Designation: C 997 – 83 (Reapproved 1993)ε1

Standard Test Methods for Chemical and Instrumental Analysis of Nuclear-Grade Sodium and Cover Gas[1]

This standard is issued under the fixed designation C 997; 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.

ε1 NOTE—Section 264, Keywords, was added editorially in April 1993.

1. Scope

1.1 These test methods provide instructions for performing chemical, radiochemical, and instrumental analyses of sodium metal and for determining impurities in cover gas.

1.2 The analytical procedures appear in the following order:

2. Referenced Documents

2.1 *ASTM Standards:*

A 370 Test Methods and Definitions for Mechanical Testing of Steel Products[2]

C 859 Terminology Relating to Nuclear Materials[3]

D 1193 Specification for Reagent Water[4]

E 146 Methods for Chemical Analysis of Zirconium and Zirconium Alloys[5]

3. Significance and Use

3.1 Sodium metal is used as a coolant (heat-transfer medium) in nuclear reactors, particularly in fast breeder reactors. An inert gas (argon, nitrogen, or helium) is used to cover sodium within a reactor and during transfer and shipping operations to protect it from oxygen and water. To be suitable for use, the metal and gas must meet specified criteria for purity as determined by analysis.

3.2 During reactor operation, chemical and radiochemical impurities resulting from corrosion and neutron activation must be maintained within specification levels established for the reactor system. The sodium and cover gas must be analyzed periodically to monitor buildup of those impurities.

3.3 These methods are applicable to the analysis of sodium and cover gas for the above purposes.

4. Reagents

4.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[6,7] 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.

5. Safety Precautions

5.1 Sodium is a reactive metal. It reacts vigorously with water and alcohol to form hydrogen, which is easily ignited

[1] These test methods are under the jurisdiction of ASTM Committee C-26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.05 on Test Methods.

Current edition approved May 27, 1983. Published August 1983.

[2] *Annual Book of ASTM Standards*, Vol 01.03.

[3] *Annual Book of ASTM Standards*, Vol 12.01.

[4] *Annual Book of ASTM Standards*, Vol 11.01.

[5] Discontinued; see 1991 *Annual Book of ASTM Standards*, Vol 03.05.

[6] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D.C. 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."

[7] Met-L-X is a tradename for a NaCl-based powder.

and which can cause an explosion. Take care when dissolving a sodium sample, and it is recommended to use a safety shield and fume hood. The proper type of fire extinguisher shall be readily available, and locally established safety precautions for handling sodium shall be followed.

5.2 Radioactive sodium must be handled in fume hoods or other protective facilities, depending upon the degree of radiation exposure involved. Locally established radiation protection and monitoring regulations shall be followed.

BYPASS SAMPLING

6. Scope

6.1 This method is required to obtain a sample for the determination of carbon by the oxyacidic flux method. In addition, it may be used for those procedures in which the sodium is dissolved directly out of the container, whether the solvent is water, alcohol, or mercury.

7. Summary of Method

7.1 A sodium sample is collected in a container that, through extended treatment in flowing sodium, has been cleaned and equilibrated isothermally with the bulk sodium.

8. Apparatus

8.1 *Sampling Vessel*, may be a section of seamless metal tubing; for example, stainless-steel tubing having an inside diameter of >⅜ in. (>9.5 mm) and an internal finish of 32 µin. AA (0.81 mµ) or better, or a vessel as shown in Fig. 1. The vessel in Fig. 1 consists of two matching sections clamped together. Its main body, that has an inside diameter of 0.855 in. (21.7 mm), tapers at each end to an inside diameter of 0.279 in. (7.09 mm). Vessels may be made of either nickel or stainless steel. Attachment of the vessel to a system is done by coupling consistent with locally approved safety practices. Provisions must be available to heat the vessel and maintain its temperature as required.

9. Reagents and Materials

9.1 *Methanol*, redistilled using a quartz or borosilicate glass still and stored in polyethylene bottles. Ethanol may be substituted for methanol.

9.2 *Nitric acid*, diluted 1-part nitric acid with 5-parts distilled water.

9.3 *Water*, distilled and passed through a high-quality mixed-bed ion exchange column and stored in a polyethylene bottle.

10. Precautions

10.1 An important safety consideration in sampling is the mode of connection of the sampler to the system. Three modes of connection for the bypass sampler are by welding, by Swagelok fittings, and by Conoseal fittings. In general, experience has shown that fewer sodium leaks are experienced when connections are welded. This is especially true at temperatures above approximately 400°C (750°F). At low pressures, Swagelok and Conoseal fittings can be used successfully at temperatures moderately above 400°C (750°F). The fittings must be installed, maintained, and monitored in accordance with locally approved safety practices.

11. Procedure

11.1 Rinse the sampling vessel successively with 1 + 5 nitric acid, water, and methanol. Dry, cap, and store until used.

11.2 Attach the sampling vessel to the system in a manner consistent with local safety practices.

11.3 Check the system as follows:

11.3.1 Check the sampling system for leaks according to locally approved operating and safety practices. Use helium-leak testing whenever possible. In that case, a helium-leak rate of $<1 \times 10^{-7}$ $cm^3 \cdot atm/s$ ($<1 \times 10^{-8}$ $m^3 \cdot Pa/s$) through the connectors or welds shall be attained. For systems that can tolerate introduction of small amounts of gas, this step may be replaced by 11.3.2.

11.3.2 Purge the vessel with an inert gas. Connect one fitting to a sampling port while continuing the purge. Discontinue the purge and immediately connect the second fitting to the other sampling port. Check the sampling system for leaks, in accordance with locally approved operating and safety practices. Use helium-leak testing whenever possible. In that case, a leak rate of $<1 \times 10^{-7}$ $cm^3 \cdot atm/s$ ($<1 \times 10^{-8}$ $m^3 \cdot Pa/s$) through the connectors or welds should be attained.

11.4 Heat the entire sampling-vessel system to a temperature greater than 100°C (212°F), taking care to heat progressively from either the solid-liquid or solid-gas interface toward the control valves. Raise the temperature of the entire system to approximately 150°C (300°F).

11.5 Establish sodium flow by opening the outlet and inlet valves in the proper sequence. If step 11.3.2 has been used, the sequence of opening first the outlet and then the inlet valve is desirable because this sequence relieves the gas pressure in the vessel to the outlet line.

11.6 Adjust the sodium-flow rate, if necessary. A minimum flow rate of 0.1 g/m (6.3×10^{-6} m^3/s) should be maintained.

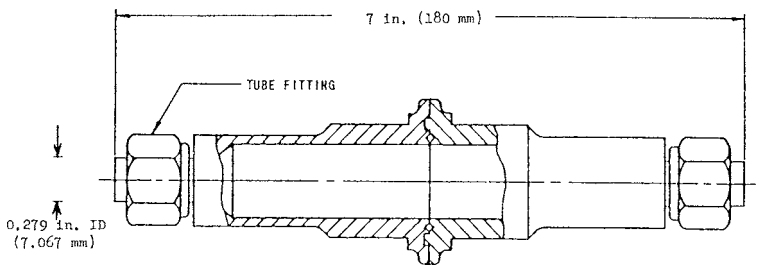

FIG. 1 Typical Sample Vessel

11.7 Increase the heat input to the sampler system if necessary to maintain the sampling vessel at the sampling temperature.

11.8 Maintain the temperature and flow rate until the vessel has equilibrated with the sodium. The time necessary for equilibration varies with the temperature of the sampling vessel. Table 1 gives the minimum equilibration time required at several selected temperatures.

NOTE 1—Steps 11.9-11.11 illustrate a typical sampling shut-down procedure. The actual steps used shall conform to locally approved operating and safety procedures.

11.9 Close the outlet valve.

11.10 Cool the sample to the freezing point of sodium <93°C (<200°F) as quickly as operational limitations will allow. Close the inlet valve at a temperature between 162°C (320°F) and 121°C (250°F) before the sodium freezes.

11.11 After the inlet and outlet lines are frozen, remove the sampling vessel.

11.12 Immediately cap the sampling vessel and mark the vessel with an identification number and an arrow indicating the direction of flow.

11.13 Deliver the vessel to the laboratory.

12. Discussion

12.1 This procedure, exclusive of equilibration time, requires approximately 4 h.

12.2 The evacuation of the sampling vessel is a time-consuming step that unnecessarily complicates the procedure. Thus, using the optional step (11.3.2), which eliminates the need to evacuate the vessel as a necessary step, is desirable. The rationale for using this option is that some systems are not subject to problems caused by the introduction of gases into the system, nor are they particularly affected by the small amounts of contaminants that may be introduced as a result of using the optional step.

OVERFLOW SAMPLING

13. Scope

13.1 This method is required to obtain a sample for those determinations that involve vacuum distillation of sodium and for the determination of carbon. It may be used for other procedures in which the sodium is dissolved in water, alcohol, or mercury.

TABLE 1 Minimum Equilibrium Time

Temperature of Sampling Vessel[A]		Minimum Equilibration Time, h
°C	°F	
540	1000	1
320	600	4
230	450	5[B]

[A] At temperatures between those given, the equilibration time should be established by interpolation.

[B] After equilibrating first at 320°C (600°F) for 1 h for all sampling temperatures below 320°C (600°F) because sodium does not appreciably wet stainless s teel at 230°C (450°F).

14. Summary of Method

14.1 A sodium sample is obtained in a cup or beaker by overflowing the container with sodium. The excess sodium returns to the system.

15. Apparatus

15.1 *Overflow Sampler*—A typical device is pictured in Fig. 2. The body of the sampler is a flanged, stainless-steel pot. The captions in the figure show the other essential features of the sampler.

15.1.1 Four level indicators are shown. During sampling, the level should be between the two center indicators. The top and bottom indicators are to show levels outside any acceptable operating range.

15.2 *Sample Cup*—This vessel may be a distillation cup or a beaker. It may be constructed of any material that will not contaminate either the sampled system or the sample itself at sampling temperature and that will not constitute an interference in subsequent analytical steps. Because the sample cup material will vary with the analysis to be performed, at least one material that is acceptable is specified in each method using overflow sampling.

15.3 *Transfer Chamber*—A typical transfer chamber is shown in Fig. 2 in position on the overflow sampler. It is an inverted flanged cup with an O-ring sealed fitting at the top. A threaded insertion rod, which makes a sliding seal through the O-ring, is screwed into the sample cup holder. A valved transfer chamber is closed at the bottom by a high-vacuum gate valve, as illustrated in Fig. 2. A valved transfer chamber ordinarily will accommodate a cup holder for one or two cups. This restriction is imposed by the need to insert the entire valved transfer chamber into the entry port of a laboratory inert-atmosphere box. By modifying the entry port, larger transfer chambers could be used. Open (that is, unvalved) transfer chambers ordinarily will accept a holder for four sample cups.

15.4 *Sampling System*—A typical and functionally adequate piping system for taking sodium samples is shown in Fig. 3. In

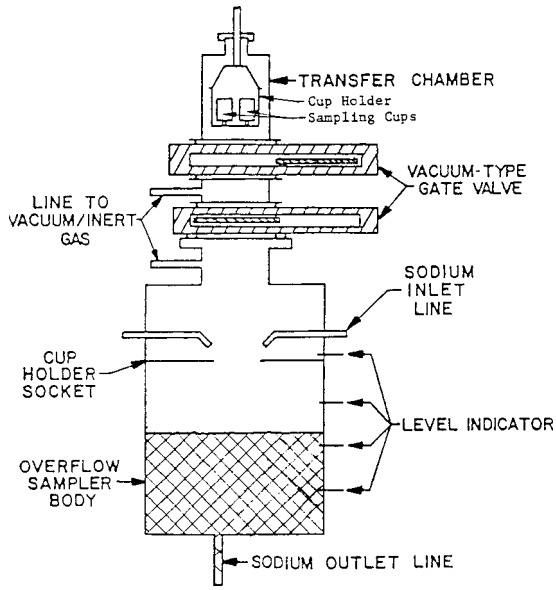

FIG. 2 Typical Overflow Sampler with Transfer Chamber Attached

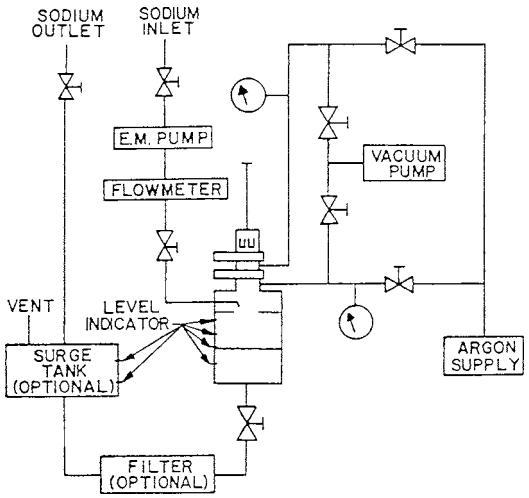

FIG. 3 Typical Sampling System

this system, sodium enters through a normally closed pneumatic bellows valve with the bellows downstream; it flows first through an electromagnetic pump and electromagnetic flowmeter and then through a manually operated bellows valve into the multiple spouts of the overflow sampler. Sodium leaves the sampler at the bottom; passing through another manually operated bellows valve, an optional filter, and an optional surge tank; and it exits through a normally closed pneumatic bellows valve with the bellows upstream.

15.4.1 A vacuum/inert-gas manifold allows measurement and adjustment of the gas pressure in the overflow sampler and in the transfer chamber.

15.4.2 Additional requirements on the system are included in Section 16.

15.5 *Multipurpose Sampler*—An alternate device for overflow sampling is the multipurpose sampler (MPS) shown in Fig. 4. This device provides three types of sampling capability in one unit. Overflow sampling is done using the sampler insert shown in Fig. 5. The MPS operation for overflow sampling is identical to that described for metal equilibration sampling, except that the sample section is operated at the sodium temperature at the system sampling point [±25°C (±45°F)], but not less than 200°C (392°F). Flow through the sampler is continued for as little as 15 min to as long as 24 h, depending upon sampling requirements.

16. Precautions

16.1 In contrast to the analytical procedures that are expected to be performed in an environment under control of the analyst, the sampling procedures must be used within the operational conditions that apply to the system being sampled.

16.2 To meet the operational restraints of some systems, this functionally adequate procedure must be expanded to include the following:

16.2.1 A leak detection system deemed adequate by local safety officials,

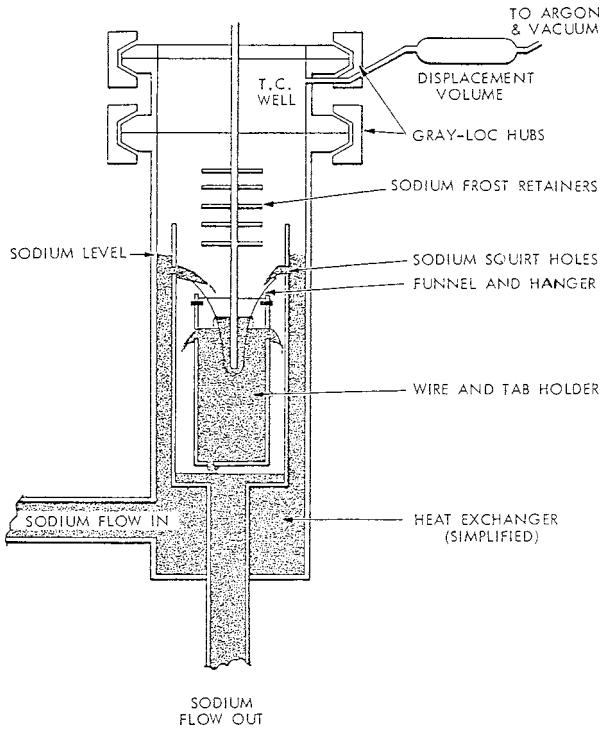

FIG. 4 Multipurpose Sampler

16.2.2 A fail-safe system of interlocks (if required by local safety practices) to close the isolation valves (normally closed pneumatic bellows valves) in an emergency,

16.2.3 Necessary biological shielding for radioactive systems, and

16.2.4 Provision for remote operation with radioactive systems and other systems considered hazardous because of high sodium pressures or temperatures.

17. Procedure

17.1 Two alternative procedures are specified. The first is for samples that must not be exposed to air or moisture; the second allows such exposure.

17.2 *Procedure for Protected Samples*:

17.2.1 Wash tantalum sampling cups successively with 1 *M* hydrofluoric acid, with aqua regia made from reagent grade acids, and finally with demineralized water. Wash titanium, quartz, and nickel cups successively with aqua regia and demineralized water.

17.2.2 Dry the cups in an oven at 110°C (230°F) for 1 h.

17.2.3 Cool the cups to room temperature, grasp with tongs, weigh, and transfer to the cup holder.

17.2.4 Retract the cup holder into the transfer chamber and close the gate valve.

17.2.5 Bring the transfer chamber to the overflow sampler and bolt or clamp the chamber to the sampler with a vacuum-tight seal.

17.2.6 Open the transfer chamber gate valve, but keep the sampler gate valve closed.

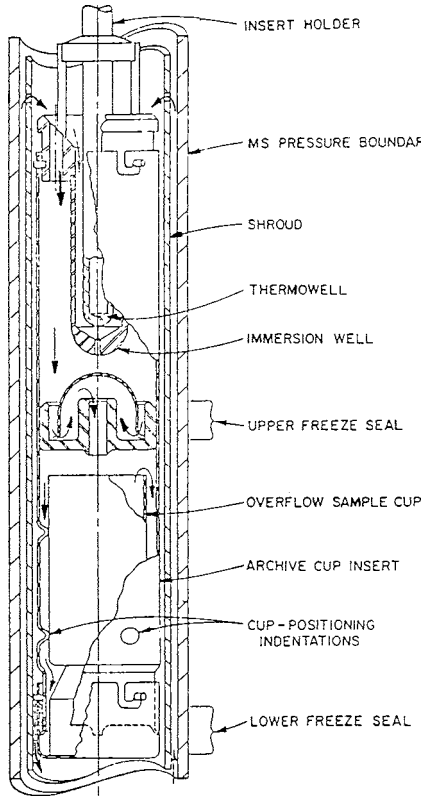

FIG. 5 Overflow Insert for Multipurpose Sampler

17.2.7 Evacuate the chamber and backfill it with inert gas for three cycles.

17.2.8 Test the assembly for leaks. The allowable in-leakage rate will be specified by the operating manual for the system or by a specific test request document. At a maximum allowable in-leakage rate, the system sodium must continue to meet operating purity requirements.

17.2.9 Correct unacceptable leaks and repeat the chamber flushing and leak test.

17.2.10 Pressurize the overflow sampler to the pressure of the sodium system.

17.2.11 Adjust the pressure in the transfer chamber to the pressure in the overflow sampler.

17.2.12 Open the gate valve at the top of the overflow sampler.

17.2.13 Lower the cup holder to the collection position and seat it in the socket provided in the overflow sampler.

17.2.14 Unscrew and raise the insertion rod.

17.2.15 Close the overflow sampler gate valve.

17.2.16 Melt the sodium in the sampler and auxiliary piping, starting at a solid-liquid or solid-gas interface. Bring the sodium to the sampling temperature. In those systems in which the sodium in the sampler and piping are kept molten, this step will be unnecessary.

17.2.17 Readjust the pressure in the overflow sampler to match the system pressure.

17.2.18 Start sodium flow in the sampler by opening the outlet and inlet valves in the appropriate order.

17.2.19 Adjust the sodium level in the sampler by changing the inert gas pressure to bring the sodium-gas interface below the sample cups.

17.2.20 Maintain sodium flow for the collection time. Normally, a flow rate of 0.1 g/m (6.3×10^{-6} m^3/s) or more should be maintained for at least 15 min.

17.2.21 Stop the sodium flow by closing inlet and outlet valves.

17.2.22 Shut off the heaters on the sampler inlet and outlet lines and allow the sodium in the lines to freeze. In those systems in which the sodium will be kept molten, this step is unnecessary.

17.2.23 Adjust the pressure in the transfer chamber to the pressure in the overflow sampler.

17.2.24 Open the sampler gate valve.

17.2.25 Lower the insertion rod, and screw it into the cup holder.

17.2.26 Retract the cup holder into the transfer chamber.

17.2.27 Close the transfer-chamber gate valve and sampler gate valve.

17.2.28 Shut off the heaters on the sampler and allow the sodium in the sampler to freeze. In those systems in which the sodium will be kept molten, this step is unnecessary.

17.2.29 Allow the sodium samples to freeze if they are not already solid.

17.2.30 Remove the transfer chamber and install another chamber with clean cups.

17.2.31 Send the transfer chamber with filled cups to the laboratory.

17.3 *Procedure for Unprotected Samples*:

17.3.1 Wash tantalum sampling cups successively with 1 *M* hydrofluoric acid, with aqua regia made from reagent grade acids, and finally with demineralized water. Wash titanium, quartz, and nickel cups successively with aqua regia and demineralized water.

17.3.2 Dry the cups in an oven at 110°C (230°F) for 1 h.

17.3.3 Cool the cups to room temperature; grasp with tongs, weigh, and transfer to the cup holder of the transfer chamber.

17.3.4 Retract the cup holder into the transfer chamber and close the chamber opening temporarily with aluminum foil or a clamp-on flange.

17.3.5 Bring the transfer chamber to the sampler and bolt or clamp the chamber to the sampler with a vacuum-tight seal.

17.3.6 Evacuate the chamber and backfill it with inert gas for three cycles.

17.3.7 Test the assembly for leaks. The allowable in-leakage rate will be specified by the operating manual for the system or by a specific test request document. At a maximum allowable in leakage, the system sodium must continue to meet operating requirements.

17.3.8 Correct unacceptable leaks and repeat the chamber flushing and leak test.

17.3.9 Pressurize the overflow sampler to the pressure of the sodium system.

17.3.10 Adjust the pressure in the transfer chamber to the pressure in the overflow sampler.

17.3.11 Open the gate valve at the top of the overflow sampler.

17.3.12 Lower the cup holder to the collection position, and seat it in the socket provided in the overflow sampler.

17.3.13 Unscrew and raise the insertion rod.

17.3.14 Close the overflow-sampler gate valve.

17.3.15 Melt the sodium in the sampler and auxiliary piping, starting at a solid-liquid or solid-gas interface. Bring the sodium to the sampling temperature. In those systems in which the sodium in the sampler and piping is kept molten, this step will be unnecessary.

17.3.16 Readjust the pressure in the overflow sampler to match the system pressure.

17.3.17 Open the outlet and inlet valves to start sodium flow to the sampler.

17.3.18 To adjust the sodium level in the sampler, change the inert gas pressure to bring the sodium-gas interface below the sample cups.

17.3.19 Maintain sodium flow for the collection time. Normally, a flow rate of 0.1 g/m (6.3×10^{-6} m^3/s) or more should be maintained for at least 15 min.

17.3.20 Close the inlet and outlet valves to stop the sodium flow.

17.3.21 Shut off the heaters on the sampler inlet and outlet lines and allow the sodium in the lines to freeze. In those systems in which the sodium in the sampler and piping will be kept molten, this step is unnecessary.

