Committee E1 on Analytical Chemistry for Metals, Ores, and Related Materials and are the direct responsibility of Subcommittee E 01.20 on Fundamental Practices and Measurement Traceability.

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²Annual Book of ASTM Standards, Vol 11.01.

³Annual Book of ASTM Standards, Vol 14.03.

⁴Annual Book of ASTM Standards, Vol 15.05.

⁵Annual Book of ASTM Standards, Vol 14.04.

⁶Annual Book of ASTM Standards, Vol 03.06.

TABLE 1 Concentration of Acids, Ammonium Hydroxide, and Hydrogen Peroxide

Name	Formula	Specific Gravity, Approximate	Reagent, Weight %		
			Nominal	Min	Max
Acetic acid	CH ₃ COOH	1.05	...	99.5	...
Formic acid	HCOOH	1.20	...	88.0	...
Hydrobromic acid	HBr	1.49	48	47.0	49.0
Hydrochloric acid	HCl	1.19	...	35.0	38.0
Hydrofluoric acid	HF	1.15	...	48.0	51.0
Nitric acid	HNO ₃	1.42	...	69.0	71.0
Perchloric acid	HClO ₄	1.67	...	70.0	72.0
Phosphoric acid	H ₃ PO ₄	1.69	...	85.0	...
Sulfuric acid	H ₂ SO ₄	1.84	...	95.0	98.0
Sulfurous acid	H ₂ SO ₃	1.03	...	6.0(SO ₂)	...
Ammonium hydroxide	NH ₄ OH	0.90	...	27.0(NH ₃)	30.0 (NH ₃)
Hydrogen peroxide	H ₂ O ₂	1.10	30	28.0	...

“Apparatus and Reagents—Apparatus and reagents required for each determination are listed in separate sections preceding the procedure. The apparatus, standard solutions, and certain other reagents used in more than one procedure are referred to by number and shall conform to the requirements prescribed in ASTM Practices E 50, for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials.”

3.2 It is assumed that the users of these practices will be trained analysts capable of performing common laboratory procedures skillfully and safely. It is expected that work will be performed in a properly-equipped laboratory.

4. Purity of Water and Reagents

4.1 *Water*—Unless otherwise indicated, references to water are understood to mean reagent water of Type II grade, as defined by Specification D 1193.

in many cases for the analyst to ensure the accuracy of his results by running blanks or checking against a comparable sample of known composition.

5. Reagents

5.1 *Concentrated Acids, Ammonium Hydroxide, and Hydrogen Peroxide*—When acids, ammonium hydroxide, and hydrogen peroxide are specified by name or chemical formula only, it is understood that concentrated reagents of the specific gravities or concentrations shown in Table 1 are intended. The specific gravities or concentrations of all other concentrated acids are stated wherever they are specified.

5.2 *Diluted Acids and Ammonium Hydroxide*—Concentrations of diluted acids and ammonium hydroxide,

TABLE 2 Physical Properties of Plastic Labware^A

Plastic ^B	Temperature Limit, ° C	Specific Gravity	Brittleness Temperature, ° C	Water Absorption, %	Flexibility	Transparency
CPE	80	0.92	-100	<0.01	excellent	translucent
LPE	120	0.95	-196	<0.01	rigid	translucent
PA	130	0.90	-40	<0.02	slight	translucent
PP	135	0.90	0	<0.02	rigid	translucent
PMP	175	0.83	-20	<0.01	rigid	clear
FEP	205	2.15	-270	<0.01	excellent	translucent
TFE	315	2.2	-265	<0.01	excellent	translucent
PC	135	1.20	-135	0.35	rigid	clear
SA	95	1.07	-25	0.23	rigid	clear
ETFE	180	1.70	-100	0.1	moderate	translucent

^A From the publications of the Nalgene Labware Div., Nalge Sybron Corp.

^B CPE, conventional (low density) polyethylene; LPE, linear (high density) polyethylene; PA, polyallomer (ethylene propylene copolymer); PP, polypropylene; PMP, polymethylpentene; FEP, fluorinated ethylene propylene; TFE, fluorinated ethylene; PC, polycarbonate; SA, styrene-acrylonitrile; ETFE, ethylene-tetrafluoroethylene copolymer.

4.2 *Reagents*—Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society when such specifications are available.⁷ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. In addition to this, it is desirable

except when standardized, are specified as a ratio stating the number of volumes of the concentrated reagent to be diluted with a given number of volumes of water, as in the following example: HCl (5 + 95) means 5 volumes of concentrated HCl (sp gr 1.19) diluted with 95 volumes of water.

5.3 *Standard Solutions*—Concentrations of standard solutions are stated as molarities or normalities, expressed decimally; or the equivalent of 1 mL of solution in terms of grams, milligrams, or micrograms of a given element expressed as “1 mL = x.xx—g, mg, or µg of...”

5.4 *Nonstandardized Solutions*—Concentrations of non-standardized solutions prepared by dissolving a given weight of the solid reagent in a solvent are specified in grams of the

⁷ “Reagent Chemicals, American Chemical Society Specifications,” Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see “Reagent Chemicals and Standards,” by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the “United States Pharmacopeia.” United States Pharmacopeial Convention, Rockville, MD 20852.

salt as weighed out per litre of solution, and it is understood that water is the solvent unless otherwise specified. For example, to prepare barium chloride solution (100 g/L) dissolve 100 g of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) in water and dilute to 1 L. In the case of certain reagents, the concentration may be specified as a weight percent. For example, H_2O_2 (3 %) means a solution containing 3 g of H_2O_2 per 100 g of solution. Other nonstandardized solutions may be specified by name only and the designation of the concentration of such solutions will be governed by the instructions for their preparation.

6. Laboratory Ware (1,2)^{8,9}

6.1 *Glassware*—Unless otherwise stated all analytical methods are carried out in borosilicate glassware.

6.1.1 *Tolerances*—All glass apparatus and vessels used in analytical work must be carefully selected and calibrated to meet the particular requirements for each operation. Standard volumetric flasks, burets, and pipets must be of Class A or B within the tolerances established by the National Institute of Standards and Technology and ASTM.⁹

6.1.2 *Types*—Glasses are available which include colored glass for the protection of solutions affected by light, alkali-resistant glass, and high-silica glass having exceptional resistance to thermal shock. Standard-taper, interchangeable, ground-glass joints are very useful in analytical work.