17.3.22 Adjust the pressure in the transfer chamber to the pressure in the overflow sampler.

17.3.23 Open the sampler gate valve.

17.3.24 Lower the insertion rod and screw it into the cup holder.

17.3.25 Retract the cup holder into the transfer chamber.

17.3.26 Close the sampler gate valve.

17.3.27 Shut off the heaters on the sampler and allow the sodium in the sampler to freeze. In those systems in which the sodium will be kept molten, this step is unnecessary.

17.3.28 Allow the sodium samples to cool to room temperature.

17.3.29 Unbolt and remove the transfer chamber.

17.3.30 Transfer the samples to the laboratory in accordance with one of the following plans:

17.3.30.1 Cover the opening of the transfer chamber with a clamp-on flange. Carry the samples to the laboratory and place them in an inert atmosphere box.

17.3.30.2 Transfer the cup holder to an evacuable transfer vessel (This may be a shatterproof vacuum desiccator). Close and evacuate the transfer vessel. Send the samples to the laboratory and transfer into an inert atmosphere box.

18. Discussion

18.1 In specifying the equipment and procedures for overflow sampling, it was assumed that the sodium in the overflow sampler should not be exposed to air because such exposure would lead to gross oxygen contamination of the system being sampled. For some systems, this assumption is not necessarily true. If oxide, hydroxide, or carbonate formed in the sampler and washed back into the system will not cause unacceptable excursions in the sodium system quality, then the gate valve at the top of the sampler may be replaced with a blank flange. The sampling procedure can be adjusted in obvious ways to compensate for this change. In particular, the sodium in the sampler must always be frozen before and during the time the sampler is opened.

18.2 Another acceptable approach to overflow sampling involves shuttling the entire sampler between the laboratory and the system being sampled. No procedure has been given for this more cumbersome approach, but the requirements of such a procedure should be apparent from an examination of Sections 14-17.

18.3 In 15.4, an optional surge tank is mentioned. In a more desirable arrangement, the sodium would be returned from the sampler in such a way that any entrained gas would be discharged and would accumulate harmlessly in the system cover gas. If there is a chance that electromagnetic pumps or flowmeters in the return line could become gas bound, then the surge tank should be provided; the accumulated gas should be vented as necessary.

18.4 This procedure takes 4 to 8 h exclusive of the time required for decay of radioactive samples.

WIRE AND FOIL EQUILIBRATION SAMPLING

19. Scope

19.1 This method is required to obtain a sample for the determination of oxygen by the vanadium wire method, hydrogen by the scandium foil method, and carbon by the Fe–12Mn method.

20. Summary of Method

20.1 A specimen of wire or metal foil is exposed to flowing sodium at 750°C (1382°F) for 4 to 24 h. The element of interest diffuses into the metal and reaches an equilibrium concentration depending upon time, temperature, and its concentration in the sodium. The metal sample is removed from the system and analyzed for the element of interest by either vacuum fusion or inert-gas fusion techniques.

21. Apparatus

21.1 Two basic types of samplers are in use for metal equilibration analyses.

21.2 *Multipurpose Sampler*—An alternate sampler device is the MPS illustrated in Fig. 4. The MPS can be utilized for three types of sampling–equilibration, overflow, and filtration. This is accomplished with three sampler inserts. The insert for equilibration sampling is shown in Fig. 6.

21.3 *Sample Transfer*—Sample inserts are removed from the sample body by disconnecting the upper Grayloc fitting and removing the insert holder. The insert is disconnected from the holder by disengaging the connection pins. The insert is then transferred to the laboratory where the samples (in this case, metal specimens) are removed in a hood or inert atmosphere box as required by the subsequent analysis.

21.4 *Sampling System*, described in Fig. 3 is typical of those used with the MPS. A sodium piping system with flowmeter, inlet and outlet valves, and a pump is required. In addition, the sampler is connected to vacuum and argon systems through a freeze seal connected to the lower Grayloc fitting in much the same manner as the sampler illustrated in Fig. 3.

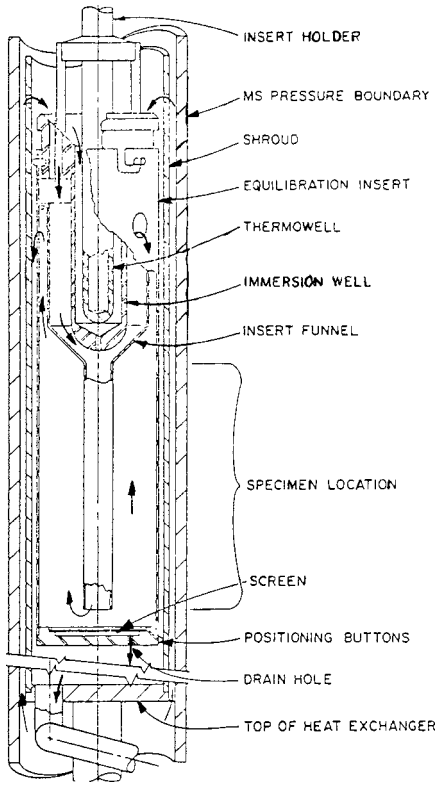

FIG. 6 Equilibrium Insert for MPS

22. Precautions

22.1 The MPS was field tested for over 18 months without incident. The sampler is connected to the piping system with Conoseal fittings, which have been used many times at system temperatures between 482 and 621°C (900 to 1150°F) without leakage. A Grayloc fitting used in removing the sample has been disconnected and reconnected over 100 times with the sampler operated at temperatures of 540 to 760°C (1000 to 1400°F). No abnormal safety problems are involved in the MPS operation.

23. Procedure

23.1 *Sample Preparation and Equilibration*:

23.1.1 The individual preparation requirements are presented in appropriate procedures for handling vanadium wire, Fe-12Mn tabs, and scandium tabs respectively. Overflow cup preparation is described in 17.2.

23.2 *Equilibration*:

23.2.1 Insert the sample holder into the sodium system.

23.2.2 Establish the required sodium flow. For the MPS, a flow of at least 0.25 g/m (1.6×10^{-5} m^3/s) is required. Normally, a flow of 0.3 to 0.4 g/m (1.9×10^{-5} to 2.5×10^{-5} m^3/s) is used.

23.2.3 Equilibrate the samples at the required flow rate and at 750 ± 2°C (1382 ± 4°F).

23.3 *Post Exposure Treatment*:

23.3.1 Turn off the heaters.

23.3.2 Close inlet valves to shut off the sodium flow.

23.3.3 Pressurize the sampler with inert gas to force sodium out of the sampler area.

23.3.4 Close outlet sodium valve.

23.3.5 Remove the sample holder from the sampler and transfer it to an inert gas glovebox.

23.3.6 Clean off residual sodium and prepare for analysis as described in the appropriate procedures.

24. Discussion

24.1 Metal equilibration sampling requires from 4 to 24 h at 750°C (1382°F), depending upon the element being determined. The total time required is approximately 8 h longer.

LABORATORY DISTILLATION OF SODIUM

25. Scope

25.1 This procedure is required to obtain a sample for the determination of fluoride, selected metals, silicon, boron, uranium, plutonium, nonvolatile alpha assay, general gamma assay, and chloride.

26. Summary of Method

26.1 Sodium is distilled in vacuum, leaving a residue which is enriched in nonvolatile impurities by a factor of approximately 10^4.

27. Apparatus

27.1 *Apparatus for Distillation Assembly*, (see Fig. 7) is made up of the following units.

27.2 *Distillation Unit*, shown in Fig. 8, is made of borosilicate glass. Details of the outer shell and the stopcock assembly appear in Fig. 9. The condenser system is detailed in Fig. 10.

27.3 *Sample Cup with Thermocouple Well*—A typical sample cup design is shown in Fig. 11. The cup is constructed of tantalum, titanium, nickel, or stainless steel. Tantalum is commercially available with purity >99.95 %, exclusive of interstitial elements. The thermocouple well extends into the pedestal of the cup.

27.4 *Thermocouple*—A chromel-alumel thermocouple is installed in the bottom part of the outer shell, as shown in Fig. 9. The thermocouple must make good physical contact with the bottom of the distillation cup.

27.5 *Vacuum Gauge and Associated Control*—The gauge should be suitable for measuring 1×10^{-3} mm Hg (130 mPa).

27.6 *Strip-Chart Recorder*—Any recorder appropriate for recording temperature with the chromel-alumel thermocouple may be used.

27.7 *Induction Generator*, rated at 2.5 kW at 450 kHz, and its output must be continuously variable from 25 to 100 % of rated power.

27.8 *Balance*, capable of weighing to ±0.1 g.

27.9 *Inert-Atmosphere Box*, shall have a purification train capable of controlling the moisture and oxygen contents of the atmosphere to <5 µL/L.

27.10 *Mechanical Pump*—A two stage mechanical pump with capacity of 25 L/min at 1×10^{-3} mm Hg (130 mPa) is satisfactory.

28. Reagents and Materials

28.1 *Helium*, welding-grade tank helium.

28.2 *Vacuum grease*.

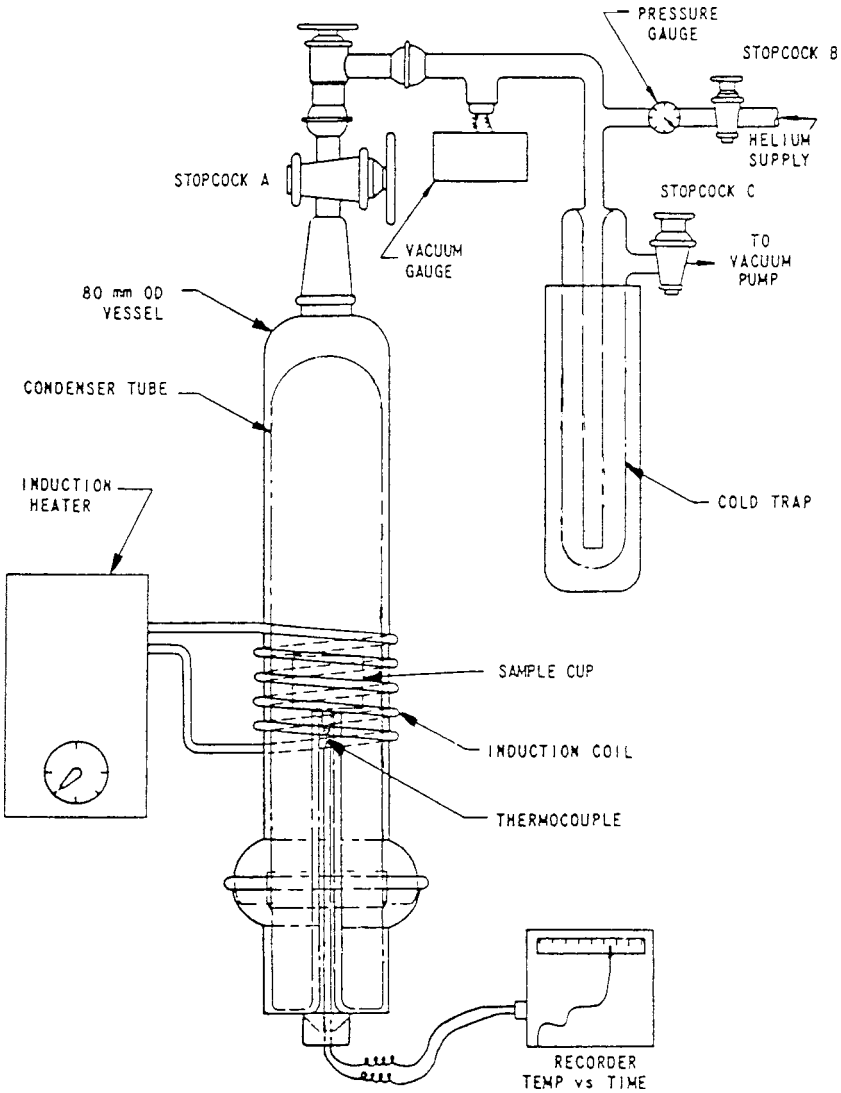

FIG. 7 Typical Vacuum Distillation Assembly

29. Precautions

29.1 In addition to normal safety practice, consider the following specific actions:

29.1.1 *Sodium Metal*—Be prepared to control a small sodium fire with Met-L-X or anhydrous sodium carbonate.

29.1.2 *Evacuated Glassware*—Perform the distillation in a hood with a transparent-front safety shield.

29.1.3 *High Voltage*—Insulate the output leads of the induction generator.

29.1.4 *Cryogenic Liquids*—When pouring liquid nitrogen or liquid argon, hold the vessel with an impervious, thermally insulating "pot-holder" pad.

30. Procedure

30.1 Transfer the distillation unit and the overflow sampling device containing the sample, obtained as in Section 17, into the glovebox.

NOTE 2—See Section 31 for comments about the desirability of exposing certain samples to laboratory air before they are distilled.

30.2 Open the sampling device, heating as required, and remove the filled sample cup.

30.3 Weigh the sample cup and record the weight.

30.4 Assemble the distillation unit with the sample cup in place (see Fig. 8). Close stopcock A.

30.5 Transfer the distillation unit from the glovebox and install it in the distillation assembly (Fig. 7).

30.6 Connect the thermocouple to the recorder.

30.7 Position the work coil of the induction heater, if necessary.

30.8 Open stopcocks A and C with stopcock B closed and evacuate the assembly to approximately 1×10^{-3} mm Hg (130 mPa). Close stopcock C and check the system for leaks with the vacuum gauge.

30.9 Cool the trap with liquid nitrogen or liquid argon.

30.10 Open stopcock B and backfill the assembly with helium.

30.11 Close stopcock B.

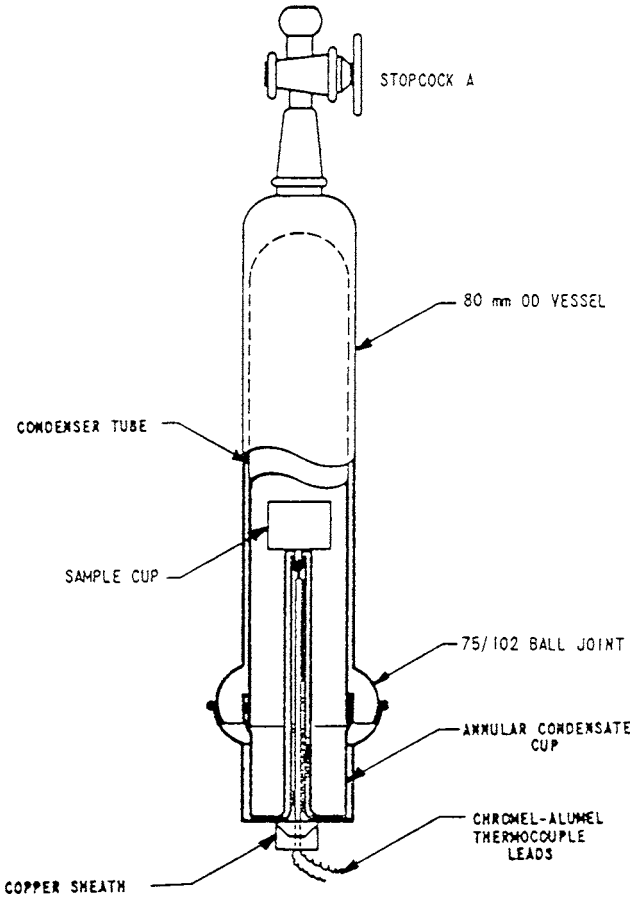

FIG. 8 Typical Sodium Distillation Unit

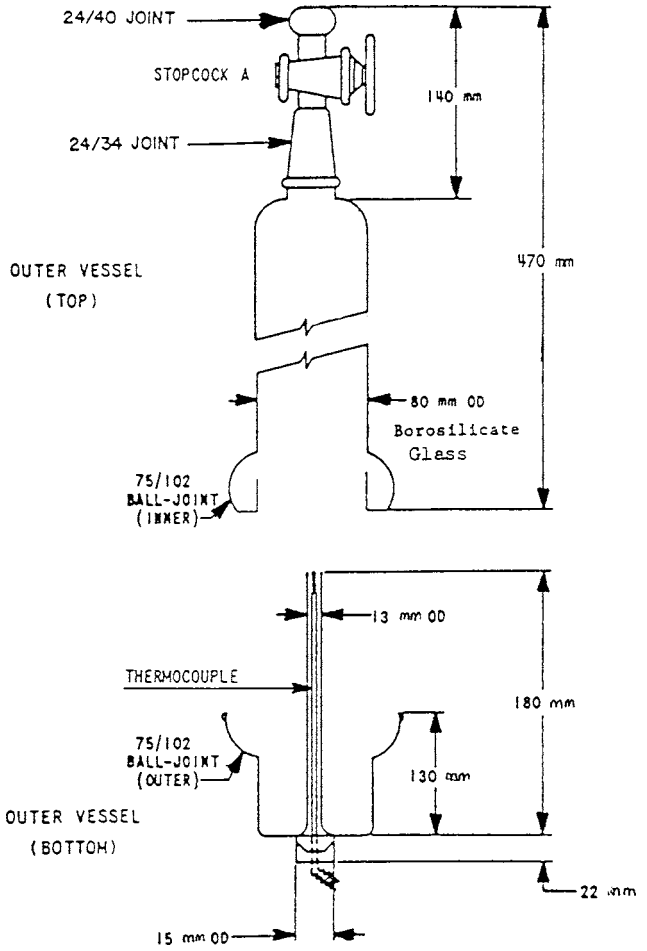

FIG. 9 Dimensions of a Typical Distillation Unit Shell

30.12 Turn on the induction heater at a power setting (previously determined) that heats the sodium slightly above melting.

30.13 Open stopcock C gradually to evacuate the system and degas the sodium for 5 min.

30.14 Adjust the power output of the induction heater to produce a rise in the temperature of the sodium of approximately 20°C/min until a sodium temperature of 300 ± 30°C is reached.

30.15 Distill at constant temperature until a sharp rise in temperature indicates that the distillation is complete.

30.16 Heat the sample cup to 400 ± 15°C.

30.17 Turn off the induction heater.

30.18 Close stopcock C. Open stopcock B momentarily to raise pressure in the system to about 1 mm Hg (130 Pa) (Thermal convection in the helium will melt the sodium drops adhering to the condenser).

30.19 Allow the system to cool to room temperature.

30.20 Open stopcock B to backfill the assembly with helium.

30.21 Open stopcocks A and B.

30.22 Disconnect the thermocouple and remove the distillation unit from the vacuum train.

30.23 Open the distillation unit, and carefully remove the sample cup (For samples of highly radioactive sodium, special shielding and handling procedures will be required and should be instituted at this point. Local safety officials should be consulted about the best manner to effect the transfer). Place the sample cup in a clean polyethylene bag or glass jar, record weights of empty and sodium-filled cup on bag or jar, and reserve for analysis. Because metallic sodium is still present in the assembly, these operations should preferably be performed in an inert atmosphere box.

30.24 Dispose of the sodium distillate in accordance with a locally approved procedure.

31. Discussion

31.1 The entire procedure requires approximately 3 to 4 h. The actual distillation requires 1.5 to 2 h.

31.2 Some metals are not quantitatively recovered in the residue under the conditions of this distillation. Zinc, cadmium, and the alkali metals, except lithium, are usually either partially or totally volatilized. Calcium and magnesium may be partially volatilized if the system is oxygen deficient. Lead may be lost if the residue is heated for prolonged time or at higher temperatures than specified. Intentional exposure to air for 1 to 5 s to produce a slight film of oxide on the surface of the sample should provide sufficient oxygen to retain up to 100 µg/g of calcium or magnesium in sodium.

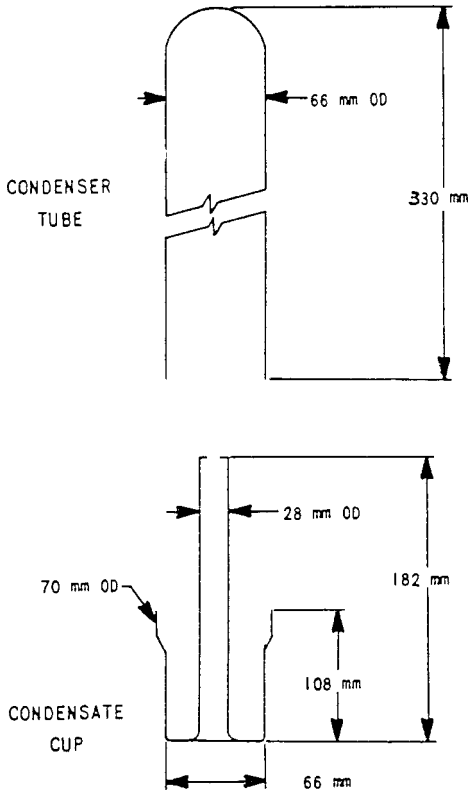

FIG. 10 Dimensions of a Typical Condenser System

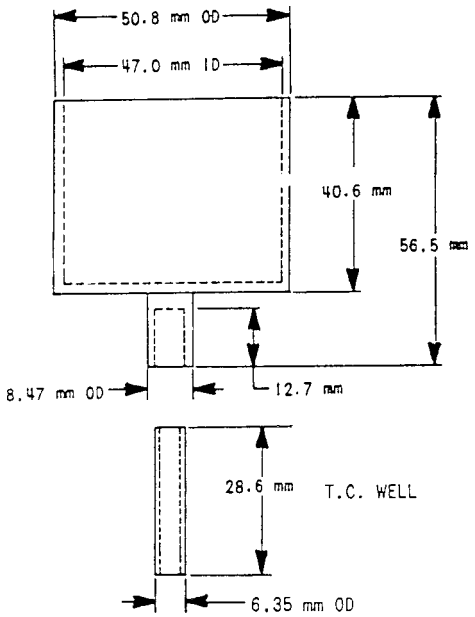

FIG. 11 Typical Sample Cup with Thermocouple Well

HYDROGEN BY HYDROGEN DIFFUSION METER

32. Scope

32.1 This procedure applies to a hydrogen diffusion meter that is installed directly in a sodium system such as a sodium loop.

32.2 The hydrogen meter operating in the equilibrium mode is applicable to the measurement of hydrogen in sodium down to the level of 0.04 μg/g. Operation of the meter in the dynamic mode shall permit measurements of hydrogen concentrations that are an order of magnitude lower than those measurable in the equilibrium mode. However, this increased sensitivity can be obtained only in systems in which calibration of the dynamic mode is possible (that is, only in systems which are at or can be adjusted to, a hydrogen level which permits equilibrium mode measurements).

33. Summary of Method

33.1 Hydrogen diffuses selectively through a nickel membrane from molten sodium into an evacuated chamber. The hydrogen concentration in sodium is proportional to the hydrogen flux through the membrane and, at equilibrium, to the hydrogen pressure in the chamber. Thus, the meter may be operated in either a dynamic mode or an equilibrium mode.

34. Apparatus

34.1 A schematic representation of a typical hydrogen meter is shown in Fig. 12.[8] Temperature control of the membrane shall be ±1°C at 500°C.

35. Procedure

35.1 *Equilibrium Mode Operation*:

35.1.1 Evacuate the system until a steady pressure reading is obtained with the ion pump opened to the system.

NOTE 3—When repeated equilibrium measurements are desired, complete evacuation of the equilibration chamber is unnecessary. It is recommended that the ion pump be opened to the membrane momentarily to reduce the pressure below the equilibrium value before proceeding to steps 35.1.2 and 35.1.3 (In this case, pressure measurements may begin immediately).

35.1.2 Isolate the equilibration chamber by valving off the ion pump. The pressure should begin to rise.

35.1.3 Take a pressure reading after 20 min and at 10 min intervals thereafter until the spread of four consecutive readings is no more than 5 % of the last reading. For pressures in the range below 5×10^{-5} mm Hg (6.6 mPa), the spread of four consecutive measurements must fall within 10 % of the last reading. This pressure plateau should be attained within 1½ h. If it is attained, record the last reading and proceed to step 35.1.4. Otherwise, take the corrective action prescribed by the meter manual and restart the measurement.

35.1.4 Correct the pressure recorded in step for the thermal transportation effect using the equation in 36.1 developed by Takaishi and Sensui. (**1**)

35.1.5 Calculate the hydrogen concentration using the equation in 36.2.

35.2 *Dynamic Mode Operation*:

35.2.1 *Calibration for Dynamic Mode*:

35.2.1.1 Fix the cold-trap temperature or add hydrogen to the system so that the concentration of hydrogen is ≥.05 μg/g.

35.2.1.2 Establish that the ion pump is open to the membrane.

[8] A hydrogen meter is commercially available from Westinghouse Nuclear Instrumentation Department, Baltimore, MD.

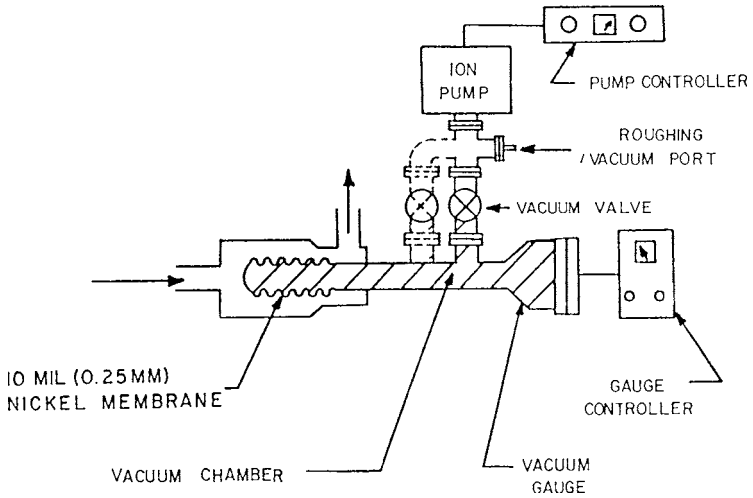

FIG. 12 Schematic Representation of a Typical Hydrogen Meter

35.2.1.3 Evacuate the system until a steady ion pump current (±5 %) is obtained.

35.2.1.4 Record this current.

35.2.1.5 Measure the hydrogen concentration in the system by operating the meter in the equilibrium mode (35.1, steps 35.1.2-35.1.5).

35.2.1.6 Record the hydrogen concentration measured in step 35.2.1.5.

35.2.1.7 Change the hydrogen level in the sodium by adjusting the cold trap temperature or by adding hydrogen and repeat steps 35.2.1.1-35.2.1.6.

35.2.1.8 Repeat step 35.2.1.7 until the concentration range of interest is covered.

35.2.1.9 Construct a calibration curve of ion current versus hydrogen concentration in sodium.

35.2.2 *Procedure for Dynamic Mode*:

35.2.2.1 Establish that the ion pump is open to the membrane.

35.2.2.2 Evacuate the system until a steady ion pump current (±5 %) is obtained.

35.2.2.3 Record this steady-state current.

35.2.2.4 Determine the hydrogen concentration in the system from the calibration curve.

36. Calculation

36.1 Correct the pressure recorded at step 35.1.3 using the following equation:

$$P_1 = P_2[(1.25 \times 10^5 B^2 + 8.0 \times 10^2 \mathrm{B} + 10.4 B^{1/2} + 1)/ (T_2/T_1 + 1.25 \times 10^5 B^2 + 8.0 \times 10^2 B + 10.48^{1/2})] \quad (1)$$

where:

P_1 = corrected pressure,
P_2 = observed pressure, mm Hg (from step 35.1.3),
T_1 = temperature of membrane, °K,
T_2 = temperature of pressure gauge, °K,
d = internal diameter of hydrogen-meter vacuum system, mm, and
B = $2[P_2 d/T_1 + T_2]$

36.2 Calculate the hydrogen concentration from the equilibrium mode of operation using the following equation:

$$S = KP_1^{1/2} \quad (2)$$

where:

S = concentration of hydrogen in ppm,
K = 4.9 ± 0.2 ppm/(mm Hg)½ [K = 56.8 ± 2.3 ppm/Pa½],
P_1 = pressure from 36.1.

37. Precision and Accuracy

37.1 Data are not available to provide information about precision and accuracy.

CARBON BY OXYACIDIC FLUX METHOD

38. Scope

38.1 This method is applicable for determining carbon in a sodium sample obtained by the Bypass Sampling Procedure. This procedure, exclusive of sampling, requires about 4 h.

38.2 This method is suitable for the determination of 0.5 to 1000 g of carbon (0.5 to 1000 µg/g in a 1-g sample of sodium). The range can be adjusted upward by recalibration of the chromatograph.

39. Summary of Method

39.1 Carbon in sodium is oxidized by combustion of a sodium sample in oxygen, and carbon dioxide is liberated by reaction with an acidic oxidizing flux. The carbon dioxide is trapped and then flushed into a gas chromatograph for measurement.

40. Apparatus

40.1 The analytical system consists of the following equipment. See the block diagram of Fig. 13.

40.2 *Gas Supply and Purification Tube*—The tube (Fig. 14) consists of a quartz tube containing copper oxide (heated to 750 ± 10°C by a tube furnace), Ascarite, and barium oxide. Helium and oxygen are passed through the tube. The gas supply pressure is 10 psig (69 kPa). The gases are supplied from gas cylinders equipped with valve-controlled flowmeters.

40.3 *Inert-Atmosphere Glovebox*—The box must have a purification system capable of controlling the impurity level of

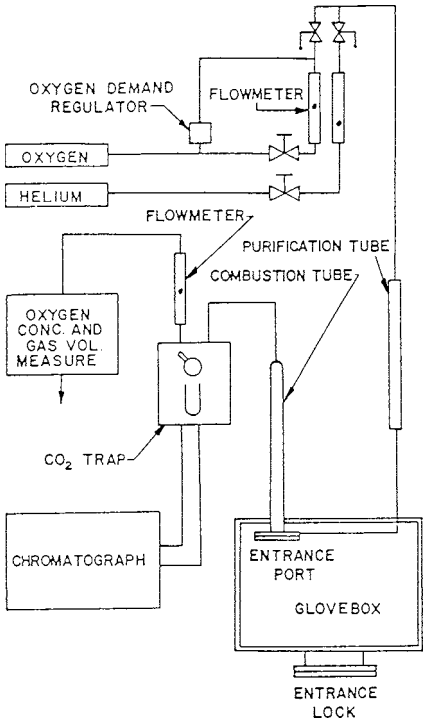

FIG. 13 Block Diagram of Analytical System

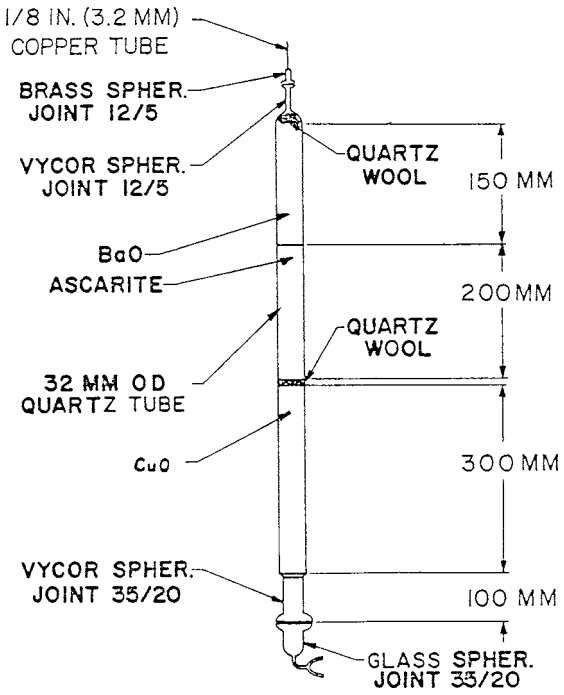

FIG. 14 Typical Gas Purification Tube

the box atmosphere. For this analysis, carbon monoxide, carbon dioxide, and hydrocarbon gases (calculated as methane) in the atmosphere must each be 1 µL/L. Oxygen and moisture must be <20 µL/L. All sampling and transfer operations must be performed in this box. The box should also be equipped with the following:

40.3.1 A sodium extruder,

40.3.2 A balance, capable of weighing to ±0.05 g,

40.3.3 Handling tools (forceps, a steel rod to move reaction bottles into and out of the combustion tube, tongs, and a notched stainless-steel bottle holder for the balance pan),

40.3.4 A powder horn, and

40.3.5 Holders for reaction bottles, shield tubes, and tools.

40.4 *Combustion Tube*, shown in Fig. 15, consists of an all metal port connected to an all quartz section by a graded seal. The port and port cover are made of Type 304 stainless steel. The carbon-free gas-tight seal is made of a wide, soft lead gasket soldered into and completely filling a machined groove in the port cover. A45° knife edge is machined on the port flange so that the knife edge is concentric with the opening to the combustion tube. The port cover is held against the knife edge on the port by four spring-loaded bolts, all tightened to the same tension by displacement limiting stops. This closure method prevents over tightening or under tightening and extends the life of the lead gasket to several months of use. Organic sealing gaskets, greases, or cements must not be used in or between the purification and combustion tubes, though they may be used elsewhere.

40.4.1 The gas line enters the combustion tube through the entrance port flange, and it is designed to flush the annular space between the port cover and the inside of the port.

40.4.2 During use, the metal port is located inside the glovebox. The quartz section penetrates the box wall and is supported by three consecutive tube furnaces outside the box. The combustion tube entry into the glovebox is made gas tight with a flat flexible silicone-rubber collar fitted tightly around the cool part of the combustion tube close to the entrance port. A metal compression fitting holds the silicone rubber to the metal glovebox wall with enough leeway to permit alignment of the tube with the tube furnace. The combustion tube is packed with copper oxide. The copper-oxide section of the tube is heated to 600 ± 10°C with the first furnace, and the reaction zone is heated to 980 ± 10°C with the second furnace.

40.5 *Carbon-Dioxide Trap*—This trap has a 3⁄16-in. (4.8-mm) outside-diameter stainless-steel tube that is 12-in. (300-mm) long containing 40 to 60-mesh molecular sieve 5A.

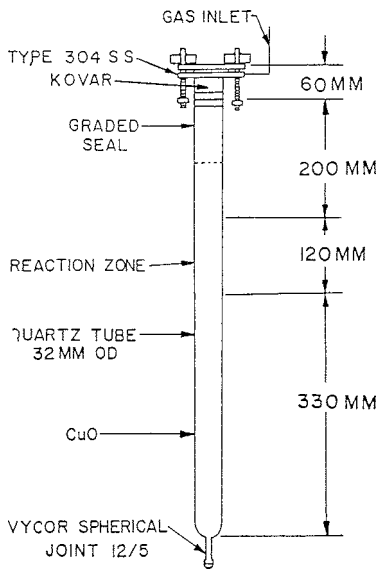

FIG. 15 Typical Combustion Tube

Provisions to heat the trap rapidly to approximately 300°C to desorb the carbon dioxide must be included.[9]

40.6 *Carbon-Dioxide Measurement System*, consists of the carbon-dioxide trap, a standard volume loop, and a gas chromatograph, as shown in Fig. 16. The gas chromatograph should be suitable for the detection of 0.1 µg of carbon as carbon dioxide.[10]

40.7 *Train-Gas Composition and Volume Measurement System*, (Fig. 17) consists of an oxygen sensor enclosed in a glass adaptor.[11]

41. Reagents and Materials

41.1 *Ascarite*, 8 to 20 mesh.
41.2 *Acetone*.
41.3 *Barium Oxide*, 10 to 20 mesh.
41.4 *Copper*, light turnings.
41.5 *Helium*, 99.95 %.
41.6 *Hydrofluoric Acid*, 28 *M*.
41.7 *Oxygen*, high purity.
41.8 *Potassium Dichromate*—Reagent-grade potassium dichromate contains 5 to 10 µg/g of carbon, that is readily removed by ignition for 1 h at 700°C.
41.9 *Quartz Wool*, preignited in air at 900 to 1000°C for 16 h.

42. Preparation of Apparatus

42.1 Clean the quartz purification tube (Fig. 14) with detergents, rinse, and then etch inside for 5 min at room temperature with 28 *M* hydrofluoric acid. Care must be taken to prevent etching of the ground joints. Rinse the tube with water to remove hydrofluoric acid and then with acetone. After evaporation of the acetone, heat the tube to red heat by means of an oxyhydrogen (not oxygen-hydrocarbon) flame.

42.2 Place a small piece of quartz wool, preignited at 900 to 1000°C for 16 h, inside the purification tube at the outlet end. Pack the tube with barium oxide to a length of 150 mm, lightly tapping to pack; add Ascarite to give an Ascarite bed length of 200 mm; and finally add a 20 to 30-mm barrier of quartz wool. Next, pack a 320-mm bed of pure copper turnings into the tube and heat the copper-filled section to 600 ± 10°C in a tube furnace. Pass a 50 % oxygen/50 % helium mixture through the tube at 80 to 100 mL/min for 16 to 24 h. Both the temperature and gas flow should be increased slowly to limit the rate of the initial oxidation of the copper. After the copper-oxide bed appears entirely black, pass only oxygen over the copper oxide for an additional 8 h.

42.3 Connect the outlet of the purification train to a flexible ⅛-in. (3.2-mm) outside diameter copper tube by either a graded glass-to-metal seal or a standard ground joint sealed with cupric phosphate cement (The cement is made by triturating copper oxide powder in 85 % phosphoric acid for about 10 min to give a creamy black paste; setting time is 24 h).

42.4 Prepare the quartz combustion tube (Fig. 15) using the same procedure used to prepare the purification tube (see 42.1).

42.5 Pack the combustion tube with approximately 320 mm of copper turnings. Convert the copper to copper oxide as described for the purification train in 42.2.

42.6 Etch the shield tubes and reaction bottles shown in Fig. 18 by immersion in 28 *M* hydrofluoric acid for 5 min at room temperature; rinse with water and acetone, and dry for 15 min at 120°C.

42.7 Clean tongs, tweezers, rod, and any other handling tools with appropriate reagents and ignite them in a hydrogen-oxygen flame until the metal shows a light oxide discoloration.

43. Calibration of Chromatograph

43.1 Fill a sample loop of known volume with standard gas (0.25 volume % carbon dioxide in helium) at known temperature and pressure, and insert the loop into the train between the

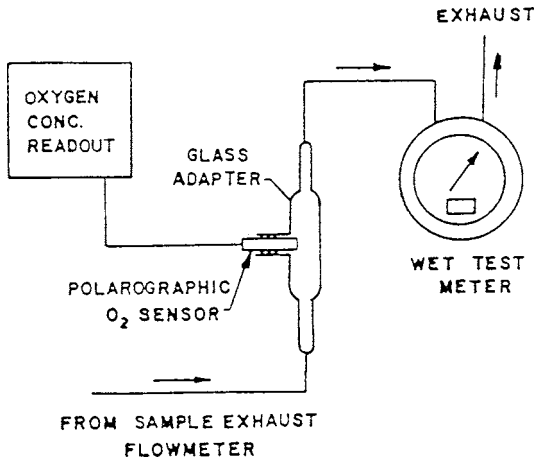

FIG. 17 Train Gas Composition and Volume Measurement

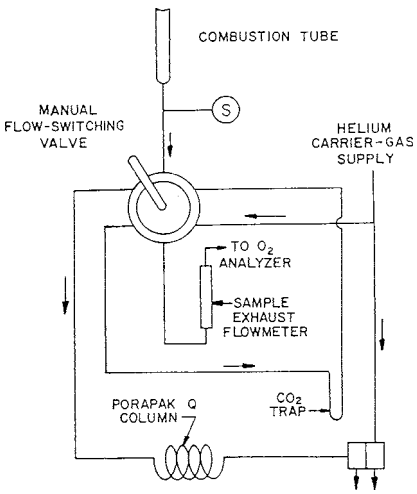

FIG. 16 Carbon Dioxide Measurement System

[9] The SKC, Inc. Model 215 Component Concentrator has been found suitable for this application. A 3/16-in. (4.8-mm) outside diameter thin wall approximately 15-mil (0.38-mm) trap must be substituted for the one supplied with the instrument. This trap contains about 0.5 g of 40 to 60-mesh molecular sieve 5A and is heated by direct application of a low-voltage, high-current electrical source.

[10] A Beckman series E analyzer equipped with a recorder having a 1-mV span was found suitable for this application. This chromatograph contained a 6-ft (1.8-m) Porapak Q column operated at 50 to 60°C and a standard two-filament thermal conductivity detector. It was operated with helium carrier gas at 100 mL/min. [A 12-ft by ¼-in. (3.7-m by 6.4-mm) outside diameter column packed with 30 to 60-mesh silica gel operated at 145°C has also been found suitable.]

[11] A Beckman Model 778 polarographic oxygen analyzer was found suitable for this application.

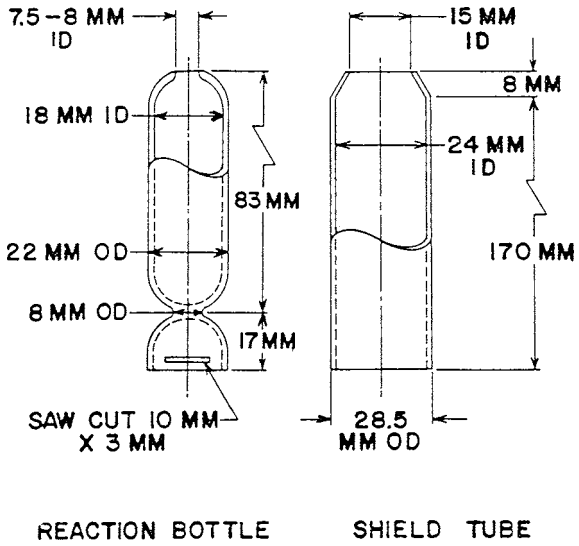

FIG. 18 Typical Reaction Bottle and Shield Tube

combustion-tube exit and the trap, point S in Fig. 16. Alternatively, inject known amounts of carbon dioxide (10 to 500 µL) into the combustion train through a septum in a tee before the combustion tube.

43.2 Trap the carbon dioxide from a stream of helium flowing at 100 mL/min.

43.3 Heat the carbon-dioxide trap and obtain the carbon-dioxide chromatogram.

43.4 Repeat the procedure, with adjustments of the chromatograph attenuator, until the desired calibration is achieved. Prepare a graph of peak height or area versus micrograms of carbon.

44. Procedure

44.1 *Preparation of Reaction Bottle*:

44.1.1 Flush the entire system including purification train, combustion train, and train-gas composition and volume measurement system with helium flowing at 100 mL/min.

44.1.2 Adjust the temperature of the copper-oxide furnace for the gas supply and purification tube to 750 ± 10°C and of the furnace for the combustion tube to 600 ± 10°C.

44.1.3 When the oxygen analyzer indicates 0.5 % oxygen, stop the flow of helium and open the combustion-tube port. To avoid oxygen contamination of the glovebox atmosphere, the combustion-tube port should never be opened if the train gas composition is above 1 % oxygen.

44.1.4 Place a clean shield tube and reaction bottle (Fig. 18) in the reaction zone, using a clean forceps (As a general rule, anything that comes in contact with the inside of the combustion tube or the sodium sample is handled or touched a minimum number of times and is touched only by point contacts).

44.1.5 Close the combustion-tube port and set the reaction zone furnace controller so that a temperature of 980 ± 10°C is attained.

44.1.6 Replace the helium with oxygen flowing at 100 mL/min.

44.1.7 Ignite for 1 h at 980 ± 10°C; replace the oxygen with helium flowing at 100 mL/min, and turn off the reaction zone furnace. Open the furnace to cool it down. To save time, cool the furnace with a fan.

44.1.8 When the furnace has cooled to 150°C and the oxygen analyzer indicates 0.5 % oxygen, remove the reaction bottle, leaving the shield tube undisturbed. The reaction bottle is always handled with forceps or by a clean steel rod which has been bent at a right angle and filed to fit the slot in the base of the bottle.

44.1.9 Grip the base of the reaction bottle, using a pair of clean tongs with serrated jaws, and place it on the double-V pan adaptor on the balance pan; allow the bottle to reach temperature equilibrium before weighing to the nearest 0.05 g. When the bottle is weighed, place it on double wedge-shaped pan adaptor made from a wide base piece of stainless steel constructed with two V-shaped notches in alignment 2 in. (50 mm) apart. Place the bottle horizontally in the notches for weighing operations, preventing the reaction bottle from rolling and preventing gross contact with the balance pan.

44.1.10 Pour 8 ± 0.1 g of potassium dichromate flux into the bottle mouth from the powder horn and reweigh the bottle.

44.1.11 Replace the bottle with the flux in the reaction zone and heat in oxygen for 1 h at 750 ± 10°C.

44.1.12 Replace the oxygen flow by helium and cool the reaction zone to 150°C. The flux must be cooled below 500°C to stop liberation of oxygen. Otherwise, the gas composition will remain above 1 % oxygen at a helium flow of 100 mL/min for an unacceptable period of time.

44.1.13 Remove the reaction bottle containing the preignited flux, cool it to glovebox temperature, and weigh it.

44.1.14 Proceed with 44.2 when running a sample or with 44.3 when running a blank.

44.2 *Aliquoting*:

44.2.1 Obtain the sample via the bypass procedure. The sodium is extruded from the bypass tube (by one of the two procedures described below) into a reaction bottle prepared as described in 44.1.

44.2.2 *Plunger-Type Sample Extrusion*:

44.2.2.1 Transfer the capped extrusion vessel into the inert-atmosphere glovebox.

44.2.2.2 Separate the two sections. Uncap one section and place it in the extrusion device shown in Fig. 15.

44.2.2.3 Force the piston into the large end to extrude sodium from the small end. Cut off and discard an initial portion of sodium.

44.2.2.4 Extrude and cut off approximately 1 g of sodium. Holding the reaction bottle vertically, insert the sodium sample as far into the bottle as possible. Reweigh the bottle and contents, and determine the sample weight by difference. Alternatively, estimate the sample weight from the number of turns of the extruder or measure the length of the extruded sodium rod. An analytical run is terminated and started over if at any time the bottle touches any part of the balance, except the double-V holder or any other item except the handling tools.