6.2 *Plastic Labware:*

6.2.1 *Tolerances*—All plastic apparatus and vessels used in analytical work must be calibrated to meet the particular requirements for each operation. Standard volumetric flasks, burets, and pipets must be of precision grade within the tolerances established by the National Institute of Standards and Technology for the corresponding types of glassware (see 6.2.4).

6.2.2 *Physical Properties*—There are a number of physical properties which influence the usefulness of plastic labware (Table 2).

6.2.3 *Compatibility*—Many reagents can affect the strength, flexibility, surface appearance, color, dimensions, or weight of plastics. The two basic modes of interaction that can cause these changes are described in 6.2.3.1-6.2.3.4.

6.2.3.1 *Chemical*—The analytical reagents can react with the polymer chain by oxidation, by attack on functional groups in or on the polymer molecule, or by depolymerization with a resultant deterioration in physical properties.¹⁰

6.2.3.2 *Physical*—Absorption of solvents in the plastic can result in softening, swelling, and permeation of the solvent through the plastic. No room temperature solvents are known for the polyolefins, however, it is better not to use them to store reagents. Reagents such as NH_3 , Br_2 , H_2S , and nitrogen oxides may be absorbed from reagent solutions by the plastic and become a source of error by subsequent release when the vessel

is used for a different analysis.¹¹ Atmospheric contaminants may diffuse through the plastic and spoil contained reagents or samples. Other polymer types may dissolve in some solvents. Plastic labware may crack from interaction of a “stress cracking agent” (present, possibly in the solution to be analyzed) with molded-in stresses. This is, however, a long-time phenomenon and is normally not a factor in analytical work because contact times usually are limited and the labware is washed regularly.

6.2.3.3 Some plastics may contain small concentrations of metals used as catalysts during manufacture. Such metals may dissolve in the analytical reagent system and cause interference, particularly when small amounts of metals are to be determined.

6.2.3.4 A general indication of the effect of individual reagents can often be obtained from manufacturers’ publications. It is important, of course, to consider that exposure time, temperature, concentration, and other reagents in the system may alter the effects of a given reagent on a given plastic. Because of these factors, the plastic labware must be thoroughly tested under the conditions of the method.¹⁰ The type of plastic labware (see footnote B of Table 2) will be found specified in the method as well as any special precautions for its use.

6.2.4 *Precautions*—Most plastic labware must not be used with strong oxidants at elevated temperatures; or exposed to localized or general temperature above the limits in Table 2.¹² With proper precaution polytetrafluoroethylene labware may be used with strong oxidizing agents at elevated temperatures (see Table 2). For the best performance new volumetric ware should be rinsed with a mild detergent according to the directions of the manufacturer before using. Plastic volumetric ware shrinks slightly as it ages; therefore, it must be recalibrated periodically. Interior surfaces of volumetric ware should not be cleaned by abrasive action.

7. Hazards (3-8)

7.1 *General Requirements*—Nearly all procedures carried out in the chemical laboratory are potentially hazardous. Each of the procedures used in these methods of chemical analysis of metals has been safely performed many times in a number of laboratories. Specific warnings are given in the methods when unusually hazardous steps are required, but the analyst must rely on his own knowledge and skill to avoid the common hazards. The following general concepts have been developed through many years of industrial laboratory operations:

7.1.1 Each person who works in a chemical laboratory should protect himself and others from harm. Each individual should adopt an attitude of anticipating potential hazards and planning means for reducing the associated risk to a tolerable level. This involves the proper implementation of approved procedures, personal protective equipment, and risk management policy.

⁸ The boldface numbers in parentheses refer to the list of references at the end of these practices.

⁹ For further information the following ASTM Standards may be consulted: Volumetric Labware: Specifications E 287, E 288, E 438, Practice E 542, Specifications E 694, E 969, and E 1044. Thermometers: Specification E 1, and Test Method E 77. Hydrometers: Specification E 100 and Test Method E 126.

¹⁰ From the publications of the Nalgene Labware Div., Nalge Sybron Corp.

¹¹ Theobald, L. S., *Analyst*, Vol 84, 1959, p. 570.

¹² Special care should be used with fluorinated materials, because at temperatures around 250°C traces of possibly hazardous vapors may be emitted. Heat in a hood or well-ventilated area.

7.1.2 The employer should provide proper physical facilities, equipment, materials and training to permit employees to work without exposure to undue hazard. The work environment should be engineered to minimize risk and control emergencies. Hoods with recommended face velocities, eye-wash and emergency shower stations should be provided. Fire alarm and fire control equipment should be installed. All employer provided risk control equipment, including personal protective equipment, should be on a regular inspection schedule. Management should adopt proper rules to promote safety by establishing low risk operating practices, good housekeeping, and proper personnel behavior. These rules should be enforced consistently and impartially. Employees shall be advised of potential hazards in accordance with applicable federal, state, and local laws and regulations.

7.1.3 Ordinary industrial hazards (such as those which cause thermal burns, slips and falls, electrical shocks, and physical injury from equipment failure or contact with stationary or moving objects) can exist in laboratories along with special chemical hazards. Employee training programs, periodic facilities inspections, and the establishment of low risk practices and procedures may be helpful in minimizing these dangers.

7.2 *Safety Plan*—Every analytical chemistry laboratory shall have a written safety plan. If the laboratory is a part of a larger facility, its plan should be a part of (or coordinated with) the overall safety plan of the larger organization. A safety plan addresses at least the following topics:

7.2.1 Definitions of areas and personnel covered,

7.2.2 General safety rules,

7.2.3 Rules covering specific areas of operations,

7.2.4 Plans and procedures for damage and injury control activities such as, building evacuations and fire fighting,

7.2.5 Lists of safety equipment according to location and type,

7.2.6 Plans for periodic safety and equipment inspections, and personnel safety training.

7.2.7 Descriptions of the duties and identities of personnel who will implement and carry out the provisions of this plan.

7.3 *Personal Protective Equipment*:

7.3.1 *Eye Protection*—Laboratory areas where chemicals are used shall be designated and appropriately posted as eye protection areas. Safety glasses with solid side shields or plastic goggles shall be required for all workers and visitors in these areas.

7.3.2 *Hand Protection*—A variety of glove types afford hand protection for different types of hazard. Rubber gloves are available in a variety of compositions that show differing forms of chemical resistance. For example, nitrile and neoprene rubbers are suitable for work with acids but show poor resistance to some organic solvents. Other materials provide protection from hot objects, cryogenic liquids, or abrasion. The appropriate style and type must be selected for each application. Gloves should be inspected before and decontaminated after each use.

7.3.3 *Miscellaneous Protective Equipment*—The following is a listing of some of the additional personal protective equipment that may be expected to find need in the metals analysis laboratory:

7.3.3.1 Face shields, portable shields, hood sash shields,

7.3.3.2 Ear plugs, sound barrier ear muffs,

7.3.3.3 Lab coats, lab aprons, sleeve protectors,

7.3.3.4 Respirators, gas masks, self-contained breathing apparatus, and

7.3.3.5 Safety shoes/boots.

7.4 *Laboratory Equipment*—This section lists common hazards associated with laboratory instruments and equipment. Reference works provide low risk practices and procedures. Suppliers and manufacturers should be consulted for specific information concerning the safe use and maintenance of their products.

7.4.1 Glass is a substance widely used in laboratory equipment. If mishandled, it can shatter into pieces with sharp edges that can inflict serious injury. Its use in pressure and vacuum systems is particularly hazardous.

7.4.2 Electrically operated equipment should always be installed in accordance with applicable local electrical codes, following the manufacturer's instructions. Proper grounding is especially important to prevent electrically conductive cabinets or cases from becoming dangerously charged if an internal short occurs. Electrical interlocks that prevent access to energized internal circuits should be kept in good operating condition and should never be defeated except as a part of carefully performed maintenance procedures. Lock-out/tag-out procedures shall be specified for any repair or maintenance operation that requires defeating electrical safety systems, or any other situation where equipment start-up could result in physical injury. Lock-out means the installation of a physical device (a lock with one key) that prevents re-energization. Tag-out means a prominently displayed clear warning sign that the equipment must not be re-energized. All personnel designated to perform such repair or maintenance shall have been adequately trained in lock-out/tag-out procedures.

7.4.3 Instruments that contain sources of radiation or radioactivity should be operated strictly in accordance with the manufacturer's instructions. Operation of instruments that produce X rays or other ionizing radiation shall conform to applicable local, state, and federal regulations (see Section 10 of Guide E 1621 for protective measures and references). Lasers, high-intensity arcs, sparks, plasmas, and ultraviolet sources can burn exposed skin. Eye protection should always be used. Commonly encountered sources of hazardous high intensity ultraviolet radiation include spectrographic emission sources, electrodeless discharge lamps, and nitrous oxide/acetylene flames.

7.4.4 Compressed gases in cylinders have the potential to cause severe damage and injury. If containers rupture or shatter, the stored energy is released suddenly with devastating force. A damaged cylinder or parts of a system and surrounding structures frequently become destructive projectiles. If the gas is toxic or explosive, its sudden release can quickly flood a vast area in a building with dangerous concentrations of the material. All inert gases present an asphyxiation hazard. The

most commonly used inert gases are nitrogen, helium, argon and carbon dioxide. Of these, the latter two are a particular concern. Argon is difficult to clear from lung passages, once inhaled, and carbon dioxide in high concentrations can paralyze the respiratory response. Standard practice is to securely chain or strap a cylinder to a firm support at all times except when it is being moved. Transportation is by means of a specially designed wheeled cart with a security chain and the protective caps should always be screwed on securely when the cylinders are being moved. Storage should be in areas kept at moderate temperatures. Combustible and oxidizing gases should be separated both in storage and in use to reduce the possibility of accidental explosions or fires. Toxic gases should be stored and used in such a manner that normal or abnormally large releases do not endanger life. In use, all gases should be trapped or released in a way that does not endanger property or life. Caution is required to be certain that gases vented outside a building do not inadvertently reenter through ventilating or air-conditioning systems. Fittings, pressure regulators, gages, valves, and tubing should be designed to safely contain the specific gas and pressures to be used in the system. Suppliers of gases and related equipment provide information on the safe use of their products.

7.4.5 Operations that release flammable, corrosive, toxic, or noxious vapors, gases, dusts, or fumes should be conducted in a suitable hood. The hood proper, ducts, and blower parts should be constructed of a material that resists chemical corrosion, solvent action, or heat generated by the process. Exhaust stacks should be positioned to ensure that hood emissions do not reenter the building through ventilating or air-conditioning systems. Periodic inspections should be provided to ensure that efficient air movement is maintained and that no holes develop in the system. Specially constructed hoods should be used for operations producing perchloric acid fumes or mists. In addition to other design features, such hoods are equipped with water valves that allow the stack and hood areas to be flushed down periodically. A regular program of flushing the stack and hood areas must be established for such hoods. Such hoods should never be used for venting easily oxidizable materials (7.5.10).

7.4.6 Equipment operating above or below atmospheric pressure should be of special heavy-walled construction. Personnel should be protected from being struck by pieces of the system if it should accidentally explode or implode.

7.4.7 Modern instruments often employ hazardous technology. Such equipment is provided with electrical interlocks, guards, and shields to protect personnel from injury. The equipment should be operated and maintained as specified by the manufacturer. All parts of the equipment, including its safety features, should be in proper working order at all times that it is being operated. Maintenance should be performed by qualified personnel who have been trained to protect themselves and others from the specific hazards present in each system.

7.4.8 Emergency safety equipment should be stored where it is plainly visible and readily available to personnel who need it. The location and manner of storing such equipment requires careful planning. No temporary or permanent storage of

equipment or material should be permitted to block access to any safety equipment. Personnel, when first assigned to a new area, should be instructed in the use of this equipment and should be reinstructed at appropriate intervals. The equipment should be inspected periodically to be sure it is in good operating condition. It should not be returned to its proper storage location after use until it is in proper condition for reuse. Examples of such equipment are emergency showers, eye wash stations, various classes of fire extinguishers, gas masks, self-contained breathing equipment, and spill control equipment.