44.2.2.5 Go to 44.4.

44.2.3 *Vice-Type Sample Extrusion*:

44.2.3.1 Transfer the capped sample tube into the glovebox.

44.2.3.2 Cut off one end of the sample tube with a tubing cutter. Discard the end section.

44.2.3.3 Hold the tube about 2 in. (50 mm) from the cut end.

44.2.3.4 Put the tubing between the jaws of the vice.[12]

44.2.3.5 Press the foot switch to actuate the vice, and squeeze one length of sodium from the tube.

44.2.3.6 Cut off the extruded sodium with a knife and discard the piece of sodium. The knife used is an all-metal scalpel that has been thoroughly washed and dried to remove sodium and carbon contamination before each use. The knife is taken into the glovebox wrapped in clean aluminum foil.

44.2.3.7 Pull the sample tube back to bring a new section of the tube between the jaws.

44.2.3.8 Actuate the vise again. Extrude and cut off about 1 g of sodium. Holding the reaction bottle vertically, insert the sodium sample as far into the bottle as possible. Reweigh the bottle and contents and determine the sample weight by difference. An analytical run is terminated and started over if at any time the bottle touches any part of the balance, except the double-V holder or any other item except the handling tools.

44.2.3.9 Go to 44.4.

44.3 *Operational Blank*:

44.3.1 An operational blank is to be obtained with each batch of samples when changes are made in the system or reagents, or when discrepant results are observed. If the operational blank is demonstrated to be stable to ±0.2 µg for at least 1 month, then one operational blank per week is sufficient.

44.3.2 The operational blank consists of performing the steps of 44.1 (preparation of reagent bottle), carrying out dummy manipulations comparable to those of 44.2 (aliquoting), and continuing the steps of 44.4 (combustion). Thus, this blank contains all the steps and manipulations involved in running a sample, except for the actual addition of the sample.

44.4 *Combustion*:

44.4.1 Place the reaction bottle in the reaction zone so that it is centered with respect to the furnace, and then turn it to position the solid flux above the sodium sample. If the solid flux is allowed to remain on the bottom in contact with the sodium during combustion, the sodium may react quite vigorously with the flux; or helium may form a gas pocket in the upper space of the bottle, expand, and blow some flux and burning sodium out of the reaction bottle.

44.4.2 Close the port and switch the train gas to flow through the carbon dioxide trap.

44.4.3 Replace helium by oxygen at 100 mL/min. After the oxygen flow is started, obtain the initial wet-test meter reading.

44.4.4 As soon as the train gas is 95 % oxygen, heat the reaction zone to 200°C. At some point during heatup, the sodium will ignite and burn to sodium oxide. If the train gas is less than 95 % oxygen, combustion will be delayed or erratic and will be accompanied by ejection of sodium oxide smoke, molten flux, and bits of burning sodium. If this occurs, reject the sample and start over.

44.4.5 If the sodium burns without significant ejection of materials from the reaction bottle, close the reaction-zone furnace and heat to 980 ± 10°C.

44.4.6 Maintain the furnace at 980 ± 10°C until 8 to 18 L of oxygen have passed through the train, then cool the reaction-zone furnace. Replace the oxygen with helium and take a wet-test meter reading.

44.4.7 When the oxygen concentration has dropped to – 0.5 %, switch the carbon dioxide trap to the chromatograph.

44.4.8 As soon as the chromatograph has stabilized with the trap in the flow path, heat the trap to introduce the carbon dioxide into the chromatograph and obtain a chromatogram. Then switch the carbon dioxide trap back to the combustion-flow path. Remove the reaction bottle.

45. Calculation

45.1 From the calibration graph prepared in 43.4, calculate the concentration of carbon using the following equation:

$$\text{Carbon, µg/g} = \text{µg C in sample} - \text{µg C in blank/g sample} \quad (3)$$

46. Precision and Accuracy

46.1 *Precision*—For carbon concentrations in the range of 0.5 to 10 µg/g, limited data gave a standard deviation of 0.3 µg/g for replicate determinations from the same bypass sample.

46.2 *Accuracy*—No standards are available for accuracy assessment. The measuring device (gas chromatograph) is calibrated using known amounts of carbon dioxide to eliminate bias in the measurement.

CARBONACEOUS GASES RELEASED BY ACID

47. Scope

47.1 This method is applicable for determining gases, released by acid from a sodium sample obtained by either the Bypass or Overflow Sampling Procedure. This procedure, exclusive of sampling, takes about 4 h.

47.2 In addition to the measurement of carbon dioxide and hydrocarbons, this procedure could be used to determine other gases released from sodium on acidic dissolution. Silane (SiH_4) and phosphine (PH_3) have been measured and hydrogen cyanide might be measured. Heavy metals, including mercury, form acetylides; however, this reaction does not affect the recovery of acetylene in this procedure.

47.3 Hydrocarbons, containing up to three carbon atoms and carbon dioxide, may typically be detected at the 0.05 to 0.2 µg/g level using a 2-g sample.

48. Summary of Method

48.1 Sodium is reacted with acid and the released gases are analyzed by gas chromatography. The reactivity of the sodium is moderated by alloying with mercury so that acid can safely be added directly to the metal.

49. Apparatus

49.1 *Gas-Handling System*—A typical apparatus suitable for preparing known dilutions of gas mixtures is shown in Fig. 19. Alternately, cylinders of diluted gas mixtures of known concentration may be used.

[12] Manco Guillotine M.C. 215 cutter obtained from the Manco Mfg. Co., Bradley, IL, has been found suitable if the jaws are replaced with hardened steel jaws that are ¾-in. (19-mm) flat and round edged (see Fig. 16). If this modified device is used, the tube end should be fitted with a reducing adapter to decrease the diameter of the extruded sodium rod to 0.28 in. (7.1 mm).

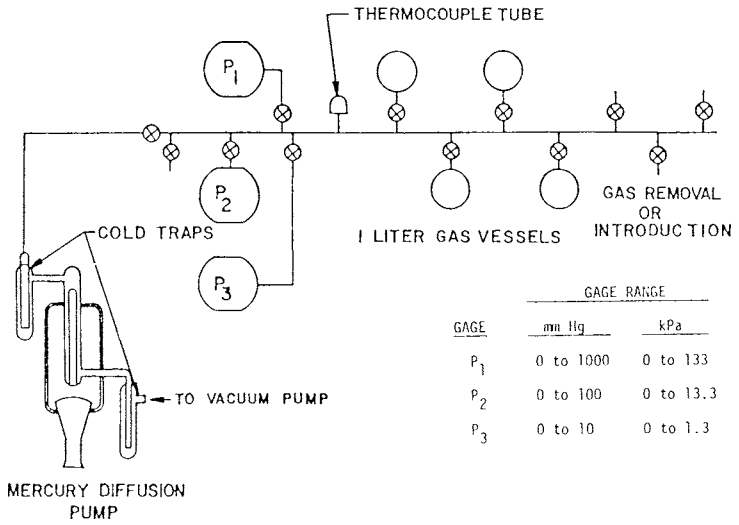

FIG. 19 Typical Gas Handling System

49.2 *Carbon-Species Apparatus*—A typical apparatus is shown in Figs. 20-22. It includes the following:

49.2.1 *Dissolver Cell and Reservoir*, as shown in Fig. 23.

49.2.2 *Condensation Traps*, 10-mm inside-diameter glass U tubes filled with glass beads and cooled with ice and dry ice.

49.2.3 *Sample Trap*, formed as a "U" from 6- by 200-mm thin-walled stainless-steel tubing and packed with 50- to 80-mesh Porapak Q.

49.2.4 *Gas Lines*, 3-mm stainless-steel tubing.

49.2.5 *Gas Chromatograph*—The chromatograph must be capable of detecting 0.3 g of carbon as carbon dioxide or methane.

49.2.6 *Inert-Atmosphere Glovebox*—A glovebox with less than 1 µL/L carbon dioxide and less than 50 µL/L oxygen and water in the atmosphere is required.

50. Reagents and Materials

50.1 *Argon*.

50.2 *Hydrochloric Acid*, 6 *N*.

50.3 *Mercury*.

50.4 *Phosphoric Acid*—Pour 100 mL of concentrated phosphoric acid into 200 mL of stirred water. Add 1 mL of 0.1 % methyl orange. Boil the mixture for 2 min and store in a glass, stoppered bottle.

51. Calibration of Chromatograph

51.1 Connect the chromatograph to the sample trap via the pull valve. Cool the trap with dry ice/methanol.

51.2 Inject 5 to 50 µg of the gases of interest through the septum.

51.3 Proceed with step 52.3.13. Plot curves of peak height versus micrograms of the gases used.

52. Procedure

52.1 *Sample Preparation*—Obtain a 2- to 3-g sample in a stainless-steel cup by the Overflow procedure or a sample in stainless-steel tubing by the Bypass procedure. Cup samples must be protected from air during transfer to the laboratory.

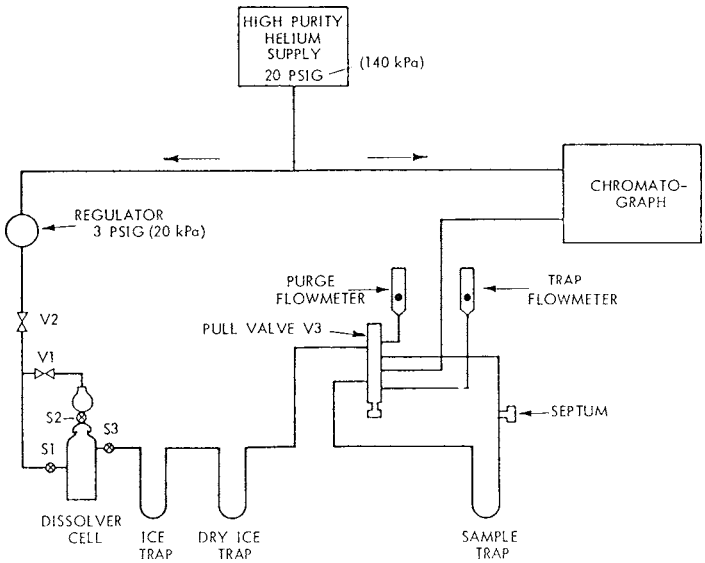

FIG. 20 Typical Carbon Species Apparatus

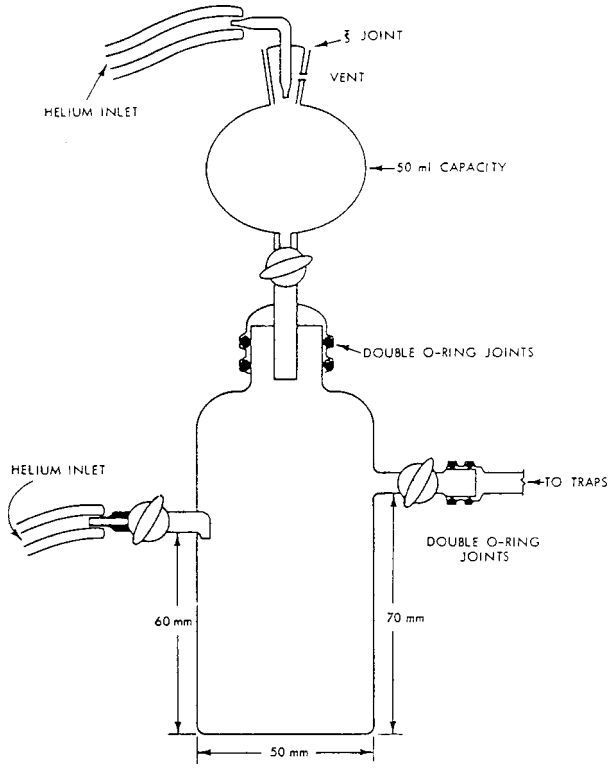

FIG. 21 Typical Dissolver Cell and Reservoir

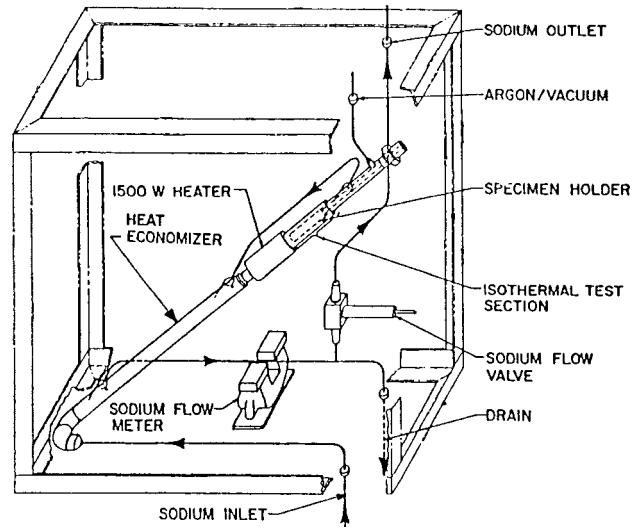

FIG. 22 Schematic of a Typical Specimen Equilibration Module

Bypass samples should be cleaned with acetone, emery paper (if heavily oxidized), 10 % volume hydrochloric acid in methanol, and finally acetone again. Take care to prevent the reagents from reaching the sodium.

52.2 *Dissolver-Cell Preparation*:

52.2.1 Put a Teflon-covered magnetic stirring bar and several drops of 6 *N* hydrochloric acid in the dissolver cell and attach the reservoir. Start purging the dissolver with carbon dioxide-free gas at 50 mL/min.

52.2.2 Direct a heat gun or small flame against the bottom of the dissolver to evaporate the acid. The acid will condense temporarily on the upper walls of the vessel and then be swept out along with any carbon dioxide that had been absorbed on the glass.

52.2.3 Close all stopcocks with the purge still flowing to prevent re-entry of air. One stopcock must be partially re-opened just prior to evacuation of the airlock for transfer to the glovebox.

52.3 *Determination of Carbonaceous Gases*:

52.3.1 In the inert-atmosphere glovebox, open the overflow-cup sampler or cut a section of bypass sample containing 2 to 3 g of sodium. Weigh the cup or tube containing the sodium.

52.3.2 Pour 25 mL of mercury in the dissolver cell and cautiously add the sample. Allow the amalgam to cool for several minutes, then attach the reservoir. With all the stopcocks closed, bring the dissolver out of the glovebox.

52.3.3 Connect stopcock No. 3 to the system and clamp the dissolver cell in place.

52.3.4 Open valve No. 2 and purge the line briefly; then connect the helium supply to stopcock No. 1. Open this stopcock to pressurize the dissolver cell with helium.

52.3.5 With the pull valve positioned to vent the system through the purge flowmeter, open stopcock No. 3 and flush several litres of helium through the system over a period of several minutes.

52.3.6 While flushing the system, fill the reservoir with phosphoric acid. Bubble argon through the acid for 2 min to remove dissolved carbon dioxide. Insert the glass stopper with the vent holes aligned and open valve No. 1 to purge air from the reservoir. Turn the stopper to close the vent and leave the reservoir under pressure.

52.3.7 Switch the pull valve to route the gas through the sample trap and immerse the trap in hot (85 to 95°C) water for 1 min to desorb gases. Replace the hot water with dry ice/methanol.

52.3.8 Chill the amalgam and the lower walls of the dissolver with an ice bath to minimize loss of evaporated water to the traps.

52.3.9 Close stopcock No. 1 and partially open stopcock No. 2 to allow acid to drip on the amalgam. The acid addition should be adjusted to keep the hydrogen evolution at 100 to 150 mL/min. Sufficient acid must be present at all times to maintain a pH of less than 5. The indicator must stay red or orange.

52.3.10 When most of the sodium has reacted, stir the amalgam vigorously with a magnetic stirrer.

52.3.11 When the hydrogen evolution starts to drop, even in the presence of a large excess of acid, close stopcock No. 2 and open stopcock No. 1 enough to purge the reaction gases from the system at 100 mL/min.

52.3.12 After purging for 10 min, switch the pull valve to connect the sample trap to the chromatograph. Stopcock No. 1 may be closed to conserve helium.

52.3.13 Allow 2 min for the system to stabilize, then remove the dry ice/methanol bath from the sample trap andquickly replace it with a hot (85 to 95°C) water bath. Start the recorder and record any peaks that appear in the next 10 min.

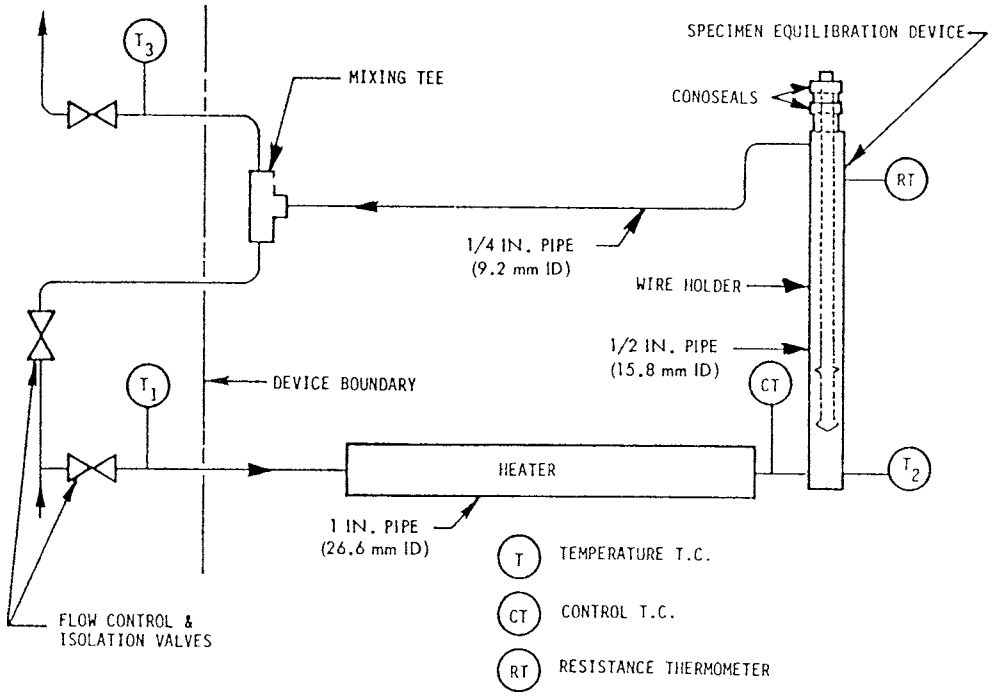

FIG. 23 Schematic of a Typical Specimen Equilibration Device

52.3.14 Open the dissolver cell; clean, dry, and weigh the empty sample tube or cup.

53. Calculation

53.1 Calculate the concentration of carbonaceous gas as follows:

$$\mu g/g \text{ gas released} = A/W \quad (4)$$

where:
A = µg gas measured, and
W = sample weight, g

54. Precision and Accuracy

54.1 Data are not available to provide information about precision and accuracy. The gas chromatograph is calibrated using known amounts of gases of interest to eliminate bias in the measurement.

CYANIDE BY SPECTROPHOTOMETRY

55. Scope

55.1 This method is applicable for determining cyanide in a sodium sample obtained by either the Bypass or Overflow Sampling Procedure. This procedure, exclusive of sampling, requires about 4 h.

55.2 This method is suitable for the determination of 0.06 to 2.4 µg of cyanide (0.03 to 1.2 ppm of cyanide in a 2-g sample of sodium).

56. Summary of Method

56.1 Cyanide in aqueous sodium hydroxide solution is converted to cyanogen chloride by reaction with Chloramine-T. The blue dye formed by reaction of cyanogen chloride with Epstein's reagent is determined spectrophotometrically.

57. Interferences

57.1 Mercury salts interfere by complexing the cyanide, but metallic mercury introduced as sodium amalgam is without effect. Unnecessary exposure of samples to mercury or mercury vapor should be avoided. Iron, chromium, and nickel at the 50-µg/g level have no effect on color development. Complex cyanide anions such as ferricyanide are decomposed by hot sodium, and they are determined as cyanide.

57.2 Proper color development requires similar ionic concentration in samples and standards as well as the absence of methanol. The salt concentration and the anions involved have a marked effect on the formation rate of the colored product and its stability. The importance of preparing both standards and unknown with identical sodium concentrations cannot be overemphasized.

58. Apparatus

58.1 *Absorption Cells*—Matched cells with 10-mm optical path lengths.

58.2 *Balance*, capable of weighing to within 0.01 g is adequate.

58.3 *Inert-Atmosphere Box*—The box must have a purification system capable of controlling the impurity levels of the atmosphere. For this analysis, the moisture and oxygen contents of the atmosphere should be 5 µL/L.

58.4 *Magnetic Stirrer*.

58.5 *Mixing Cylinders*—Stoppered 100-mL graduated cylinders of alkali-resistant plastic.

58.6 *pH Meter*.

58.7 *Safety Shield*, for use during dissolution of sodium.

58.8 *Spectrophotometer*—A Bechman Model B instrument has been found suitable.

59. Reagents and Materials

59.1 *n-Butanol*.

59.2 *Chloramine-T Solution*—Dissolve 0.20 g of chloramine-T in 100 mL of water. Make fresh on the day of use.

59.3 *Concentrated Cyanide Standard*—Dissolve 0.19 g of sodium cyanide in 500 mL of water containing 1.0 g of sodium hydroxide. This solution contains 200 µg of cyanide per millilitre.

59.4 *Dilute Cyanide Standard*—Dilute 1.0 mL of the concentrated cyanide standard to 1000 mL with water. The dilute standard must be made fresh on the day of use.

59.5 *Epstein's Reagent*—Stir 500 mL of water with 1 g of 3-methyl-1-phenyl-2-pyrazolin-5-one (Eastman 1397) for 1 h. Filter through glass wool to remove undissolved crystals. Add to this solution 100 mL of fresh, reagent grade, pyridine containing 0.1 g of 3,3`-dimethyl-1,1`-diphenyl-[4 , 4` - bi - 2 pyrazoline] - 5 , 5` - dione (Eastman 6969). Store in a dark bottle and make fresh on the day of use.

59.6 *Methanol*.

59.7 *Sodium Hydroxide Solution*—Dissolve 170 g of sodium hydroxide in sufficient water to make 1 L of solution. Store in a polyethylene bottle and protect from unnecessary contact with air.

59.8 *Sulfuric Acid, 4 M*—Cautiously pour 220 mL of concentrated sulfuric acid into about 700 mL of water. Add sufficient water to make 1 L.

59.9 *Tartaric Acid Solution*—Dissolve 10 g of tartaric acid in sufficient water to make 100 mL of solution.

59.10 *Water*—Pass tap deionized water through a high-quality commercial mixed-bed ion-exchange column.

60. Precautions

60.1 Cyanide poisoning can occur from ingestion or skin absorption of cyanide salts or from inhalation of hydrogen cyanide gas, which forms when even the weakest acids contact sodium cyanide. Handle solid sodium cyanide with care. Dispose of cyanide residues in compliance with local safety procedures.

60.2 The dissolution of sodium in methanol could result in the ignition of the alcohol and hydrogen. This operation should be carried out behind a shield and on a nonflammable surface.

61. Calibration

61.1 Prepare standard samples by pipeting 10 mL of sodium hydroxide solution into each of four 100-mL beakers. Add 0, 1, 2, and 4 mL of dilute cyanide standard to the beakers and proceed with steps 62.2.2-62.2.5.

61.2 Prepare a calibration curve of absorbance versus total micrograms cyanide added.

62. Procedure

62.1 *Sample Preparation*—Separate treatments for the preparation of two different types of samples, a bypass sample and an overflow sample, are as follows:

62.1.1 *Bypass Sampling*:

62.1.1.1 To obtain a sodium sample in a bypass tube, use the Bypass Sampling Procedure.

62.1.1.2 Rinse the exterior of the tube with deionized water and methanol.

62.1.1.3 Dry the tube and transfer it to the inert-atmosphere box. If no other determinations are to be done on this sample, the transfer is unnecessary.

62.1.1.4 Cut off at least a 1-in. (25-mm) section from the end of the sample tube with a tubing cutter. Discard the end section.

62.1.1.5 Cut off and weigh a section containing approximately 2 g of sodium.

62.1.1.6 Remove the sample from the inert-atmosphere box and dissolve it in approximately 30 mL of anhydrous methanol in a 150-mL stainless-steel beaker.

62.1.1.7 Remove the section of bypass tube while rinsing with water. Add a total of 50 mL of water to the solution and boil off the methanol.

62.1.1.8 Dry the tube section, weigh it, and record the weight.

62.1.1.9 Dilute the aqueous sodium hydroxide solution to 100 mL in a graduated mixing cylinder.

62.1.1.10 Go to 62.2.

62.1.2 *Overflow Sampling*:

62.1.2.1 Obtain a sodium sample weighing about 50 g in an overflow cup by the Overflow Sampling procedure (If the sample size is appreciably larger or smaller than 50 g, adjust all volumes in steps 62.1.2.3-62.1.2.5, accordingly). Tantalum is a suitable cup material.

62.1.2.2 Weigh the cup plus sample and record the weight.

62.1.2.3 Place the cup in a stainless-steel beaker and dissolve the sodium in approximately 450 mL of methanol.

62.1.2.4 Remove the sample cup while rinsing with water. Add a total of 200 mL of water to the solution and boil off the methanol.

62.1.2.5 Dry the cup, weigh it, and record the weight.

62.1.2.6 Transfer the aqueous sodium hydroxide solution to a 250-mL volumetric flask, and dilute it to the mark with water.

62.1.2.7 Transfer an aliquot of the solution, containing approximately 2 g of sodium, to a graduated mixing cylinder and dilute to 100 mL.

62.1.2.8 Go to 62.2.

62.2 *Cyanide Determination*:

62.2.1 From the mixing cylinder, pour an aliquot containing exactly 1.00 g of sodium into a 100-mL beaker. Add a magnetic stirring bar.

62.2.2 Dilute the sample to between 60 and 70 mL. While stirring, add 2 mL of tartaric acid solution.

62.2.3 Insert the electrodes from a pH meter, continue to stir, and add 4 *M* sulfuric acid from a buret until the pH is 5.5 ± 1. Approximately 5 mL of acid will be required.

62.2.4 Transfer the solution to a 100-mL volumetric flask and add 1.0 mL of Chloramine-T solution. Quickly cap, then shake for 1 min.

62.2.5 Add 10 mL of Epstein's Reagent, mix, and dilute to volume. After 1.5 h, transfer the solution to a separatory funnel, add 12 mL of *n*-butanol, and shake for 1 min. Drain off the

aqueous layer and pipet a portion of the butanol into a 10-mm absorption cell. Read the absorbance at 630 nm using water as a reference blank. At room temperature, the color is stable for at least 30 min.

63. Calculation

63.1 From the calibration curve, determine the micrograms of cyanide in the 1-g portion of sample.

63.2 The concentration of cyanide in micrograms per gram is equal to the micrograms of cyanide in the 1-g portion of the sample (63.1).

64. Precision and Accuracy

64.1 *Precision*—For cyanide concentrations between 0.1 and 1.0 g/g, limited data indicate that the range of replicate determinations from the same sample should be no greater than 25 % (relative).

64.2 *Accuracy*—No standards are available for accuracy assessment. The average recovery of cyanide when analyzing standards with sodium is 95 %, and individual recoveries are consistently above 85 %.

OXYGEN BY THE EQUILIBRATION METHOD USING VANADIUM WIRES

65. Scope

65.1 This method is applicable for determining oxygen in sodium using the Wire and Foil Equilibration Sampling Procedure. This procedure requires 3 to 4 h, excluding equilibration time.

65.2 This method is applicable in the range of 10 to 1000 µg of oxygen in vanadium (0.1 to 15 µg/g of oxygen in sodium with the amount of vanadium wire sample usually available). The range can be extended down to 0.003 µg/g of oxygen in sodium if vanadium wire samples of 0.1 g are available.

66. Summary of Method

66.1 A vanadium wire is immersed in flowing sodium at 750°C (1382°F) for a time sufficient to establish equilibrium with respect to oxygen. Subsequent measurement of the oxygen concentration in the wire is related to the concentration of active oxygen in sodium at that temperature by means of the distribution coefficient.

67. Interferences

67.1 Temperature-induced equilibrium shifts involving oxygen and other impurities can theoretically affect the oxygen concentration determined by this procedure if the equilibration occurs at a temperature other than the system temperature. Extensive experience indicates that this is not a problem in measuring the oxygen in a 300–650°C (572–1202°F) system.

68. Apparatus

68.1 *Specimen-Equilibration Device Options*—Fig. 22 is a schematic drawing of the Specimen Equilibration Module for use on reactors and large sodium systems. Fig. 23 is a schematic drawing of a typical specimen-equilibration device for use on small experimental systems. Fig. 24 shows a typical basket-type specimen holder and a second specimen-equilibration device. The basket-type holder may be used with either an equilibration device or an equilibration module. A typical sample holder that may be used with static pots that have access ports and inert-gas locks above the sodium is shown in Fig. 25. A holder of similar design may also be used with modular- or device-type apparatus.

68.2 *Electropolishing Apparatus*—Fig. 26 shows a typical electropolishing apparatus. The electrolysis cell consists of a 250-mL tall-form beaker with a cylindrical cathode (>1000 mm^2) near the bottom. Platinum or tantalum are suitable cathode materials. The lead from this electrode is insulated with shrink-fit TFE-fluorocarbon or polyethylene. The anode contact is made through spring-loaded forceps with platinum tips. The electrolysis cell rests on a magnetic stirrer. Direct current is supplied from batteries or a rectifier capable of providing up to 4 A at 4 to 25 V.[13]

68.3 *Oxygen-Determination Apparatus*, capable of determining 0.1 to 1.5 % oxygen in vanadium metal by an inert gas or vacuum-fusion technique.[14]

68.4 *Magnetic Stirrer*—TFE-fluorocarbon-coated stirring bars.

68.5 *Forceps*—Self-locking type.

[13] A Hewlett-Packard Model 700 with thermal conductivity detectors and a 3-mm by 2-m Porapak Q column has been found satisfactory.

[14] A LECO RO-16 Oxygen Determinator, manufactured by the Laboratory Equipment Co., has been used successfully.

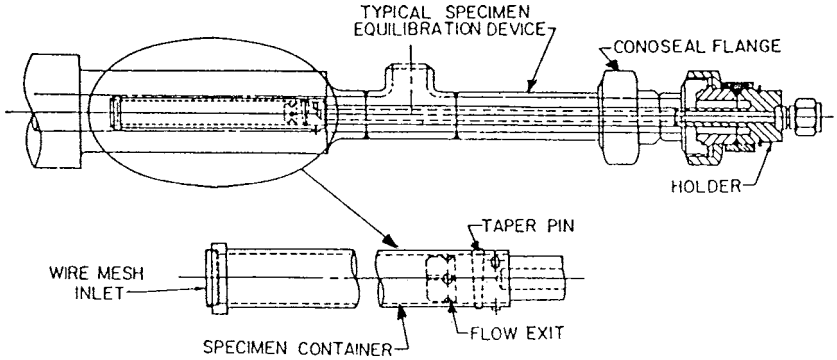

FIG. 24 Typical Basket-Type Sample Holder and Equilibration Device

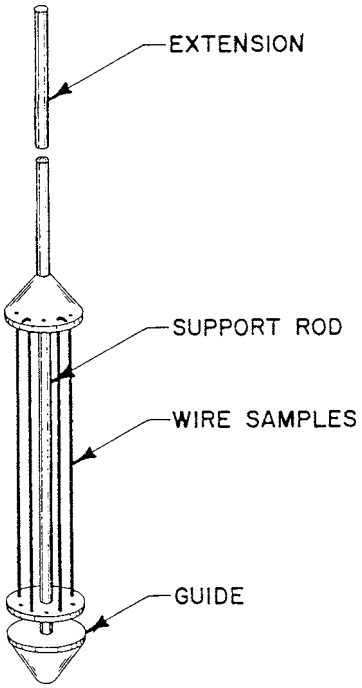

FIG. 25 Typical Sample Holder for Use on Static Sodium Pots with Access Ports and Inert-Gas Locks Above the Sodium Level

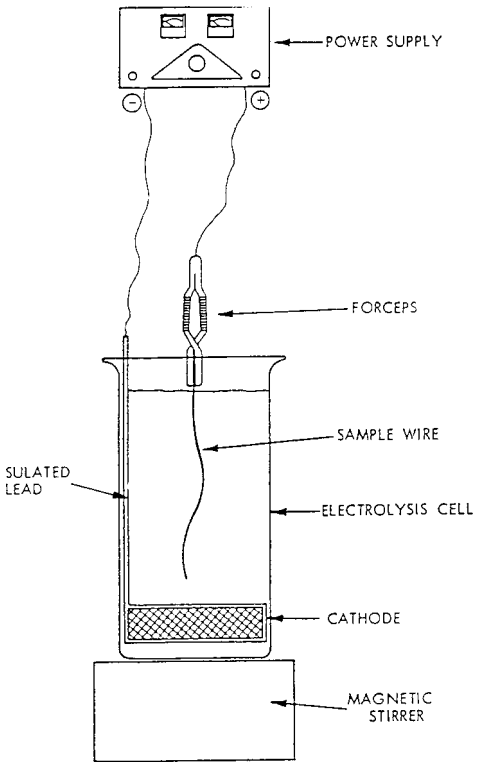

FIG. 26 Typical Electropolishing Apparatus

69. Reagents and Materials

69.1 *Acetone*, technical grade.

69.2 *Electropolishing Solution*—Cautiously add 200 mL of concentrated sulfuric acid to 800 mL of chilled methanol while stirring. Store in a glass bottle. Discard after use.

69.3 *Ethanol*, technical grade.

69.4 *Lintless Tissue*, Cel-Fibe Wipes No. 1745, or equivalent.

69.5 *Nickel Flux*, LECO part 763-065 or equivalent.

69.6 *Oxygen Standards*, approximately 100 and 300 µg/g oxygen in steel.[15]

69.7 *Vanadium Wire High Purity*, annealed, 0.25-mm (0.010-in.) or 0.50-mm (0.020-in.) diameter with a tolerance of 0.005 mm (0.0002 in.). Typical impurity concentrations are: <300 µg/g total metallic impurities (titanium + zirconium + hafnium shall be <20 µg/g), <300 µg/g total of oxygen, nitrogen, hydrogen, and carbon (none of which shall be >150 µg/g).[16] The wire surface shall be smooth and free of scale, showing only fine drawing marks. This surface must also be free of galling and pitting marks. Ductility and surface condition of the wire must be such as to permit bending the wire 180° about its own diameter without surface cracking. The ductility of the wire shall be sufficient to withstand, without fracture, six bends about its own diameter. A general description of the bend test is found in 14 and S22 at A 370A 370.

70. Precautions

70.1 Observe the usual precautions for handling sodium, acids, and flammable liquids. Avoid electrical sparks when electropolishing to prevent ignition of the polishing solution.

71. Calibration of Vacuum-Fusion Analyzer

71.1 Check the instrument in accordance with the instruction manual and the precautions in 70.1. Determine a crucible blank, and standardize the instrument with one high (approximately 300 µg of oxygen) and one low (approximately 100 µg of oxygen) standard.

72. Procedure

72.1 *Wire Preparation and Equilibration*:

72.1.1 Cut the vanadium wire into lengths suitable for the intended sampler, and coil it into helices or straighten as required.

72.1.2 Degrease the wire with acetone. Handle the degreased wire with forceps or clean cotton gloves.

72.1.3 Place the wire in the wire holder. If straight wire is used in a basket-type holder, the wire must be formed into a "U" and inserted with the curve toward the wire-mesh bottom. If a holder like that in Fig. 25 is used, fix the wires in place by bending their ends around the holder. Typically 300 to 500 mm of 0.25-mm diameter wire or 100 to 150 mm of 0.50-mm diameter wire is exposed in an equilibration.

72.1.4 Insert the sample holder into the sodium system.

72.1.5 Choose an equilibration time from Table 2 and find the minimum flow-rate parameter for the estimated concentration of oxygen in the sodium (if no reliable concentration estimate is available, assume 0.01 µg/g). The equilibration time for 0.25-mm diameter wires must be in the range of 4 to 30 h. The equilibration time for 0.50-mm diameter wires must be in the range of 16 to 120 h.

[15] LECO Oxygen Standards, Stock Numbers 501-645 and 501-646 have been found satisfactory.

[16] Vanadium wire of sufficient purity has been obtained from the Materials Research Corp., Orangeburg, NY 10962.

TABLE 2 Flow-Rate Parameter for Vanadium-Wire Equilibration

Oxygen Concentration in Sodium, µg/g	Equilibration Time for 0.25-mm Wire, h				
	4	5	10	20	30
	Equilibration Time for 0.50-mm Wire, h				
	16	20	40	80	120
	Minimum Flow-Rate Parameter, gpm/mm of wire				
10.0	1.5×10^{-5}	1.2×10^{-5}	6.0×10^{-6}	3.0×10^{-6}	2.0×10^{-6}
1.0	7.4×10^{-5}	5.9×10^{-5}	3.0×10^{-5}	1.5×10^{-5}	1.0×10^{-5}
0.1	2.2×10^{-4}	1.8×10^{-4}	9.2×10^{-5}	4.4×10^{-5}	2.9×10^{-5}
0.01	3.3×10^{-4}	2.6×10^{-4}	1.3×10^{-4}	6.6×10^{-5}	4.4×10^{-5}
	Minimum Flow-Rate Parameter, $m^3/(s \cdot mm)$				
10.0	9.5×10^{-10}	7.6×10^{-10}	3.8×10^{-10}	1.9×10^{-10}	1.3×10^{-10}
1.0	4.7×10^{-9}	3.7×10^{-9}	1.9×10^{-9}	9.5×10^{-10}	6.3×10^{-10}
0.1	1.4×10^{-8}	1.1×10^{-8}	5.8×10^{-9}	2.8×10^{-9}	1.8×10^{-9}
0.01	2.1×10^{-8}	1.6×10^{-8}	8.2×10^{-9}	4.2×10^{-9}	2.8×10^{-9}

72.1.6 To find the minimum sodium flow rate, multiply the length of the wire sample (in millimetres) by the minimum flow-rate parameter.

72.1.7 Establish at least the minimum sodium flow rate through the equilibration device and equilibrate the wires at 750 ± 2°C (1382 ± 4°F) for the chosen time.

72.2 *Post-Equilibration Treatment*:

72.2.1 *Procedure for Nonradioactive Systems*:

72.2.1.1 Shut off sodium flow by closing inlet and outlet valves.

72.2.1.2 Pressurize the equilibration device with inert gas, open the drain valve, and drain the sodium from the equilibration device. If drainage at 750°C (1382°F) is prohibited by level safety practices, cool the sodium in the device at a rate of at least 50°C/min (122°F/min) down to 500°C (932°F) before draining the sodium. To cool, for example, turn off the heaters and flow cool sodium over the wires.

72.2.1.3 Shut the drain valve and inert-gas inlet valve.

72.2.1.4 Cool the equilibration device to a convenient temperature, not less than 110°C (230°F).

72.2.1.5 Pull the wire holder from the equilibration device. Insert a holder to close the device.

NOTE 4—If withdrawal of wires at temperatures ≥110°C (≥230°F) is prohibited by local safety practices, omit steps 72.2.1.4 and 72.2.1.5 and substitute steps and .

72.2.1.5.1 Cool the equilibration device to ambient temperature.

72.2.1.5.2 Pull the wire holder from the equilibration device. If the wire holder does not pull free easily, reseal the equilibration device, reheat it to about 150°C (300°F) and repeat steps 72.2.1.2-. Finally, insert a spare holder to close the device.

72.2.1.6 Dissolve the sodium adhering to the holder in about 1000 mL of technical-grade ethanol. The large volume of ethanol prevents excessive heating of the wires.

72.2.1.7 Rinse holder and wires with water and allow the wires to dry.

NOTE 5—For the rest of the procedure, the wires must be handled with forceps.

72.2.1.8 Remove the wires from the holder. Only straight portions of the wire are used for analysis. Make cuts, as necessary, at least 3 mm from each bend.

72.2.1.9 Separate the wires for archival storage from those for immediate analysis.

72.2.1.10 Store the archival wires in a capped vial that is properly identified.

72.2.1.11 Fill the electrolytic cell with electropolishing solution. Grasp the sample wire with the forceps and adjust the anode position so that the forcep tips just contact the liquid and the wire is centered in the cell. The wire may be cut or bent into a "J" if it is too long. With the stirrer at a low speed, start the electrolytic current and adjust the voltage to provide a current of 5 to 10 mA/mm for 0.25-mm wire or 10 to 20 mA/mm for 0.50-mm wire. Polish each end of the wire for 30 s to reduce the diameter 0.03 to 0.05 mm. Rinse the wires in water, then methanol. Handle cleaned wires only with forceps.

72.2.1.12 Determine the oxygen content of the wire by a standard inert gas-fusion or vacuum-fusion technique (for example, by Methods E 146E 146, or if a vacuum-fusion analyzer is used, by the procedure described in 72.3).

72.2.2 *Procedure for Radioactive Systems*:

72.2.2.1 Shut off sodium by closing inlet and outlet valves.

72.2.2.2 Pressurize the equilibration device with inert gas, open the drain valve, and drain the sodium from the equilibration device.

NOTE 6—If drainage at 750°C (1382°F) is prohibited by local safety practices, cool the sodium in the device at a rate of at least 50°C/min (122°F/min) down to 500°C (932°F) before draining the sodium. Cooling may be accomplished, for example, by turning off the heaters and flowing cool sodium over the wires.

72.2.2.3 Shut the drain valve and the inert-gas inlet valve.

72.2.2.4 Cool the equilibration device to a convenient temperature not less than 110°C (230°F).

NOTE 7—If withdrawal of wires at temperatures ≥110°C (230°F) is prohibited by local safety practices, substitute steps , , and for steps 72.2.2.4, 72.2.2.5, and 72.2.2.6 respectively.

72.2.2.4.1 Cool the equilibration device to ambient temperature.

72.2.2.5 Wait until the radiation has decayed to an acceptable level.

72.2.2.5.1 Wait until activity has decayed to a tolerable level.

72.2.2.6 Pull the wire holder from the equilibration device. Insert a holder to close the device. Follow local radiation safety practices during this operation.

72.2.2.6.1 Pull the wire holder from the equilibration device. If the wire holder does not pull free easily, reseal the equilibration device, reheat it to about 150°C (300°F), and

repeat steps 72.2.2.2-. Finally, insert a spare holder to close the device. Follow local radiation safety practices during this operation.

72.2.2.7 Fasten the wire holder into a metal test tube carrier with a matching coupling at its open end.

72.2.2.8 Send the protected wire holder to the laboratory.

72.2.2.9 Dissolve the sodium adhering to the holder in about 1000 mL of technical-grade ethanol (the large volume of ethanol prevents excessive heating of the wires). Perform this operation in a hood or hot cell, following local radiation safety practices. If alcohol is not appropriate for removal of the sodium (in a hot cell, for example) mercury may be used instead of alcohol.

72.2.2.10 Rinse the holder and wires with water and allow the wires to dry.

NOTE 8—For the rest of the procedure, the wires must be handled with forceps.

72.2.2.11 Remove the wires from the holder. Only straight portions of the wire are used for analysis. Make cuts, as necessary, at least 3 mm from each bend.

72.2.2.12 Separate the wires for archival storage from those for immediate analysis.

72.2.2.13 Store the archival samples in a capped glass or metal vial that is properly identified.

72.2.2.14 Fill the electrolytic cell with electropolishing solution. Grasp the sample wire with the forceps, and adjust the anode position so that the forcep tips just contact the liquid and the wire is centered in the cell. The wire may be cut or bent into a "J" if it is too long. With the stirrer at a low speed, start the electrolytic current and adjust the voltage to provide a current of 5 to 10 mA/mm for 0.25-mm wire or 10 to 20 mA/mm for 0.50-mm wire. Polish each end of the wire for 30 s to reduce the diameter 0.03 to 0.05 mm. Rinse the wires in water, then methanol. Handle cleaned wires only with forceps.

72.2.2.15 Determine the oxygen content of the wire by a standard inert gas-fusion or vacuum-fusion technique (for example, by Methods E 146E 146, or if a vacuum-fusion analyzer is used, by the procedure described in 72.3).

72.3 *Determination of Oxygen by Vacuum Fusion Analyzer*:[17]

72.3.1 Cut ¼ in. (6.4 mm) off each end of the wire sample.

72.3.2 Cut the rest of the wire into lengths just under ⅜ in. (9.5 mm) and place them into clean glass vials (about 10 pieces are obtained per wire).

72.3.3 Select and weigh a sample, based upon the estimated oxygen concentration, that will contain 100 to 300 µg of oxygen.

72.3.4 Put a nickel flux spiral into a new graphite crucible and insert the crucible into the lower electrode (without the nickel flux, the wires do not always completely fuse).

72.3.5 Transfer the weighed group of wire sections to the empty sample loader with forceps. Using a flashlight, ascertain that all wires are at the bottom of the loader. Occasionally, a wire will not fall to the bottom and may hang up in the loader.

72.3.6 Slide the sample holder to the left after ascertaining that the furnace assembly is open. The furnace assembly must be open to prevent nitrogen pressure from blowing wires out of the holder.

72.3.7 Close the furnace assembly and proceed according to the instruction manual.

NOTE 9—Successful operation requires that both a purge and a measure pressure be approximately 12 psig (83 kPa) and that they be equal within 0.1 psig (0.7 kPa).

NOTE 10—Effective operation requires the maintenance of a fixed-nitrogen purge rate of 0.8 to 2.0 L/min. To prevent blockage of the purge gas-exit orifice by particulates, the LECO RO-16 instrument is equipped with a paper filter in the line. This filter may become plugged and will require removal and replacement. The LECO instruction manual covers this maintenance step.