7.5 *Reagents*—Reagent chemicals are normally used in small quantities and by personnel who have been instructed in their hazardous properties. Laboratories shall maintain a file of hazardous property data (Material Safety Data Sheets) for chemicals stored for use. Operating personnel shall have free access to the complete file at all times. However, since nearly all chemicals are hazardous under some circumstances, it is critically essential for all personnel to avoid inhaling or ingesting any chemicals and to permit no substances (with the exception of soap and water) to contact the skin. Some substances or combinations of substances are much more hazardous than others and are normally handled with gloves, protective clothing, barriers, or with other special precautions. Mouth pipetting should never be used. Because of the hazards of inadvertent contamination, it is prudent to establish and maintain a policy that forbids food, drink, tobacco, and cosmetic use in laboratories. A few of the more commonly used hazardous reagents are listed in the sections below. The analyst is cautioned to understand the properties of *any* reagent or combination of reagents before using them for the first time. Every step of a new procedure should be carefully planned, keeping in mind the potentially hazardous properties of the reacting materials and the resulting products. The plan should be designed for low-risk handling, even in the event of such unexpected occurrences as unusually rapid reactions, evolution of large quantities of gases, spillage, or accidental breakage or failure of equipment.

7.5.1 Storage of reagents, chemicals, and solvents should take into account their physical and chemical properties. The general classes of materials that should be stored separately are: bulk acids, strong oxidizers, volatile and flammable solvents, and water-sensitive materials. The latter (for example, calcium carbide and metallic sodium) should be stored where they cannot come in accidental contact with water from such sources as fire protection sprinklers, safety showers, accidental flooding, or leaks. Solvents and other highly flammable materials may require special explosion and fire-resistant storage.

7.5.2 All reagents should be considered hazardous, although some are much more dangerous than others. In many cases, inhalation, ingestion, skin contact, or combination thereof can lead to chronic or acute poisoning, and some chemicals have carcinogenic effects, or mutagenic effects on the unborn. In general, organic solvents have high vapor pressures at room temperatures, are flammable, and form explosive mixtures over a range of concentrations in air, and cause physiological changes in the human body if inhaled, ingested, or absorbed

through the skin. Chloroform, carbon tetrachloride, and benzene are examples of solvents with known serious harmful effects. Smoking and open flames or sparking electrical equipment should not be permitted in areas where solvents are stored or used.

7.5.3 Beryllium and its compounds, dry or in solution, present a serious health hazard. Ingestion or inhalation of dusts or sprays containing these materials must be avoided.

7.5.4 Elemental mercury has an appreciable vapor pressure. Hazardous concentrations can build up in the air in enclosed spaces where liquid mercury is exposed. Standard practice is to store mercury in strong, tightly closed containers and to transfer mercury in such a manner that a spill can be contained and thoroughly cleaned up at once.

7.5.5 Mineral dusts that contain any of a number of heavy metals, asbestos, beryllium, chromium compounds, or fluorides are hazardous.

7.5.6 Hydrogen cyanide and alkali cyanides are very toxic substances and should be used in an efficient fume hood. Cyanides must be disposed of with care, avoiding contact with acid that releases highly toxic hydrogen cyanide gas.

7.5.7 Hydrogen sulfide is more toxic than hydrogen cyanide. It is readily detected at low concentrations because of its powerful “rotten egg” smell, but the sense of smell becomes a very unreliable means of detection at higher concentrations. Procedures in which hydrogen sulfide is used or produced (for example, acid dissolution of metal sulfides) should be performed in an efficient fume hood.

7.5.8 Nitric acid fumes and the reaction products of nitric acid with reducing agents (such as metals) are noxious and highly toxic. Reactions with nitric acid should be performed in an efficient fume hood.

7.5.9 The corrosive action of acids and bases on materials, including human tissues, is well known. It is standard practice to use eye protection and protective clothing when handling these materials.

7.5.10 Perchloric acid can be used safely, but only under carefully prescribed conditions. Dilute perchloric acid has the same hazardous properties as other strong acids, but the concentrated acid, especially when it is hot, reacts rapidly and often with violently explosive force with oxidizable materials. Only well-established procedures should be employed for perchloric acid oxidations and the procedures should be followed *exactly* as written. Specially designed hoods are specified for handling perchloric acid fumes and any hood in which perchloric acid may be fumed should not be used for other operations that permit easily oxidizable material to collect in the ducts or blower.

7.5.11 Hydrofluoric acid produces very serious burns which may or may not be painful on first contact. Such burns often damage bone and other tissue within the body. Standard procedure is to use gloves and protective clothing when handling this reagent. After the material is added, the closed container, gloves, and all surfaces that may later be touched are

rinsed with large quantities of water. Even one drop of hydrofluoric acid on the skin or fingernail must receive immediate first-aid and medical attention should be promptly sought.

7.5.12 Halogens (fluorine, chlorine, bromine, and iodine) are hazardous materials. Procedures in which halogens are used or produced should be performed in an efficient fume hood. Bromine is the most commonly used halogen in the chemical analysis of metals. Liquid bromine vaporizes at room temperature; its fumes attack organic material and are highly irritating to eyes and lungs. The liquid causes burns and blisters. Inhalation, ingestion, and skin contact with both vapor and liquid must be avoided. Work only in an efficient exhaust hood with proper protective equipment. Familiarity with proper first-aid procedures is essential.

7.5.13 Hydrogen peroxide is commonly used at concentrations of 30 % and lower. At these concentrations the reagent is safer to handle than at higher concentrations but must still be treated as a very serious hazard; it is a very strong oxidizing agent, causes serious burns, and may decompose violently if contaminated.

7.5.14 Sodium peroxide is used both as an aqueous solution reactant and a molten salt flux. It is a very strong oxidant and must be considered a very serious hazard. In particular, sodium peroxide fusions with some sample materials may result in violent or explosive reactions. Such fusions should never be attempted with highly reactive or unknown samples. Sodium peroxide fusions must be performed following well-established procedures with samples of known reactivity and proper safety practices and equipment must be used.

7.5.15 *Spill Control*—Kits are commercially available for dealing with various types of chemical spills. It is also possible to assemble a variety of materials for dealing with such emergencies. Where such equipment is stored and who uses it should be specified in safety planning.

7.5.16 *Disposal of Laboratory Reagents*—As with all work in chemical laboratories, the chemical analysis of metals generates chemical wastes which must be disposed of by means which pose the least harm to health and the environment. All pertinent federal, state, and local laws and regulations shall be strictly followed.¹³

7.6 *Confined Space*—If repair, maintenance, or work of any kind requires personnel to enter a confined space, as defined by the applicable regulations, such personnel shall have been adequately trained in confined space safety procedures.

¹³ A valuable reference on the subject of the disposal of laboratory wastes is: *Prudent Practices for Disposal of Chemicals from Laboratories*, National Research Council, National Academy Press, Washington, D.C. 1983.

APPARATUS

8. General

8.1 Apparatus required in the methods of chemical analysis of metals, and referred to by number in the separate sections on apparatus which appear in the chemical methods preceding the procedures, must conform to the requirements prescribed below for the particular apparatus specified.¹⁴

9. Apparatus No. 1—Apparatus for Determination of Total Carbon by Direct-Combustion

9.1 The apparatus must be suitable for the direct combustion of the metal in purified oxygen and have a suitable purifying train following the furnace. For amounts of carbon above approximately 300 μg , the evolved CO_2 is collected in an absorbent of inert-base impregnated with NaOH . For amounts of carbon above approximately 1600 μg , an ordinary analytical balance may be used to weigh the absorption bulb. For smaller amounts special weighing techniques must be used. Fig. 1 shows a typical arrangement of the apparatus. Because of the diversity of apparatus by which correct results may be obtained in the determination of carbon, the recommendations given in 9.1.1-9.1.9 are intended to indicate what is acceptable rather than to prescribe definitely what must be used.

NOTE 2—Caution: Induction furnaces are capable of inflicting high-frequency burns and high-voltage shocks. All guards must be maintained properly. The furnace must be disconnected from the power line whenever electrical repairs or adjustments are made.

9.1.1 *Combustion Apparatus*—Any apparatus that will heat the sample to the required combustion temperature may be used. Furnaces with wire-wound heating elements generally are limited to a maximum temperature of 1200°C; resistance furnaces equipped with nonmetallic heating elements and induction furnaces (**Caution**, Note 2) and may be operated at temperatures above 1400°C. Some types of induction furnaces contain as integral units the oxygen purifier, catalyzer, particle filter, and carbon dioxide purifier (see 9.1.3, 9.1.7, 9.1.8, and 9.1.9).

9.1.2 *Combustion Tubes*—Tubes may be of porcelain, sillimanite, clay, quartz, or platinum and must be gas tight at operating temperatures. Quartz is susceptible to devitrification when used intermittently at temperatures above 1000°C and may then become porous. Tubes 760 mm (30 in.) long with an inside diameter of 32 mm (1¼ in.), tapered at one end, are generally used with resistance furnaces and are convenient for the small fused silica crucible that is used for the determination of graphitic carbon in cast iron.

9.1.3 *Oxygen Purifiers*—The purity of the oxygen must not be less than 99.5 %. It must be passed through two reduction pressure valves (approximately 207 kPa (30 psig) and 14 to 28 kPa (2 to 4 psig), respectively), or a suitable two-stage reduction valve to provide an even and adequate flow of oxygen. Organic matter is an undesirable impurity; therefore, the oxidation catalyst tube, *E* in Fig. 1, heated to a temperature above 450°C, must be used when the presence of organic contaminants in the oxygen is suspected. Usually organic contaminants are not present, and the catalyst tube *E* (Fig. 1) may be omitted.

9.1.4 *Boats and Covers*—The boats and covers may be of aluminum oxide, clay, zircon, nickel, or platinum. Nickel boats should be made of sheet nickel containing less than 0.02 % carbon. Before use, new boats and covers must be preheated at a minimum of 1100°C in oxygen or air for at least 15 min or until a constant blank is obtained. To prevent damage to the tube by spattering, a platinum, nickel, or ceramic cover or ceramic sleeve, open at both ends to allow free access of oxygen, should be placed over the boat.

9.1.5 *Material for Lining Boats*—Aluminum oxide, 60-mesh or finer, specially prepared for carbon determinations is satisfactory. Ignited low-silica chrome ore, or zirconium oxide, properly sized and freed from materials causing a blank, may be employed.

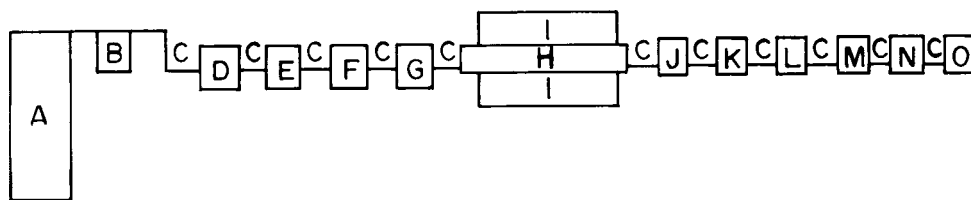
9.1.6 *Accelerators*—Accelerators are described in the respective methods.

9.1.7 *Catalysts for Resistance Furnace*—Ironized asbestos, copper oxide, platinized quartz or asbestos, or platinum gauze is placed in the exit end of the combustion tube when determining graphitic carbon in cast iron. In other instances when these catalysts are used to ensure complete combustion of carbon to carbon dioxide, it is questionable whether they are of any value except to serve as baffles to hold back finely divided solid metallic oxides, since they soon become fouled. When such baffles are used, the fixed sulfur should be burned out after not more than 200 samples have been run. This may be accomplished by drawing the exit end of the combustion tube into the hot zone while oxygen is passed through. When carbon determinations are made on materials containing high sulfur, baffles are not used in the exit end of the tube, but a special SO_2 absorber or purifier is placed between the tube and the CO_2 absorber.