72.3.8 Record the readout.

72.3.9 Open the furnace assembly to relieve the nitrogen pressure when the determination is complete. Using a flashlight and a mirror, check up into the sample cavity to ascertain that no wires are hung up. If a wire section has hung up, remove and weigh it, and correct the sample weight.

72.3.10 Analyze a standard that will correspond to the level of the oxygen in the samples after approximately every six determinations.

73. Calculation

73.1 Calculate the oxygen concentration in the vanadium-wire sample as follows:

$$\text{Oxygen in vanadium, weight \%} = (A - B)\ 100/C \quad (5)$$

where:

A = oxygen content of sample, mg,
B = oxygen content of fusion blank, mg, and
C = weight of sample, mg.

73.2 Determine the oxygen concentration in sodium (in micrograms per gram) corresponding to the weight percent oxygen in the equilibrated vanadium wire by reference to Table 3, interpolating linearly between tabulated values if necessary.

73.3 Table 3 was prepared using the following equation, applicable to the equilibrium oxygen distribution between vanadium and sodium at 750°C (1382°F).

$$\ln (N_{O_v} / N_{O_{Na}}) = -28.22 + 39.42\ (1 - N_{O_v})^2 \quad (6)$$

where:

N_{O_v} = atom fraction of oxygen dissolv ed in vanadium, and
N_{O_v} = atom fraction of oxygen dissolved in sodium.

74. Precision and Accuracy

74.1 *Precision*—For the concentration range of 0.5 to 5 µg/g of oxygen in sodium, the relative standard deviation is expected to be within 10 %. For sample results in that concentration range, one laboratory reported relative standard deviations ranging from 1 to 7 % for 10 sets of triplicate determinations made over a period of several months.

74.2 *Accuracy*—No standards are available for accuracy assessment. The oxygen analyzer is calibrated to eliminate bias in the measurement of oxygen contained in the vanadium wire.

[17] A LECO RO-16 Oxygen Determinator has been used successfully.

TABLE 3 Corresponding Equilibrium Oxygen Concentrations, Vanadium Versus Sodium at 750°C (1382°F)

V, Weight % 0	Na, µg/g 0	V, Weight % 0	Na, µg/g 0	V, Weight % 0	Na, µg/g 0
0.01	0.003	0.51	0.537	1.01	3.441
0.02	0.006	0.52	0.560	1.02	3.556
0.03	0.010	0.53	0.585	1.03	3.674
0.04	0.013	0.54	0.610	1.04	3.797
0.05	0.017	0.55	0.637	1.05	3.922
0.06	0.021	0.56	0.664	1.06	4.052
0.07	0.025	0.57	0.692	1.07	4.185
0.08	0.030	0.58	0.721	1.08	4.322
0.09	0.034	0.59	0.751	1.09	4.463
0.10	0.039	0.60	0.782	1.10	4.609
0.11	0.044	0.61	0.815	1.11	4.758
0.12	0.049	0.62	0.848	1.12	4.912
0.13	0.054	0.63	0.882	1.13	5.071
0.14	0.060	0.64	0.918	1.14	5.234
0.15	0.066	0.65	0.954	1.15	5.402
0.16	0.072	0.66	0.992	1.16	5.575
0.17	0.078	0.67	1.032	1.17	5.752
0.18	0.085	0.68	1.072	1.18	5.935
0.19	0.092	0.69	1.114	1.19	6.123
0.20	0.099	0.70	1.157	1.20	6.317
0.21	0.107	0.71	1.201	1.21	6.516
0.22	0.115	0.72	1.247	1.22	6.721
0.23	0.123	0.73	1.295	1.23	6.931
0.24	0.131	0.74	1.344	1.24	7.148
0.25	0.140	0.75	1.395	1.25	7.371
0.26	0.149	0.76	1.447	1.26	7.600
0.27	0.159	0.77	1.501	1.27	7.835
0.28	0.169	0.78	1.556	1.28	8.078
0.29	0.179	0.79	1.614	1.29	8.327
0.30	0.190	0.80	1.673	1.30	8.583
0.31	0.201	0.81	1.734	1.31	8.846
0.32	0.213	0.82	1.797	1.32	9.117
0.33	0.225	0.83	1.862	1.33	9.396
0.34	0.237	0.84	1.929	1.34	9.682
0.35	0.250	0.85	1.998	1.35	9.976
0.36	0.264	0.86	2.069	1.36	10.278
0.37	0.278	0.87	2.142	1.37	10.589
0.38	0.292	0.88	2.218	1.38	10.908
0.39	0.307	0.89	2.296	1.39	11.237
0.40	0.323	0.90	2.377	1.40	11.574
0.41	0.339	0.91	2.459	1.41	11.921
0.42	0.356	0.92	2.545	1.42	12.277
0.43	0.373	0.93	2.633	1.43	12.643
0.44	0.391	0.94	2.724	1.44	13.019
0.45	0.410	0.95	2.817	1.45	13.405
0.46	0.429	0.96	2.914	1.46	13.802
0.47	0.449	0.97	3.013	1.47	14.210
0.48	0.470	0.98	3.115	1.48	14.629
0.49	0.491	0.99	3.221	1.49	15.060
0.50	0.514	1.00	3.329	1.50	15.502

FLUORIDE BY SPECIFIC ION ELECTRODE

75. Scope

75.1 This method is applicable for determining fluoride in a solution obtained from a sodium sample using the Laboratory Distillation Procedure. This procedure takes about 1 h after preparation of the sample solution.

75.2 This method is suitable for the determination of 0.2 to 20 µg of fluoride (0.01 to 1 µg/g in a 25-g sample of sodium). The range can readily be adjusted upward.

75.3 The sample solution prepared by this procedure is also suitable for chloride determination by specific ion electrode. Chloride should be measured first because of the relatively higher risk of contamination.

76. Summary of Method

76.1 Fluoride is separated from sodium by vacuum distillation, and then is determined electrometrically using a fluoride-specific ion electrode.

77. Interferences

77.1 Since ion activity in solutions is temperature dependent, temperature changes during measurement will appear as meter drift. This can be minimized by not allowing the solution containers to rest directly on the warm stirrer.

78. Apparatus

78.1 *pH Meter*, suitable for use with specific ion electrodes, with expanded scale.

78.2 *pH Electrode*.

78.3 *Fluoride-Specific Ion Electrode*.

78.4 *Magnetic Stirrer*—Small plastic-covered stirring bars are required.

78.5 *Plastic Cups*—Size and shape depends upon electrodes used. They should permit the use of 5-mL samples and a stirring bar.

78.6 *Reference Electrode*—Use of a double-junction type calomel electrode is required if prevention of chloride contamination of the sample is desired.

79. Reagents and Materials

79.1 *Fluoride Working Standard*, 0.01 mg F^-/mL. Dilute 10 mL of the sodium fluoride standard to 1 L. Freshly prepare on the day of use.

79.2 *Ionic Strength/pH Buffer*—Dissolve 85 g of sodium nitrate and 57 mL of glacial acetic acid in 500 mL of water. Add 4 g of cyclohexylene dinitrilo tetracetic acid dissolved in 25 mL of 1 *M* sodium hydroxide. Titrate to pH 5.3 ± 0.2 with 5 *M* sodium hydroxide and dilute to 1 L.

79.3 *Sodium Fluoride Standard*, 1 mg F^-/mL. Dissolve 2.210 of sodium fluoride in water and dilute to 1 L. Store in plastic.

79.4 *Water*, distilled, passed through a high-quality commerical mixed-bed ion-exchange column. Store in a polyethylene bottle.

80. Calibration

80.1 Prepare standards by adding 0.10, 0.25, 0.50, and 1.0 µg of fluoride (10, 25, 50, and 100 µL of working standard) to 5 mL portions of buffer.

80.2 Immerse the tips of the specific ion and reference electrodes in each standard in turn, stirring with a magnetic stirrer until the millivolt reading is constant. Record the readings and plot a calibration curve on semilog paper with the fluoride concentration on the log scale in µg/5 mL.

NOTE 11—For instruments designed especially for use with specific ion electrodes, the calibrate and slope controls may be used to adjust the instrument to read directly in concentration units.

81. Procedure

81.1 Obtain a distillation residue by the Laboratory Distillation Procedure. Use a nickel cup.

81.2 Compute the sample weight from information recorded on the distillation residue container (step 30.23).

81.3 Rinse the cup with 3 mL of buffer solutions and two 1-mL portions of buffer solution.

81.4 Combine all washings in a small plastic cup.

81.5 Immerse the tips of the specific ion and reference electrodes into the solution, stirring with a magnetic stirrer until the millivolt reading is constant.

81.6 Record the reading.

82. Calculation

82.1 Obtain the micrograms of fluoride in the sample solution from the calibration curve.

82.2 Calculate the fluoride concentration in the sodium as follows:

$$\text{Fluoride, } \mu g/g = A/W \quad (7)$$

where:

A = µg of fluoride/5 mL, and
W = weight of sample, g.

83. Precision and Accuracy

83.1 *Precision*—For fluoride concentrations between 0.02 and 1.0 µg/g, limited data indicate that the range of replicate determinations from the same sample should be no greater than 25 % (relative).

83.2 *Accuracy*—No standards are available for accuracy assessment. The fluoride electrode is calibrated to eliminate bias in the measurement of fluoride after separation from the sodium sample.

CHLORIDE BY SPECIFIC ION ELECTRODE

84. Scope

84.1 This method is applicable for determining chloride in a solution obtained from a sodium sample using the Laboratory Distillation Procedure. This procedure takes about 1 h after preparation of the sample solution.

84.2 This method is suitable for the determination of 10 to 100 µg of chloride (1 to 10 µg/g of chloride in a 10-g sample of sodium). The range can readily be adjusted upward.

84.3 The sample solution prepared by this procedure is also suitable for fluoride determination by specific ion electrode. Chloride should be measured first because of the relatively higher risk of contamination.

85. Summary of Method

85.1 Chloride is separated from sodium by vacuum distillation, and then is determined electrometrically using a chloride-specific ion electrode.

86. Interferences

86.1 Since ion activity in solutions is temperature dependent, temperature changes during measurement will appear as meter drift. This can be minimized by not allowing the solution containers to rest directly on the warm stirrer.

87. Apparatus

87.1 *pH meter*, shall be an expanded-scale type suitable for use with the specific ion electrode.

87.2 *pH Electrode*.

87.3 *Chloride-Specific Ion Electrode*.

87.4 *Reference Electrode*—Use of a double-junction type calomel electrode is required to prevent chloride contamination.

87.5 *Magnetic Stirrer*—Teflon-covered stirring bars are required.

87.6 *Plastic Cups*—Size and shape depends on the electrodes used. They should permit the use of 5-mL samples and a stirring bar.

88. Reagents and Materials

88.1 *Chloride-Working Standard*, (50 µg Cl^-/mL). Dilute 5 mL of sodium chloride standard to 100 mL with buffer. Freshly prepare on the day of use.

88.2 *Ionic Strength/pH Buffer*—Dissolve 85 g of sodium nitrate and 57 mL of glacial acetic acid in 500 mL of water. Add 4 g of cyclohexylene dinitrilo tetracetic acid dissolved in 25 mL of 1 *M* sodium hydroxide. Tirate to pH 5.3 ± 0.2 with 5 *M* sodium hydroxide and dilute to 1 L.

88.3 *Sodium Chloride Standard*, (1 mg Cl^-/mL). Dissolve 1.649 g of sodium chloride in buffer and dilute to 1 L with buffer.

88.4 *Water*—Pass distilled water through a high-quality commercial-mixed bed ion exchange column. Store in a polyethylene bottle.

89. Calibration

89.1 Prepare standard solutions containing 1, 2, 3, 5, 10, and 20 µg Cl^-/mL by diluting 0.5, 1.0, 1.5, 2.5, 5.0, and 10.0 mL of chloride-working standard to 25 mL with buffer.

89.2 Immerse the tips of the specific ion and reference electrodes in each standard in turn, stirring with a magnetic stirrer until the millivolt reading is constant. Record the readings and plot a calibration curve on semilog paper with the chloride concentration on the log scale in micrograms per millilitre.

NOTE 12—For instruments designed especially for use with specific ion electrodes, the calibrate and slope controls may be used to adjust the instrument to read directly in concentration units.

90. Procedure

90.1 Obtain a distillation residue prepared by the Laboratory Distillation Procedure. Use a nickel cup.

90.2 Compute the sample weight from the information recorded on the distillation residue container (step 30.23).

90.3 Rinse the cup with a total of 5 mL of buffer in two portions.

90.4 Combine the rinses in a small plastic cup.

90.5 Immerse the tips of the specific ion and reference electrodes into the solution, stirring with a magnetic stirrer until the millivolt reading is constant.

90.6 Record the reading.

91. Calculation

91.1 Obtain the concentration of chloride in solution in micrograms per millilitre from the calibration curve.

91.2 Calculate the chloride concentration in the sodium as follows:

$$\text{Chloride, } \mu g/g = A \times B/W \quad (8)$$

where:
A = Cl^- concentration in sample solution, µg/mL,
B = volume of sample solution, mL, and
W = weight of sample, g.

92. Precision and Accuracy

92.1 *Precision*—For chloride concentration of about 5 µg/g, limited data indicate that the range of replicate determinations from the same sample should be no greater than 20 % (relative).

92.2 *Accuracy*—No standards are available for accuracy assessment. The chloride electrode is calibrated to eliminate bias from the measurement of chloride after separation from the sodium sample.

TRACE METALS BY ATOMIC-ABSORPTION OR FLAME-EMISSION SPECTROPHOTOMETRY

93. Scope

93.1 This method is applicable for determining the following trace metals in sodium using atomic-absorption or flame-emission spectrophotometry after sodium distillation: Ag, A 370, Au, Ba, Bi, Ca, Co, Cr, Cu, Fe, In, Li, Mg, Mn, Mo, Ni, Pb, Sc, Sn, Sr, Ti, and V. This procedure requires 6 to 8 h after sampling and distillation.

93.2 Typical working ranges for the various elements are shown in column 4 of Table 4.

94. Summary of Method

94.1 The residue from distillation of sodium is dissolved in aqua regia, diluted, and aliquots of the solution are analyzed by standard techniques of atomic absorption or flame-emission spectrophotometry.

TABLE 4 Calibration Ranges and Lower Limits of Analysis

Element	Measurement Method[A]	Medium	Typical Working Range: Metal Concentration, µg/g	Analytical Limit[B], µg/g
Aluminum	AA	Alcoholic	1.0 to 10	0.6
Barium	FE	Alcoholic	0.25 to 2.5	0.05
Bismuth	AA	Alcoholic	0.25 to 1.0	0.04
Calcium	AA	Alcoholic	0.04 to 0.12	0.02
Cobalt	AA	Alcoholic	0.04 to 0.24	0.02
Chromium	AA	Alcoholic	0.024 to 0.12	0.02
Copper	AA	Alcoholic	0.04 to 0.24	0.02
Gold	AA	Aqueous	0.1 to 2.0	0.05
Indium	AA	Aqueous	0.0 to 1.5	0.02
Iron	AA	Alcoholic	0.08 to 0.32	0.05
Lead	AA	Alcoholic	0.04 to 5.0	0.02
Lithium	FE	Alcoholic	0.005 to 0.05	0.005
Magnesium	AA	Alcoholic	0.01 to 0.1	0.005
Manganese	AA	Alcoholic	0.008 to 0.048	0.005
Molybdenum	AA	Alcoholic	0.12 to 0.5	0.07
Nickel	AA	Alcoholic	0.08 to 0.32	0.05
Scandium	AA	Aqueous	0.2 to 4.0	0.1
Silver	AA	Aqueous	0.04 to 6.0	0.04
Strontium	AA	Alcoholic	0.01 to 0.1	0.01
Tin	AA	Aqueous	0.8 to 30	0.5
Titanium	AA	Aqueous	0.2 to 4.0	0.1
Vanadium	AA	Aqueous	0.2 to 4.0	0.1

[A] AA = atomic absorption, FE = flame emission.
[B] For a 50 g sample of sodium.

95. Apparatus

95.1 *Atomic-Absorption and Flame-Emission Spectrophotometer*—Any commercially available, dual-function, grating instrument, or laboratory-assembled equivalent instrument may be used.

95.2 *Premix Burners*—For nitrous oxide-acetylene, air-acetylene triple-slot Boling head, and air-acetylene single slot.

NOTE 13—Flameless atomizers provide much greater sensitivity for many metals than conventional burners and may be substituted where applicable.

95.3 *Hollow Cathode Lamps*, as needed for the elements determined.

96. Reagents and Materials

96.1 *Acetylene*, 99.6 % minimum purity.

96.2 *Air*, dry, compressed gas in a cylinder, or a suitably filtered lab supply.

96.3 *Aqua Regia*—Freshly prepare by mixing 1 part concentrated nitric acid and 3 parts concentrated hydrochloric acid.

96.4 *Concentrated Hydrochloric Acid*—Prepare approximately 12 *N* acid by saturating ice-cooled redistilled water with electronic-grade hydrochloric acid gas. Store in a polyethylene bottle. Commercial electronic-grade acid may be used if suitably low blanks are obtained.

96.5 *Ethanol-Sodium Chloride Solution*, redistilled ethanol containing 200 µg/mL dissolved sodium chloride. Check the solution to assure absence of trace-metal impurities.

96.6 *Ethyl Alcohol, 95 %*—Distill alcohol in a fused silica or borosilicate glass still and store in a polyethylene bottle.

96.7 *Hydrochloric Acid, 2 N*—Prepare by diluting previously prepared 12 *N* acid with redistilled water. Store in a polyethylene bottle.

96.8 *Hydrochloric Acid-Sodium Chloride Solution*, 2 *N* hydrochloric acid containing 200 µg/mL sodium chloride.

96.9 *Lanthanum Solution*—Dissolve 1.17 g of lanthanum oxide in 10 mL concentrated hydrochloric acid and dilute to 1 L with water.

NOTE 14—The analyst has considerable freedom in choosing the concentrations of the working standard solutions. If it becomes necessary or desirable, change the dilution volume of the sample solution and the concentration of lanthanum added.

96.10 *Nitric Acid*—Distill concentrated nitric acid in a fused-silica still. Store in a Teflon bottle. Commercial electronic-grade acid may be used if suitably low blanks are obtained.

96.11 *Nitrous Oxide*, 98.0 % minimum purity.

96.12 *Sodium Chloride*—Check the specific batch used for impurities of interest or use a high-purity material.

96.13 *Standard Metal Solutions*, 1 mg/mL in 2 *N* hydrochloric acid containing 200 µg/mL sodium chloride. Prepare by dissolving pure metals or compounds of known stoichiometry in a minimum amount of acid and diluting as necessary. The working standard solutions and the blank solution must all be adjusted to contain approximately the same concentration of sodium chloride as the sample. Solutions containing approximately 200 µg/mL sodium chloride normally result when a residue from the procedure in 99 is used. However, should

experience show that the concentration of sodium chloride in the sample solutions differ from 200 µg/mL by ±25 %, adjustments must be made.

96.14 *Water*—Distill ion-exchange water in a fused-silica still. Store in a polyethylene bottle.

97. Precautions

97.1 In addition to the demands of ordinary laboratory technique, the following specific hazards shall be considered.

97.1.1 Acetylene is inherently unstable and its decomposition can be triggered by shock, elevated temperature, contamination, or contact with catalytic surfaces. Do not discharge the gas at pressures higher than 15 psig (100 kPa). Do not distribute it through copper tubing. Consult the Matheson Gas Data Book for further safety recommendations.

97.1.2 Use nitrous oxide with adequate ventilation. Nitrous oxide is an anesthesia in high concentrations. Inhalation of small amounts may produce a type of hysteria.

98. Calibration

98.1 Calibration is done each time that a sample is analyzed by alternately aspirating standards, samples, and blanks (step 99.12). The calibration curves are prepared by following step 99.14.

99. Procedure

99.1 Obtain a distillation residue from approximately 50 g of sodium by the Laboratory Distillation Procedure. Use a tantalum cup.

99.2 Remove the distillation cup from its container. Record the weights marked on the container that was used to transfer the cup from the sample site to the laboratory.

99.3 Add 1.5 mL aqua regia to the cup containing the distillation residue. Tilt and rotate the cup to moisten its inner surface.

99.4 Add 1 mL of lanthanum solution to prevent depression of calcium and magnesium and enhancement of molybdenum responses.

99.5 Dilute the solution in the cup of 5 mL with water. Carefully heat the cup in near-boiling water for 5 min.

NOTE 15—If aqueous solutions are not to be prepared for tin determinations or for determining other elements at higher concentrations, omit steps 99.6-99.8.

99.6 Transfer the sample solution by transfer pipet and syringe to a 25-mL volumetric flask. Rinse the cup with 2 *N* hydrochloric acid and add the washings to the volumetric flask.

99.7 Dilute to volume with 2 *N* hydrochloric acid.

99.8 Pipet 5 mL of solution to be used for the determination of tin (and, possibly, for high concentration impurities) and reserve for step 99.12. If the increased sensitivity obtainable with organic solutions is not necessary (that is, if the concentrations involved are high enough to be determined precisely in aqueous media), omit steps 99.8 and 99.9.

99.9 Evaporate the sample solution to dryness but do not bake it; add 1 mL of concentrated hydrochloric acid to the residue and dilute to 25 mL with ethanol.

99.10 Prepare aqueous or alcoholic sample blank solutions, as needed. To prepare aqueous blanks, add 6 mL of aqua regia and 4 mL of lanthanum solution to a 100-mL volumetric flask and dilute to volume with the hydrochloric acid-sodium chloride solution. To prepare alcoholic blanks, add 6 mL of aqua regia and 4 mL of lanthanum solution to a quartz beaker, evaporate to dryness, dissolve the residue to 4 mL of concentrated hydrochloric acid, and dilute to 100 mL with the ethanol-sodium chloride solution.

99.11 Prepare aqueous or alcoholic single-element standard solutions or mixed-element working standards as needed to define the calibration curves. To prepare aqueous working-standard solutions, add 6 mL of aqua regia, 4 mL of lanthanum solution, and appropriate aliquots of standard solution to separate 100-mL volumetric flasks. Dilute to volume with the hydrochloric acid-sodium chloride solution. To prepare alcoholic working-standard solutions, add 6 mL of aqua regia, 4 mL of lanthanum solution, and appropriate aliquots of standard solution to a quartz beaker, evaporate to dryness, dissolve the residue in 4 mL of concentrated hydrochloric acid and dilute to 100 mL with the ethanol-sodium chloride solution.

99.12 With the spectrophotometer adjusted to the proper settings (see Table 5 and Table 6 for typical settings), alternately aspirate the standard, sample, and blank solutions for 5 to 15 each.

NOTE 16—The sample, standard, and blank solutions should be grouped (alcoholic versus aqueous) and all solutions in a group aspiration consecutively. The order in which the groups are aspirated is unimportant.

99.13 Readjust the spectrophotometer settings for the next metal to be determined, if necessary, and repeat step 99.12.

99.14 Prepare a calibration curve for each element to be determined by plotting µg/25 mL of standard solution versus the instrument reading obtained.

99.15 From the calibration curves, obtain the total amount of each element in each sample solution. After back extraction into an acid medium, zinc and cadmium are determined by atomic-absorption spectrophotometry.