9.1.8 *Catalyst for Induction Furnace*—A catalyst such as copper oxide heated to about 300°C must be used to ensure complete conversion of CO to CO_2 .

9.1.9 *Carbon Dioxide Purifiers*—The purifiers that follow the combustion tube must remove finely divided solid metallic oxides and oxides of sulfur and selenium, dry the gases before they enter the weighed CO_2 absorber, and protect the absorber from outside effects. Finely divided solid metal oxides are removed from the gases during their passage through the glass wool. The SO_2 given off by materials containing sulfur is removed by MnO_2 , or by platinized silica gel heated to about 400°C. Water vapor is absorbed in the tube containing $\text{Mg}(\text{ClO}_4)_2$. Additional components in the purification train may be required when materials containing very high amounts of

¹⁴ In addition to the requirements for apparatus given in these practices, reference should be made to the requirements set forth in the *Annual Book of ASTM Standards*, for the following: D 1100, "Specification for Filter Paper for Use in Chemical Analysis;" E 70, "Test for pH of Aqueous Solutions with the Glass Electrode;" E 145, "Specification for Gravity-Convection and Forced-Ventilation Ovens;" E 147, "Specification for Apparatus for Microdetermination of Nitrogen by Kjeldahl Method;" E 287, "Specification for Burets;" E 288, "Specification for Volumetric Flasks;" E 319, "Testing Single-Arm Balances;" E 438, "Specification for Glasses in Laboratory Apparatus;" E 617, "Specification for Laboratory Weights and Precision Mass Standards;" E 675, "Specification for Interchangeable Stopcocks and Stoppers;" E 676, "Specification for Interchangeable Taper- Ground Joints."



- A — Cylinder of oxygen.
 B — Reduction valve.
 C — Rubber tubing.
 D — Flowmeter.
 E — Heated oxidation catalyst tube containing CuO or platinum to destroy organic contaminants or CO, if their presence is suspected in the oxygen.
 F — Tower containing 20 to 30-mesh CO₂ absorber covered with a 13-mm (½-in.) layer of anhydrous magnesium perchlorate (Mg(ClO₄)₂) to remove moisture.
 G — Manometer.
 H — Combustion tube.
 I — Electric furnace, resistance-type with appropriate temperature controls, or induction-type with appropriate power input indicating device.
 J — Glass tube lightly packed with glass wool to remove solid particles.
 K — Bottle containing asbestos impregnated with manganese dioxide (MnO₂), or heated platinized silica gel, to remove sulfur gases from the stream. For alternative purification trains see 9.1.9.
 L — U-tube containing anhydrous Mg(ClO₄)₂. (For alternative purification trains see 9.1.9.)
 M — Heated oxidation catalyst tube containing CuO or platinized silica gel to ensure complete conversion of CO to CO₂ when using an induction furnace. When using a resistance-type furnace for determining graphitic carbon in cast iron, ironized asbestos or a similar catalyst should be placed in the exit end of the combustion tube.
 N — Absorption bulb with exit stopcock containing 20 to 30-mesh CO₂ absorber. A layer of glass wool is placed in the bottom and top of the bulb, and the CO₂ absorbent is covered with a layer of anhydrous Mg(ClO₄)₂ approximately 13 mm (½ in.) in thickness.
 O — Flowmeter.

FIG. 1 Apparatus No. 1—Typical Arrangement for Determination of Carbon by the Direct-Combustion Method

sulfur or of halides are being analyzed. A second tube containing MnO₂ may be used when the sulfur content is very high; MnO₂ has also been reported to remove chlorides. Chlorides may also be removed by pumice impregnated with a mixture of sodium thiosulfate and potassium iodide or by a tube containing 20 to 30-mesh zinc metal heated to 300 to 325°C. Other materials may be substituted for those listed; for example, potassium permanganate solution may replace the MnO₂, and H₂SO₄ may be used for removing water vapor, provided satisfactory results are obtained. The materials used in the purification train must be checked frequently to ensure that their absorbing capacity has not been exhausted.

9.1.10 *Gravimetric Determination of Carbon Dioxide by Absorption Bulbs*—No special types of absorption bulbs are recommended, although the Fleming, Miller, and Turner bulbs have proved satisfactory. When charged with absorbent, the bulbs must not weigh over 200 g, and they must always be weighed filled with oxygen. An adequate and uniform time interval between the combustion and the weighing must be maintained.

9.1.11 *Gravimetric Determination of Carbon Dioxide by Carbon Dioxide Absorbents*—The most desirable absorbent for CO₂ is 20 to 30-mesh inert base impregnated with NaOH, followed by anhydrous Mg(ClO₄)₂ at the exit end. The latter absorbs the water that is formed during the absorption reaction but not held by the unused CO₂ absorbent.

10. Apparatus No. 2—Filtering Crucible (9)

10.1 Fritted-glass filtering crucibles or porous-bottom porcelain filtering crucibles are recommended for general use. These crucibles are available in different sizes and porosities. When use above 150°C is specified, the porous porcelain crucibles should be used. Glass crucibles used at temperatures above 150°C require slower heating and cooling. Gooch

crucibles, with fixed or removable perforated bottoms, made of porcelain, fused silica, or platinum and of the following sizes as specified, are also recommended: 10, 20, 25, and 35 mL.

10.1.1 *Purification of Asbestos for Gooch Crucibles*—Digest a good grade of commercial shredded asbestos in HCl on a steam bath for several hours. Filter on a Büchner funnel and wash with water. Repeat the acid digestion until soluble iron has been removed. Filter and wash the fibers to remove chlorides. If the Gooch crucible is to be used for a particular operation, it may be desirable to introduce at this point further treatments of the asbestos. For example, if the Gooch crucible is intended for use in the bismuthate method for manganese, digest the asbestos for 1 to 2 h with hot HNO₃ (1 + 2) after chlorides have been washed out, to make sure of the elimination of the chlorides and to oxidize traces of ferrous iron. If the Gooch crucible is to be used in combustions for carbon, dry the asbestos, ignite it under oxidizing conditions until all carbonaceous matter has been consumed, and again mix with water.