TABLE 5 Typical Parameters for Atomic Absorption

Hollow Cathode Lamp Use	Wave Length, nm	Burner Type	Flame Oxidant[A]
Copper	324.7	Single Slot	Air
Bismuth	223.1	Triple Slot	Air
Calcium	422.7	Triple Slot	Air
Chromium	357.9	Triple Slot	Air
Cobalt	240.7	Triple Slot	Air
Gold	242.8	Triple Slot	Air
Indium	303.9	Triple Slot	Air
Iron	248.3	Triple Slot	Air
Lead	283.3	Triple Slot	Air
Magnesium	285.2	Triple Slot	Air
Manganese	280.0	Triple Slot	Air
Nickel	232.0	Triple Slot	Air
Silver	328.1	Triple Slot	Air
Aluminum	309.3	Nitrous Oxide	N_2O
Molybdenum	313.3	Nitrous Oxide	N_2O
Scandium	391.2	Nitrous Oxide	N_2O
Strontium	460.7	Nitrous Oxide	N_2O
Tin	286.3 or 224.6	Nitrous Oxide	N_2O
Titanium	365.3	Nitrous Oxide	N_2O
Vanadium	318.4	Nitrous Oxide	N_2O

[A] Acetylene is the fuel in all cases.

TABLE 6 Typical Parameters for Flame-Emission Spectrometry

Element	Wave Length, nm	Burner Type	Flame Oxidant[A]
Barium	553.6	Nitrous Oxide	N_2O
Lithium	670.8	Triple Slot	Air

[A]Acetylene is the fuel in both cases.

100. Calculation

100.1 Calculate the concentration of each element in the sample as follows:

$$\text{Concentration of element, } \mu g/g = A \times B/C - D \quad (9)$$

where:

A = weight of element from calibration curve, µg,
B = dilution factor (1.25 for alcoholic solutions when step 99.8 is performed; in all other instances, 1.0),
C = weight of sample plus container, g, and
D = weight of empty container, g.

101. Precision and Accuracy

101.1 *Precision*—For the concentrations given in column 4 of Table 4, limited data indicate that a relative standard deviation of 25 % may be expected. This is expected to approach 5 to 15 % as the upper portion of the working range is approached.

101.2 *Accuracy*—No standards are available for accuracy assessment. The instruments are calibrated to eliminate bias from the measurements of the metals in solutions prepared from the residues after vacuum-distilling sodium.

CADMIUM AND ZINC BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY

102. Scope

102.1 This method is applicable for determining cadmium and zinc in sodium using atomic-absorption spectrophotometry. This procedure, exclusive of sampling, requires about 3 h.

102.2 The detection limit is 0.6 µg of zinc or cadmium (0.06 µg/g zinc or cadmiuim in a 10-g sample of sodium).

103. Summary of Method

103.1 Sodium metal is dissolved in an alcohol-water solution, and zinc and cadmium are separated by extraction into dithizone-chloroform.

104. Interferences

104.1 Zinc seems to be ubiquitous; contamination from glassware, paper, and plastics is commonplace. It is frequently found that vessels must be soaked overnight in 1 *M* hydrochloric acid prior to use.

105. Apparatus

105.1 *Atomic-Absorption Spectrophotometer*—Any commercially available grating instrument or laboratory-assembled equivalent instrument may be used.

105.2 *Quartzware*, used for the dissolving of sodium and for the storing of strongly acidic and alkaline solutions.

105.3 *Hollow Cathode Lamps*—Zinc and cadmium lamps are needed for this procedure.

105.4 *Safety Shield*—For use during dissolution of sodium.

106. Reagents and Materials

106.1 *Acetylene*, 99.6 % minimum purity.

106.2 *Air*—Dry, compressed air in a cylinder, or a suitably filtered laboratory supply.

106.3 *Ammonium Acetate Buffer, 1 M*—Dissolve 15.4 g ammonium acetate in 50 mL of water and adjust the pH to 8 with the ammonium hydroxide prepared above. Add 20 mL chloroform and 5 drops of 0.1 % dithizone in chloroform. Extract for 2 min and discard the extract. Repeat the extraction until the dithizone solution remains green, indicating the removal of all zinc and cadmium contaminants. Wash twice with the 20-mL portions of chloroform. Dilute to 100 mL with water.

106.4 *Ammonium Hydroxide*—Prepare by saturating ice-cooled, deionized water with ammonia gas.

106.5 *Cadmium Standard Solutions*—Dissolve a known weight of $CdCl_2 \cdot 2½\ H_2O$ in 2 *N* hydrochloric acid and by suitable dilution, prepare a series of working standard solutions in the range 0.1 to 1.0 µg of Cd/mL 2 *N* hydrochloric acid.

106.6 *Chloroform.*

106.7 *Concentrated Hydrochloric Acid, 2 N*—Prepare approximately 12 *N* acid by saturating ice-cooled, deionized water with hydrochloric acid gas. Store in a polyethylene bottle.

106.8 *Deionized Water*—Pass distilled water through a high-quality commercial mixed-bed ion exchange column. Store in a polyethylene bottle.

106.9 *Dithizone in Chloroform*—Prepare a 0.1 % solution by dissolving 0.1 g of dithizone in 50 mL of chloroform. Extract the dithizone from the chloroform by using four 50-mL portions of 1 % ammonium hydroxide (concentrated ammonium hydroxide diluted 1 + 99). Combine the ammonium hydroxide extracts and acidify with hydrochloric acid. Extract the dithizone from the acidified solution with 25-mL portions of chloroform and dilute to 100 mL with chloroform.

106.10 *Hydrochloric Acid, 2 N*—Prepare by diluting previously prepared 12 *N* acid. Store in a polyethylene bottle.

106.11 *Methyl Alcohol*, absolute.

106.12 *Zinc Standard Solutions*—Dissolve a known weight of zinc metal in hydrochloric acid and by suitable dilution, prepare a series of working standard solutions in the range 0.1 to 1.0 µg of zinc/mL 2 *N* hydrochloric acid.

107. Precautions

107.1 The dissolution of sodium in methanol could become vigorous enough to ignite the hydrogen and methanol vapors. The dissolution must be carried out in a beaker; a flask or bottle that could permit an explosive atmosphere to build up should never be used. The dissolution beaker should be contained in a metal tray or pan to retain any spilled alcohol. To eliminate the chance of igniting a large amount of methanol, the methanol added during the dissolution process should be poured into the separatory funnel from a second beaker rather than directly from the bottle.

107.2 See 97.1.1 regarding acetylene.

108. Calibration

108.1 Calibration is done each time that a sample is analyzed by aspirating standards, sample, and blank at step 109.17. Calibration curves are prepared by following step 109.18.

109. Procedure

109.1 Obtain a 10 to 12-g sodium sample by the Overflow Sampling Procedure. Borosilicate glass or quartz beakers have been found suitable.

109.2 Weigh the sample plus beaker and place it in a 500-mL quartz beaker.

109.3 Dissolve the sample by dripping methyl alcohol-water mixture (90 mL methyl alcohol + 30 mL water) from a separatory funnel onto the sodium at the rate of one drop per s.

109.4 Cool the beaker in ice and acidify the solution with 35 to 40 mL of 12 *N* hydrochloric acid.

109.5 Remove the sample beaker. Dry and weigh it.

109.6 Heat the solution on a hot plate and boil gently for about 10 min to remove most of the alcohol. Record the exact quantity of acid added so that a proper reagent blank may be prepared.

109.7 Cool, and transfer the solution to a 500-mL separatory funnel. Dilute to about 250 mL with water.

109.8 Add 5 mL 1 *M* ammonium acetate and adjust the pH to 8 with ammonium hydroxide.

109.9 Add 15 mL of chloroform and 5 drops of the 0.1 % dithizone in chloroform.

109.10 Extract for 2 min and drain the extract into a 125-mL separatory funnel.

109.11 Perform three more extractions and combine all of the extracts.

109.12 Wash the solution with 10 mL of chloroform and combine the wash with the extracts.

109.13 Discard the aqueous phase.

109.14 Add 8 mL of 2 *N* hydrochloric acid to the extracts and back extract by shaking for 3 min.

109.15 Reject the chloroform phase and collect the acid phase in a 10-mL volumetric flask. Dilute to volume with 2 *N* hydrochloric acid.

109.16 Prepare a reagent blank solution as follows:

109.16.1 Evaporate the acid and alcohol from a mixture of 90 mL alcohol + 30 mL water plus the volume of 12 *N* hydrochloric acid used to acidify the dissolved sample.

109.16.2 Add 5 mL of 1 *M* ammonium acetate buffer and dilute to 200 mL with water.

109.16.3 Adjust to pH 8 with ammonium hydroxide and follow steps 109.9-109.15.

109.17 Measure the absorption of the 0.1 to 1.0 µg/mL working standard solutions of zinc and cadmium, of the reagent blank, and of the sample.

109.18 Plot calibration curves in terms of micrograms of zinc or cadmium versus absorption.

109.19 Read micrograms of zinc and cadmium from the calibration curves.

110. Calculation

110.1 Calculate the concentration of zinc or cadmium in the sodium sample as follows:

$$\text{Zinc or cadmium, µg/g} = A/(B - C) \times 1/E \quad (10)$$

where:

A = weight of zinc or cadmium, µg,
B = weight of sample plus beaker, g,
C = weight of empty beaker, g, and
E = extraction efficiency (approximately 0.9).

NOTE 17—E may be checked by measuring the fraction recovered of known quantities of zinc and cadmium added to a sodium chloride solution previously purified by dithizone extraction and processed through the procedure.

111. Precision and Accuracy

111.1 *Precision*—For concentrations of cadmium or zinc between 0.1 and 1.0 µg/mL, limited data indicate that the range of replicate measurements made on a sample solution should be no greater than 25 % (relative). No results are available from actual sodium samples.

111.2 *Accuracy*—No standards are available for accuracy assessment. The instrument is calibrated to eliminate bias from the measurements made on sample solutions.

POTASSIUM BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY

112. Scope

112.1 This method is applicable for determining potassium in sodium using atomic-absorption spectrophotometry. This procedure, exclusive of sampling, requires about 2 h.

112.2 This method is suitable for the determination of from 10 to 500 µg/g of potassium in a 1-g sodium sample. The range can be extended by the use of additional standards.

113. Summary of Method

113.1 A sample of sodium is dissolved, acidified, and diluted to volume. Potassium is determined by atomic-absorption spectrophotometry without separation from sodium.

114. Interferences

114.1 If the potassium level is below 5 µg/g, an ultra-pure grade of sodium carbonate is required. Selected batches of sodium carbonate are suitably low in potassium to be used in preparing standards for most sodium samples.

115. Apparatus

115.1 *Atomic-Absorption Spectrophotometer*—Any commercially available grating instrument or laboratory-assembled equivalent instrument may be used.

115.2 *Polypropylene Graduated Vessels*—Graduated cylinders and flasks are used as volumetric ware for samples and working standards.

116. Reagents and Materials

116.1 *Hydrochloric Acid*—Redistill approximately 5 *M* hydrochloric acid from a quartz still and store it in TFE-Fluorocarbon bottles.

116.2 *Methanol*, with less than 0.1 µg/g potassium. Alternatively, redistill methanol from a quartz still and store in plastic bottles.

116.3 *Methyl Orange Indicator*—Dissolve 0.05 g of methyl orange in 100 mL of water.

116.4 *Potassium Standard Solution*—Dissolve 0.1907 g of potassium chloride, dried at 110°C, in 100 mL of water to make a 1 mg/mL standard.

116.5 *Sodium Stock Solution*—Select anhydrous sodium carbonate for low potassium content. Add a few drops of methyl orange indicator to 23 g of sodium carbonate in a large beaker. Add redistilled hydrochloric acid slowly and with vigorous stirring until the indicator remains red and the salt is completely in solution. Dilute to 1000 mL to make a 1 g/100-mL sodium solution.

116.6 *Water*—Pass distilled water through a high-quality mixed-bed ion-exchange column and store it in a polyethylene bottle.

116.7 *Working Standards*—Dilute 0, 50, 100, 250, and 500 µL of potassium standard (0, 50, 100, 250, and 500 µg K) to 100 mL with the sodium stock solution.

117. Precautions

117.1 The dissolution of sodium in methanol could become vigorous enough to ignite the hydrogen and methanol vapor. Therefore, the dissolution should be carried out in an open vessel. A flask or bottle that could permit an explosive atmosphere to build up should never be used. The dissolution vessel should be contained in a metal tray or pan to retain any spilled methanol. To reduce the chance of igniting a large amount of methanol, the methanol added during the dissolution process should be poured from a small beaker rather than directly from a reagent bottle. The reaction should be carried out in a hood.

118. Calibration

118.1 Calibration is done each time that a sample is analyzed by aspirating the sample and standard solutions at step 119.2.5. A calibration curve is prepared by following step 119.2.6.

119. Procedure

119.1 *Sample Preparation*—Separate treatments are described below for two different types of samples: a bypass sample and an overflow sample.

119.1.1 *Bypass Sample*:

119.1.1.1 Obtain a sodium sample in a bypass tube by the Bypass Sampling Procedure.

119.1.1.2 Rinse the exterior of the sample tube with dilute hydrochloric acid, water, then methanol. Allow the tube to dry.

119.1.1.3 Cut off a 1-cm section from the end of the sample tube with a tubing cutter. Discard this section.

119.1.1.4 Cut off and weigh a section containing 1.0± 0.1 g of sodium.

119.1.1.5 Dissolve the sample in 15 mL of methanol contained in a 100-mL TFE-fluorocarbon beaker. Cover the beaker with a plastic watch glass or short-stem funnel to prevent loss of spray.

119.1.1.6 Retrieve the empty tubing section, weigh it, and calculate the actual sodium weight.

119.1.1.7 Proceed to 119.2.

119.1.2 *Overflow Cup Sample*:

119.1.2.1 Obtain a sodium sample weighing approximately 30 g in an overflow cup by the Overflow Sampling procedure. If appreciably larger or smaller samples are obtained, adjust the volumes in Steps 119.1.2.3 and 119.1.2.4 accordingly. Nickel, quartz, and tantalum cups have been found suitable.

119.1.2.2 Weigh the cup plus sample.

119.1.2.3 Place the cup in a 1200-mL stainless-steel beaker and dissolve the sodium in 450 mL of methanol. Cover the beaker with a plastic watch glass or short-stem funnel to prevent loss of spray.

119.1.2.4 Transfer the solution to a 500-mL polypropylene volumetric flask and dilute to volume.

119.1.2.5 Pipet an aliquot of solution containing 1.0± 0.1 g of sodium into a 100-mL TFE-fluorocarbon beaker.

119.2 *Determination of Potassium*:

119.2.1 Add 10 to 20 mL of water and several drops of methyl orange indicator to the beaker containing the sample.

119.2.2 Add sufficient dilute hydrochloric acid to weakly acidify the solution, that is, to turn the indicator from orange to red.

119.2.3 Remove methanol by evaporating the sample at low heat until crystals start to form.

119.2.4 Cool the sample and dilute to 100 mL with water.

119.2.5 Measure the absorbance of the sample solution and the standards at 766.5 nm, preferably with a low wave-length filter in the light path to block the intense sodium light.

119.2.6 Using the readings obtained from the standards, plot a calibration curve of absorbance versus micrograms of potassium. Determine the weight of potassium in the sample or aliquot by referring to this curve.

120. Calculation

120.1 The concentration of potassium in sodium is calculated using the following equation:

$$\text{Potassium, µg/g} = AF/B - C \quad (11)$$

where:

A = weight of potassium in sample or aliquot, µg,
B = weight of sample plus bypass tube or cup, g,
C = weight of empty bypass tube or cup, g, and
F = aliquot factor.

121. Precision and Accuracy

121.1 *Precision*—For concentrations of about 100 µg/g, limited data indicate that the range of replicate determinations should be no greater than 10 % (relative).

121.2 *Accuracy*—No standards are available for accuracy assessment. The instrument is calibrated to eliminate bias from the measurement of potassium in sample solutions.

RUBIDIUM AND CESIUM BY FLAME SPECTROPHOTOMETRY

122. Scope

122.1 This method is applicable for determining rubidium and cesium in sodium using flame spectrophotometry. This procedure, exclusive of sampling, takes about 6 h in addition to the time required to evaporate the methanol.

122.2 The detection limits are 0.2 µg for each element (0.05 µg/g for each element in a 4-g sample of sodium).

123. Summary of Method

123.1 Rubidium and cesium are separated from sodium in aqueous solution by absorption on the inorganic cation exchanger ammonium-12-molybdophosphate (AMP). The AMP is dissolved and rubidium and cesium are determined by scanning flame-emission spectrophotometry with potassium added to repress ionization.

124. Interferences

124.1 As an ion exchanger, AMP has two undesirable properties; it is slightly soluble and it is such a fine material that flow through a thick bed of pure AMP is extremely slow. The combined batch and column technique described here was devised to cope with these problems.

125. Apparatus

125.1 *Scanning Double-Beam Flame Spectrophotometer*, equipped with a 3-slot air-acetylene burner and a strip chart recorder. Alternatively, an atomic-absorption spectrophotometer may be used if wavelength scanning is not available.

125.2 *Ion-Exchange Columns*—Borosilicate-glass columns 10-mm inside diameter by 150-mm long, with the top enlarged to a 100-mL reservoir.

125.3 *Safety Shield*, for use during dissolution of sodium.

126. Reagents and Materials

126.1 *Ammonium Hydroxide, 2 M*—Prepare by saturating ice-cooled deionized water with ammonia gas. Assay the solution and dilute to 2 *M*. Store in a well-capped polyethylene bottle.

126.2 *Ammonium - 12 - Molybdophosphate (AMP)*[18]—Prepare by the direct method of J. Van R. Smit, et al. (**2**)

126.3 *AMP/Cotton*—Dissolve 5 g of AMP in 15 mL of 2 *M* ammonium hydroxide. Add this solution to ten 10 by 40-mm cotton dental rolls or equivalent (about 4 g of absorbent cotton). Squeeze to uniformly distribute the solution, then add 100 mL of 8 *M* nitric acid to reprecipitate the AMP in the cotton. Wash once with water and once with wash solution. The cotton should be squeezed or pressed with each change of liquid to displace the previous liquid.

126.4 *Bromcresol Green Indicator*—Dissolve 40 mg of bromcresol green in 100 mL of ethanol.

126.5 *Hydrochloric Acid*—Redistill 6 *M* acid from a quartz still and store it in a polyethylene bottle.

126.6 *Methanol*—Redistill methanol from a quartz still, and store it in a polyethylene bottle.

126.7 *Nitric Acid*—Redistill concentrated acid from a quartz still. Store in a Teflon bottle.

126.8 *Potassium Chloride Solution*—Dissolve 6.4 g of potassium chloride containing less than 5 µg/g each of rubidium and cesium in sufficient water to make 100 mL of solution.

126.9 *Rubidium-Cesium Dilute Standard, 20 µg/mL*—Dilute 10 mL of the stock standard to 100 mL with wash solution (0.3 *M* hydrochloric acid).

126.10 *Rubidium-Cesium Stock Standard, 200 µg/mL*—Dissolve 71 mg of rubidium chloride and 63 mg of cesium chloride (both dried at 150°F) in 250 mL of wash solution.

126.11 *Wash Solution, 0.3 M hydrochloric acid*—Dilute 50 mL of concentrated hydrochloric acid to 1 L and store in a polyethylene bottle.

126.12 *Water*—Pass deionized water through a high-quality commercial mixed-bed ion exchange column and store in a capped polyethylene container.

127. Precautions

127.1 The dissolution of sodium in methanol could become vigorous enough to ignite the hydrogen and methanol vapors. The dissolution must be carried out in an open vessel, never a flask or bottle that could permit an explosive atmosphere to build up. The vessel should be contained in a metal tray or pan to retain any spilled alcohol. Additional alcohol added during the dissolution process should be poured from a beaker rather than directly from the bottle to eliminate the chance of igniting a large amount of alcohol.

127.2 See 97.1.1 regarding acetylene.

128. Calibration

128.1 Calibration is done each time that a sample is analyzed by aspirating samples and standard solutions at step 129.12. Calibration curves are prepared by following step 129.13.

129. Procedure

129.1 Obtain a bypass sample by the Bypass Sampling Procedure.

129.2 Cut off and discard about 1 in. (25 mm) from the end of the sample.

129.3 Cut off a section containing 3 to 4 g of sodium and weigh it.

129.4 Dissolve the sample in 50 mL of methanol in a polypropylene beaker.

129.5 Add two drops of bromcresol green indicator, then cautiously add 2 mL of 6 *M* hydrochloric acid in excess of that required to turn the indicator from blue to yellow.

129.6 Add sufficient water to dissolve the precipitated sodium chloride and transfer the solution to a glass beaker, leaving the sample tube behind. Wash and dry the sample tube and weigh it. Compute the sample weight.

129.7 Evaporate the methanol by heating until almost dry. Evaporation by heating overnight is often convenient. Dissolve the crystals and dilute to about 75 mL with wash solution (0.3 *M* hydrochloric acid).

129.8 Add 50 to 75 mg of AMP to the cooled solution and stir with a magnetic stirrer for at least 15 min. In the meantime, prepare the ion exchange column by pressing an AMP-loaded cotton roll (or equivalent) into the bottom of the column.

129.9 Pour the sample solution and AMP from the beaker onto the column. Wash the residual solution and AMP onto the column with about 10 mL of the wash solution. Rinse the walls down with two 5-mL portions of wash solution, allowing the column to drain completely before each addition.

129.10 Recover rubidium and cesium by adding 2 *M* ammonium hydroxide to the column in increments of 1 to 2 mL

[18] A similar material is available from Bio-Rad Laboratories.

until 9.7 mL has eluted from the column and has been collected in a 10-mL volumetric flask containing 0.3 mL of potassium chloride solution. All of the AMP should have dissolved.

129.11 Mix the eluted solution and scan the flame spectrum over the range of 777 to 784 nm for rubidium and 849 to 855 nm for cesium. The instrument settings will depend on the particular instrument used.

129.12 Prepare working standards by diluting 0, 0.2, 0.5, and 1.0 mL of rubidium-cesium dilute standard (0, 4, 10, and 20 µg of rubidium and cesium) to 10 mL with elutant solution and 0.3 mL of potassium chloride solution. Run these standards consecutively with the sample.

129.13 Prepare a calibration curve of relative emission intensity versus micrograms of rubidium or cesium from the standards. Read the micrograms of rubidium and cesium in the sample from this calibration curve.

130. Calculation

130.1 The concentration of rubidium or cesium in sodium is calculated as follows:

$$\text{Rubidium or cesium, } \mu g/g = A/W \quad (12)$$

where:
A = rubidium or cesium found in the sample, µg,
W = sample weight, g.

131. Precision and Accuracy

131.1 *Precision*—For concentrations of about 5 µg/g, limited data indicate that the range of duplicate determinations should be no greater than 10 % (relative).

131.2 *Accuracy*—No standards are available for accuracy assessment. The instrument is calibrated to eliminate bias from the measurements made on sample solutions.