10.1.2 *Preparation of Filter Pad for Gooch Crucible*—Prepare three sizes of asbestos suspended in water: coarse, medium, and fine. Pour some of the coarse asbestos into the crucible and drain. Then add the medium fibers and drain under gentle suction. Tamp down gently, especially at the sides, with the flattened end of a glass rod. Finally, add a layer of the fine asbestos and drain under stronger suction. Then wash with distilled water and drain under full suction until no fibers pass into the filtrate. The pad should be 2 to 3 mm thick and weigh 50 to 100 mg.

11. Apparatus No. 3—Apparatus for pH Measurements and Potentiometric Titrations

11.1 See Willard, Merritt, Jr., and Dean (10) for an excellent discussion of potentiometers for pH and potentiometric measurements.

11.1.1 *Apparatus No. 3A for pH Measurement*—A number of pH meters are commercially available. Many of these instruments can accept a variety of electrodes and therefore can be used also for potential measurements. Although both line- and battery-operated pH meters are manufactured, the former is recommended for laboratory work because this type of pH meter contains an electronic or transistorized potentiometer which makes the emf balancing operation entirely automatic. Electrometer tube input is used on both the electronic and transistorized pH meters.

11.1.1.1 The pH meter must have electrode standardization (or asymmetry potential) and manual or automatic temperature compensation controls. The dial must read in pH directly, and permit readings that are accurate to at least ± 0.01 pH unit. For higher accuracies it is recommended that a pH meter with an expanded scale be used.

11.1.1.2 Because there is no accurate method for determining the absolute potential of an individual electrode, two electrodes are used for pH measurements. These are called the reference and indicator electrodes. By international agreement the hydrogen electrode is the standard indicator electrode for pH, but it is inconvenient to use and subject to several limitations. The most widely used reference electrode is the saturated calomel electrode. It is most often used as a pencil-type unit that is immersed directly in the solution, but may also be utilized as an external cell (to prevent possible contamination) contacting the solution by means of a salt bridge. The silver - silver chloride reference electrode is also convenient to use, but it is more difficult to prepare than the saturated calomel electrode. The mercurous sulfate reference electrode may be used in solutions in which the chloride ions that diffuse out of the calomel cell might be harmful.

11.1.1.3 The most commonly employed indicator electrode is the glass electrode. The quinhydrone and antimony - antimonous oxide electrodes are used to a much less extent. Combination electrodes containing both the indicator and reference units are also available. The tips of the electrodes containing solutions must be covered with rubber caps when the electrodes are disconnected from the meter and stored. When pH measurements are not being made the electrodes connected to the pH meter should be kept in a beaker containing water. Prior to measuring the pH of a solution the electrodes must be thoroughly washed with water especially if they have been left standing for a long period of time.

11.1.2 *Apparatus No. 3B for Potentiometric Titrations*—Instruments for detecting the end points in pH (acid-base), oxidation-reduction, precipitation, and complexation titrations consist of a pair of suitable electrodes, a potentiometer, a buret, and a motor-driven stirrer. Titrations are based on the fact that when two dissimilar electrodes are placed in a solution there is a potential difference between them. This potential difference depends on the composition of the solution and changes as the titrant is added. A high-impedance electronic voltmeter follows the changes accurately. The end point of the titration may be determined by adding the titrant until the potential difference attains a predetermined value or by plotting the potential difference versus the titrant volume, the titrant being added until the end point has been passed.

11.1.2.1 An elaborate or highly sensitive and accurate potentiometer is not necessary for potentiometric titrations because the absolute cell voltage needs to be known only approximately, and variations of less than 1 MV are not significant. Such instruments should have a range of about 1.5 V and a readability of about 1 MV. Many of the pH meters satisfying the requirements for Apparatus No. 3A are also suitable for potentiometric titrations.

11.1.2.2 The electrode system must consist of a reference electrode and an indicator electrode. The reference electrode maintains a constant, but not necessarily a known or reproducible potential during the titration. The potential of the indicator electrode does change during the titration; further, the indicator electrode must be one that will quickly come to equilibrium.

11.1.2.3 Saturated calomel and silver-silver chloride half-cells may be used as reference electrodes. In oxidation-reduction titrations tungsten may be used as the reference electrode with platinum as the indicator electrode. Where the hydrogen-ion activity remains constant throughout the titration, the glass electrode may be used as the reference electrode with platinum as the indicator electrode for oxidation-reduction titrations or silver in argentometry for precipitation reactions. Graphite has also been used as a reference electrode.

11.1.2.4 In addition to the indicator electrodes already cited, the glass electrode is used for this purpose in acid-base titrations, but in rare instances a hydrogen, quinhydrone, or antimony electrode may be preferred. In oxidation-reduction reactions the bright platinum or platinum-rhodium alloy may be in the form of wire or foil. Mercury is used as the indicator electrode in certain complexometric titrations. Silver may be used for argentometric halide precipitation reactions.

11.1.2.5 Initially, a titration of the constituent in question is performed manually, and the volumes of titrant added and the corresponding potential differences are noted. By use of established techniques (10) the end point potential is determined. For the analytical determinations, titration may be continued to a preset potential, the end point being signaled by a null meter, with or without automatic termination of the titration. This technique is applicable to reasonably rapid reactions involving strong oxidants and reductants, precipitates not more soluble than silver chloride, and ionization constants greater than that of boric acid.

11.1.2.6 Other techniques may be used for both slow and fast reactions. These include automatic recording of the titration curve on a strip chart, and the recording of the titrant end point volume on a tape. In the latter, an adjustable print-out delay prevents undertitrating when the reaction is slow.

11.1.2.7 Further detailed requirements for this apparatus are given in Method E 70.

12. Apparatus No. 4—Apparatus for Determination of Sulfur by Evolution

12.1 *Apparatus No. 4A*—The apparatus shown in Fig. 2 may be used for determining sulfur by the evolution method in testing materials that are soluble in HCl (1 + 1). It should consist of a 300-mL Florence flask fitted with a “sulfur-free” two-hole rubber stopper carrying a thistle tube and a second glass tube dipping into a beaker containing ammoniacal $ZnSO_4$ or $CdCl_2$ solution.

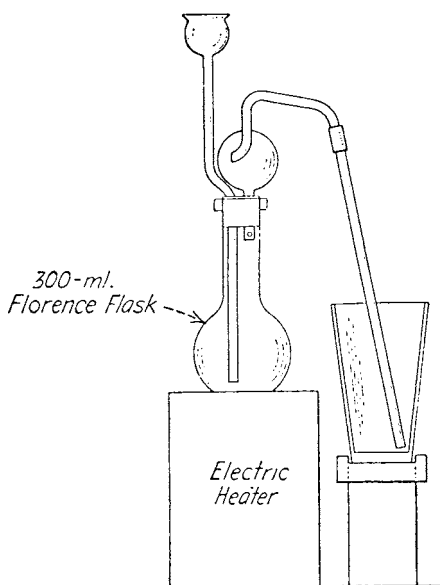


FIG. 2 Apparatus No. 4A for Determination of Sulfur by Evolution Method

13. Apparatus No. 6—Apparatus for Determination of Arsenic by Distillation

13.1 A simplified solution-distillation apparatus recommended for the determination of arsenic is shown in Fig. 3. The apparatus consists of a 300 or 500-mL Erlenmeyer flask with a standard-taper, ground-glass stopper carrying a distillation tube, a thermometer, and pressure regulator tube that comes within 3 to 6 mm ($\frac{1}{8}$ to $\frac{1}{4}$ in.) of the bottom of the flask.

13.2 *Thermometer*—A 76-mm partial immersion thermometer, having a range from -20 to $+150^{\circ}\text{C}$, conforming to the requirements for ASTM Partial Immersion Thermometer IC as prescribed in Specifications E 1 is recommended.

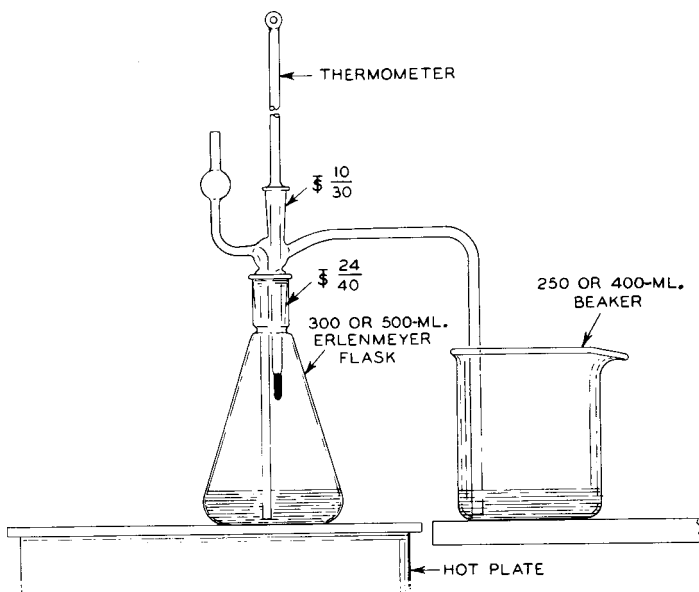


FIG. 3 Apparatus No. 6 for Determinations of Arsenic by Distillation

14. Apparatus No. 7—Apparatus for Reduction of Tin

14.1 *Apparatus No. 7A*—When tin is to be reduced to the stannous state and determined by titration with standard iodine or iodate solution, air must be excluded during the reduction and titration to prevent oxidation of the stannous tin. This exclusion of air is usually accomplished by keeping the solution under a blanket of gaseous CO_2 and may be accomplished in a variety of ways. One of the simplest methods is by means of the apparatus shown in Fig. 4 in which the reduction of the tin solution is made in a flask capped with a rubber stopper containing an L-shape siphon tube. When reduction is complete, the end of the siphon is dipped into a saturated solution of NaHCO_3 and set aside to cool. When cool, the stopper is removed and the solution titrated.

14.2 *Apparatus No. 7B*—For work of high accuracy, it is best to keep the tin solution under gaseous CO_2 . Fig. 5 shows one of the many forms of apparatus that may be used when gaseous CO_2 is employed. It consists of a flask closed with a three-hole rubber stopper containing an inlet tube for CO_2 , an air condenser, and a hole for the buret (glass plugged). During reduction a very slow stream of CO_2 is passed through the flask. When reduction is complete, the flow is increased to maintain a protecting blanket of CO_2 during the cooling and titration.

15. Apparatus No. 8—Jones Reductor

15.1 The Jones reductor has the dimensional requirements shown in Fig. 6. It consists of a column 19 mm in diameter and 250 mm in length, of 20 to 30-mesh amalgamated zinc. To amalgamate the zinc, shake 800 g of zinc (as free of iron as possible) with 400 mL of HgCl_2 solution (25 g/L) in a 1-L flask for 2 min. Wash several times with H_2SO_4 (2 + 98), and then thoroughly with water. The reductor, when idle, should always be kept filled with distilled water to above the top of the zinc.

15.2 When the reductor is to be used for the determination of columbium in steel, the reducing column should be 19 mm in diameter and 760 mm in length. One filling should suffice for about six determinations of columbium.

16. Apparatus No. 9—Electrodes for Electroanalysis

16.1 *Electrodes*—Platinum electrodes of the stationary type are recommended as described in 16.1.1 and 16.1.2, but strict

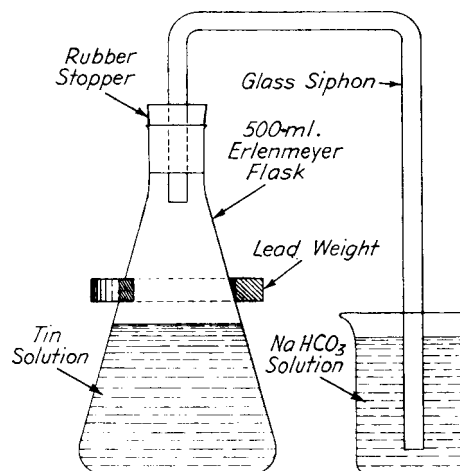


FIG. 4 Apparatus No. 7A for Reduction of Tin