SILICON BY SPECTROPHOTOMETRY

132. Scope

132.1 This method is applicable for determining silicon in sodium using spectrophotometry after sodium distillation. This procedure, exclusive of sampling and distillation, takes about 4 h after dissolution of residue from distillation.

132.2 This method is suitable for the determination of 5 to 40 µg of silicon (0.5 to 4 µg/g of silicon in a 10-g sample of sodium). The range can be adjusted by changing the sample size.

133. Summary of Method

133.1 Silica is separated from sodium by vacuum distillation of sodium metal and then is determined colorimetrically by the molybdenum-blue method.

134. Interferences

134.1 Phosphate, arsenate, and titanium interfere with this analysis.

135. Apparatus

135.1 *Distillation Cup*—A tantalum cup of 10-mL capacity (Since titanium interferes in this determination, titanium cups should not be used).

135.2 *Spectrophotometer*, with matched 10-mm cells.

135.3 *pH Meter*.

135.4 *Centrifuge*.

135.5 *Magnetic Stirrer*, with TFE-fluorocarbon-covered stirring bars.

135.6 *TFE-fluorocarbon Beakers*.

135.7 *Polyethylene Test Tube*.

136. Reagents and Materials

136.1 *Ammonium Hydroxide Solution*—Saturate silica-free water, cooled in an ice bath, with ammonia. Store the solution in a polyethylene bottle.

136.2 *Boric-Acid Solution*—Dissolve 40 g of boric acid in 800 mL of lukewarm silica-free water. Cool, dilute to 1 L, and store in a plastic bottle.

136.3 *Deionized Water*, silica-free. Pass distilled water through a high-quality commercial mixed-bed ion exchange column. Store in a polyethylene bottle.

136.4 *Hydrochloric Acid*, concentrated, silica-free.

136.5 *Hydrofluoric Acid*, concentrated, silica-free.

136.6 *Molybdic-Acid Solution, 10 %*—Dissolve 7 g of ammonium molybdate in 35 mL of water in a TFE-fluorocarbon beaker, using a magnetic stirrer and a TFE-fluorocarbon-coated stirring bar. Add 35 mL of dilute hydrochloric acid (120 mL of concentrated acid diluted to 250 mL with water). Pour the acid rapidly. Prepare the solution fresh on each day of use.

136.7 *Nitric Acid*, concentrated, silica-free.

136.8 *Reducing Solution*—Dissolve 27 g of sodium bisulfite, 2 g of sodium hydroxide, and 0.5 g of 1-amino-2-naphthol-4-sulfonic acid in 250 mL of water and store in a plastic bottle. The solution is stable for approximately one month if it is kept in a refrigerator.

136.9 *Silicon Standard Solution*—Prepare a standard silicon solution containing 1.0 mg silicon dioxide/mL (0.47 mg silicon/mL) by diluting a commercially available sodium silicate standard with silica-free water.[19] Store in a polyethylene bottle. The resulting solution is stable indefinitely.

136.10 *Silicon Working Standard*—Dilute 1 mL of the silicon standard solution to 100 mL with silica-free water and store in a polyethylene bottle. The resulting solution, containing 4.7 µg Si/mL, is stable for several months.

136.11 *Sulfuric Acid-Tartaric Acid Solution*—Slowly add 125 mL of concentrated sulfuric acid to 300 mL of silica-free water. Dissolve 8 g tartaric acid and dilute the solution to 500 mL.

137. Calibration

137.1 Prepare standard solutions containing 0 to 40 µg silicon by pipeting working standard solution into 100-mL Teflon beakers and carrying out steps 138.8-138.14.

137.2 Prepare a calibration curve of micrograms silicon versus absorbance.

[19] Acculate ampoules containing sodium silicate standard supplied by Anachemia Chemicals, Inc. have been found suitable.

138. Procedure

138.1 Obtain a distillation residue from approximately 10 g of sodium in a tantalum cup by following the Laboratory Distillation Procedure.

138.2 Record the weights of the sodium filled and empty cups as marked on the transfer vessel.

138.3 Add 2 drops of concentrated nitric acid, 5 drops of concentrated hydrochloric acid, and 3 mL of water to the residue. Warm the cup in a boiling-water bath and stir the solution with a TFE-fluorocarbon stirring rod.

138.4 Transfer the solution to a polyethylene test tube. Wash the cup with 5 mL water. Add 3 drops of hydrofluoric acid and let the solution stand overnight.

138.5 Centrifuge to remove any insoluble residue.

138.6 Prepare an acid blank by using 2 drops of concentrated nitric acid, 5 drops of concentrated hydrochloric acid, 3 drops of hydrofluoric acid, and 5 mL of water.

138.7 Transfer the sample and blank to 100-mL Teflon beakers.

138.8 Add 20 mL of boric-acid solution.

138.9 Add to each, 2 mL of 10 % molybdic acid and immediately adjust the pH to 1.3 using either ammonium hydroxide or hydrochloric acid. Let stand 10 min.

138.10 Add 5 mL of sulfuric-tartaric acid solution and mix by swirling.

138.11 Immediately add 1 mL of reducing solution and mix by swirling.

138.12 Transfer the solutions from the TFE-fluorocarbon beakers to a 50-mL volumetric flask and dilute to the mark with water.

138.13 Let the solutions stand for 20 to 30 min for color development.

138.14 Measure the absorbance of the solutions in 10-mm cells at 800 nm against water as a blank.

139. Calculation

139.1 Read the micrograms of silicon in the sample and blank from the calibration curve.

139.2 Calculate the concentration of silicon in sodium as follows:

$$\text{Silicon, } \mu g/g = A - B/W \times 100/R \quad (13)$$

where:

A = silicon in sample, µg,
B = silicon in blank, µg,
W = weight of sample, g, and
R = percent recovery.

NOTE 18—Recovery of silicon (added as sodium silicate) from sodium by the vacuum-distillation technique is close to 100 %. Assume R to be 100 or determine it by carrying a spiked sample through the analysis.

140. Precision and Accuracy

140.1 *Precision*—For concentrations from 1 to 4 µg/g, limited data indicate that the range of replicate determinations should be no greater than 25 % (relative).

140.2 *Accuracy*—No standards are available for accuracy assessment. Recovery of silicon (added as sodium silicate) from sodium is expected to be 100 %.

BORON BY SPECTROPHOTOMETRY

141. Scope

141.1 This method is applicable for determining boron in sodium using spectrophotometry after sodium distillation. This procedure, exclusive of sampling and distillation, requires about 2 h.

141.2 This method is suitable for the determination of 0.25 to 3.5 µg of boron (0.025 to 0.35 µg/g of boron in a 10-g sample of sodium). The range can be adjusted by changing the sample size.

142. Summary of Method

142.1 Trace boron is separated from sodium by vacuum distillation of the sodium sample and then is determined by a colorimetric method using curcumin as a reagent.

143. Interferences

143.1 Fluoride, nitrate, and titanium ions interfere by complex formation.

144. Apparatus

144.1 *Tantalum or Nickel Cup*, used for collecting approximately 10 g of sodium (Since titanium interferes in this determination, titanium cups should not be used).

144.2 *Spectrophotometer*, with matched 10-mm cells.

144.3 *Platinum Dishes*—Nickel crucibles may be substituted.

144.4 *Polyethylene Stirring Rods*.

144.5 *Centrifuge*.

144.6 *Polycarbonate Centrifuge Tubes*.

NOTE 19—The use of borosilicate glassware should be avoided throughout the procedure.

145. Reagents and Materials

145.1 *Boron Standard Solution, 1 mg boron/mL*—Dissolve 5.715 g orthoboric acid in 500 mL of water and dilute to 1 L. Store in a polyethylene bottle.

145.2 *Boron Working Standard Solution, 10 µg boron/mL*—Dilute 10 mL of the boron standard solution to 1 L with water. Keep in a polyethylene bottle and freshly prepare on the day of use.

145.3 *Curcumin-Acetic Acid*—Dissolve 0.125 g of curcumin in 100 mL of glacial acetic acid. This reagent, stored in polyethylene bottles, is stable for several months if kept in the dark.

145.4 *Deionized Water*—Pass distilled water through a high-quality commercial mixed-bed ion exchange column. Store in a polyethylene bottle.

145.5 *Ethyl Alcohol, 95 %*—If commercial alcohol leads to high blanks, distill it in a fused silica still and store it in a polyethylene bottle.

145.6 *Sodium Hydroxide Solution, 10 %*—Dissolve 10 g of sodium hydroxide pellets in 100 mL of water in a polyethylene beaker. Store in a polyethylene bottle.

145.7 *Sulfuric-Acetic Acid Reagent*—Cautiously add 50 mL of concentrated sulfuric acid to 50 mL of glacial acetic acid stirring constantly.

146. Calibration

146.1 Pipet 0, 1, 2, and 3.5 µg of boron into platinum dishes and follow the procedure in steps 147.3-147.11, excluding the blank at step 147.11.

146.2 Plot the absorbance versus micrograms of boron to obtain the calibration curve.

147. Procedure

147.1 Obtain a distillation residue from approximately 10 g of sodium in a tantalum or nickel cup using the Laboratory Distillation Procedure.

147.2 Compute the sample weight from the information recorded on the transfer vessel holding the cup and residue (step 30.23).

147.3 Add 0.5 mL of 10 % sodium hydroxide to the distillation residue in the sample cup and stir with a polyethylene rod.

147.4 Evaporate the solution in the sample cup gently to dryness.

147.5 Add 1.5 mL of curcumin-acetic acid reagent and warm the sample cup gently to dissolve the residue.

147.6 Cool the sample cup to room temperature and add 1.5 mL of sulfuric acid-acetic acid reagent.

147.7 Stir well with a polyethylene rod and allow to stand for 15 min.

147.8 Dilute the mixture by stirring in about 15 mL of ethyl alcohol, and transfer the resulting slurry to a dry 50-mL volumetric flask.

147.9 Rinse the sample cup with ethyl alcohol and add the rinses to the volumetric flask.

147.10 Adjust the volume to 50 mL with ethyl alcohol. The insoluble salts, although apparently voluminous, represent less than 1 % of the volume of the solution.

147.11 Mix the solution and centrifuge a portion of it in a polycarbonate tube. Measure the absorbance in a 10-mm cell at 555 nm on a spectrophotometer. A reagent blank is prepared similarly using a platinum dish rather than a sample cup.

148. Calculation

148.1 Determine the micrograms of boron in the sample and in the blank using the calibration curve.

148.2 Calculate the boron concentration in sodium as follows:

$$\text{Boron, µg/g} = A - B/W \times 100/R \quad (14)$$

where:

A = boron in sample, µg,
B = boron in the blank, µg,
W = weight of the sample, g, and
R = percent recovery of boron.

NOTE 20—Recovery of boron, added as boric acid or sodium borate to sodium metal, is 90 to 95 %. Assume R to be 95, or determine it by carrying spiked samples through the distillation and analysis.

149. Precision and Accuracy

149.1 *Precision*—For concentrations from 0.1 to 0.35 µg/g, limited data indicate that the range of replicate determinations should be no greater than 25 % (relative).

149.2 *Accuracy*—No standards are available for accuracy assessment. Recovery of boron (added as boric acid or sodium borate) from sodium is expected to be between 90 to 95 %.

URANIUM BY FLUORIMETRY

150. Scope

150.1 This method is applicable for determining uranium in sodium using fluorimetry after sodium distillation. This procedure, exclusive of sampling and distillation, requires about 1 h.

150.2 The detection limit is 0.1 µg of uranium (0.002 µg/g uranium in a 50-g sample of sodium).

151. Summary of Method

151.1 The residue from a vacuum distillation is dissolved in nitric acid and transferred to an acid-deficient aluminum nitrate salting solution; uranium is extracted into hexone to separate it for fluorometric analysis. An aliquot of the hexone extract is transferred to a platinum cup, evaporated to dryness, and the residue fused with sodium fluoride/2 % lithium fluoride. The uranium content of the fused fluoride bead is measured fluorometrically.

152. Apparatus

152.1 *Fluorophotometer*, must be equipped with a light source for inducing fluorescence of uranium and must be capable of measuring the fluorescence of 0.01 µg of uranium.

152.2 *Platinum Dishes*, usually matched with the particular fluorophotometer in use. In general, they should have a diameter consistent with the geometry of the instrument holder and a central depression deep enough to hold approximately 0.4 g of fused flux.

152.3 *Platinum-Iridium Loop*—The loop must have a diameter consistent with the diameter of the platinum dishes

152.4 *Meker Burner*.

152.5 *Laboratory Centrifuge*.

152.6 *Centrifuge Cones*, 15-mL capped type.

152.7 *Pellet Press*—A device to prepare 0.4-g pellets of flux.

153. Reagents and Materials

153.1 *Flux*, 98 % sodium fluoride/2 % lithium fluoride (powder).

153.2 *Hexone* (methyl isobutyl ketone).

153.3 *Nitric Acid*, concentrated.

153.4 *Nitric Acid, 2 N*—Add 130 mL of concentrated nitric acid to 500 mL of distilled water and dilute to 1 L.

153.5 *Salting Solution*, 1.9 *M* aluminum nitrate, acid deficient, and 0.019 *M* tetrapropyl ammonium nitrate. Dissolve 725 g of $Al(NO_3)_3 \cdot 9H_2O$ in a minimum amount of water with the aid of heat. Slowly add 95 mL concentrated ammonium hydroxide and 39 mL of a 10 % solution of tetrapropyl ammonium hydroxide. Stir until solution is complete, maintaining the temperature below 50°C to prevent decomposition of the tetrapropyl ammonium nitrate. Dilute to 1 L with deionized water.

153.6 *Uranium Standard Solution*, 0.5 µg uranium/mL in 2 *N* nitric acid.

NOTE 21—All reagents and glassware must be free of uranium.

154. Calibration

154.1 Calibration is done each time that samples are analyzed by preparing standards that are carried through the procedure with the samples. A calibration curve is prepared by following step 155.16.

155. Procedure

155.1 Obtain a distillation residue from approximately 50 g of sodium by using the Laboratory Distillation Procedure. Use a tantalum cup. Remove the distillation cup from its container. Record the weights marked on the container.

155.2 Add 1.5 mL of concentrated nitric acid to the distillation residue. Tilt and rotate the cup to moisten the inner surface.

155.3 Add about 3.5 mL of water to the cup.

155.4 Carefully heat the cup in near boiling water for 5 min.

155.5 Transfer the sample solution to a 30-mL beaker. Rinse the cup into the beaker with 5 mL of 2 *N* nitric acid.

155.6 Evaporate the solution to approximately 0.5 mL, cool, and add 5 mL of the aluminum nitrate salting solution.

155.7 Transfer the solution from the beaker to a 15-mL capped centrifuge cone. Rinse the beaker with an additional 5 mL of salting solution and transfer the washings to the centrifuge cone.

155.8 Accurately pipet 2 mL of hexone into the centrifuge cone and extract the uranium by thoroughly mixing for 3 min.

155.9 Centrifuge for 2 min to separate the phases.

155.10 Pipet 500-µL aliquots of the hexone extract into three of the platinum dishes and evaporate to dryness under a heat lamp.

155.11 Pipet a 200-µL aliquot of the uranium standard into one of the sample dishes to serve as a check for possible fluorescence quenching.

NOTE 22—The fluorescence of the spiked sample aliquot should equal the fluorescence of 200 µL of uranium standard plus the fluorescence of the unspiked sample. If the fluorescence is less than this value, quenching is indicated and the sample should be reanalyzed.

155.12 Prepare additional standards by pipeting 50, 100, and 200 µL of uranium standard solution into clean platinum dishes as required. Evaporate solutions to dryness under the heat lamp.

155.13 Add a pellet (approximately 0.4 g) of sodium fluoride per 2 % lithium fluoride flux to each of the platinum dishes, including a dish for the blank.

155.14 Hold the platinum dish with the wire loop just above the reducing portion of the flame to fuse the flux in each dish over a Meker burner. After the flux is entirely liquefied, remove the dish from the flame and allow the melt to solidify. Then, return the melt to the flame and, after the liquid phase is again obtained, remove the dish and let it cool for approximately 30 min.

NOTE 23—Fuse and cool all fluxes in the same set under the same conditions, since the fluorescence is affected by fusion temperature, cooling rate, etc.

155.15 Measure the fluorescence of the fused samples, standards, and blank.

155.16 Prepare a calibration curve of (fluorescence of standard–fluorescence of blank) versus micrograms of uranium.

155.17 For each aliquot of sample, determine (fluorescence of sample aliquot–fluorescence of blank) and read the uranium content of the aliquot from the calibration curve.

156. Calculation

156.1 Calculate the uranium concentration in sodium as follows:

$$\text{Uranium, } \mu g/g = 4A/W \quad (15)$$

where:

A = weight of uranium in sample aliquot, µg, and
W = weight of sodium sample, g.

157. Precision and Accuracy

157.1 *Precision*—No information is available to determine precision.

157.2 *Accuracy*—No standards are available for accuracy assessment. The instrument is calibrated to eliminate bias from the measurement of uranium in sample solutions.

OXYGEN BY OXYGEN METER

158. Scope

158.1 This method applies to an oxygen meter that is installed directly in a sodium system such as a sodium loop. Calibration requires 6 to 8 h, whereas only a few minutes are required for the measurement of oxygen.

158.2 Theoretically, there is no sensitivity limit to the oxygen meter (electrochemical cell) in that each factor of 10 change in oxygen activity should produce a voltage change of 0.075 V. In actual practice, the meter has been used to measure active oxygen as low as 0.01 µg/g.

159. Summary of Method

159.1 A solid electrolyte-electrochemical cell that consists of a yttria-doped thoria ceramic tube containing a gaseous reference electrode is immersed in a liquid sodium stream. The resultant cell voltage is used as a continuous, on-line measure of the oxygen activity in the sodium.

160. Apparatus

160.1 A schematic representation of a typical oxygen meter is shown in Fig. 27.[20] Temperature control of the electrolyte tube shall be ±1°C at 400°C.

161. Precautions

161.1 The insertion and withdrawal of vanadium wires requires opening the sodium system. It is imperative that the equilibration chamber be isolated from the rest of the system during this operation. Furthermore, removal of the excess sodium from the wire and its holder could lead to small sodium or solvent fires. Be prepared to handle such fires.

[20] Oxygen meters are commercially available from Westinghouse Nuclear Instrumentation Dept., Baltimore, MD and General Electric Energy Systems & Technology Dept., Sunnyvale, CA.

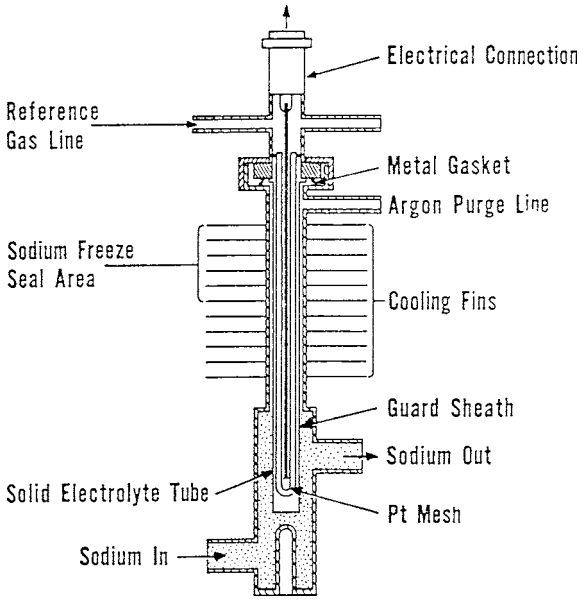

FIG. 27 Oxygen Meter Schematic

161.2 Once the meter has been demonstrated to be leak tight, the only precaution that must be taken is to assure that the cooling fins are maintained at a temperature well below (>10°C) 100°C. To prevent damage to the ceramic electrolyte, the temperature of the sodium in contact with the electrolyte should be changed gradually.

162. Calibration

162.1 With the sodium system under steady-state conditions (that is, constant sodium, cold trap, and meter temperatures), prepare and equilibrate a set of vanadium wires in accordance with the procedure given in 72.1.

162.2 Record the meter readings, either continuously or every half hour, during the wire equilibration.

162.3 Withdraw the vanadium wires from the system and determine their oxygen content in accordance with the procedure given in 72.2.

162.4 Determine the oxygen concentration in the sodium in accordance with the procedure given in 72.2.1.12.

162.5 Readjust the cold-trap temperature, if practical, to produce a factor of two change in oxygen concentration and repeat steps 162.1-162.4 at least once more.

162.6 Construct a calibration curve by plotting the log of the oxygen concentration as established by the wires against the average meter voltage obtained during the equilibration. Alternatively, the above data may be used to establish the following calibration equation:

$$E = K_1 - K_2 \log A \qquad (16)$$

where:

E = meter reading,
K_1 and K_2 = experimentally determined constants for the meter, and
A = concentration of oxygen in sodium, µg/g.

163. Procedure

163.1 Establish that the meter temperature is within ± 10°C of the temperature used to calibrate the meter.

NOTE 24—The stipulation that all meter readings must be made within ±10°C of the calibration temperature is based on the following assumptions:

(1) The temperature coefficient of the meter is ±0.5 mV/°C,

(2) The desired precision of the measurement of the oxygen concentration is 10 %, and

(3) Corrections of the meter readout for temperature is not permitted.

Should operation of a particular meter on a system call for more stringent or less stringent conditions than given above, the stipulation in the procedure for measurement should be altered accordingly.

163.2 Record the meter reading.

163.3 Establish the concentration of oxygen in the sodium by referring to the calibration curve or to the calibration equation.

164. Precision and Accuracy

164.1 Data are not available to provide information about precision and accuracy.

CARBON BY EQUILIBRATION METHOD

165. Scope

165.1 This method is applicable for determining carbon in sodium by an equilibration method using iron-manganese tabs. This procedure, exclusive of equilibration, requires about 4 h.

165.2 This method is applicable for active carbon concentrations in sodium in the range 0.05 to 10 µg/g.

166. Summary of Method

166.1 A metal tab of Fe-12Mn is immersed in flowing sodium at 750°C (1382°F) until equilibrium with respect to carbon is reached. Subsequently, the carbon concentration in the tab is measured and the concentration of active carbon is calculated.

167. Apparatus

167.1 *Equilibration Module*—Fig. 22 is a schematic drawing of the specimen-equilibration module for use on reactors and large sodium systems. Fig. 23 is a schematic drawing of a typical specimen-equilibration device for use on small experimental systems.

167.2 *Carbon-Determination Apparatus*, capable of determining 10 to 200 µg of carbon in 500 mg of ferrous alloy by the combustion technique.[21]

167.3 *Forceps*—Dissecting forceps.

168. Reagents and Materials

168.1 *Accelerator*—Tin metal.[22]

168.2 *Acetone*.

168.3 *Carbon Standard*—National Bureau of Standards Type 335 Steel (0.1 % carbon) has been found suitable.

168.4 *Ethanol*, technical grade and absolute reagent grade.

[21] The LECO WR-12 Carbon Determinator or the LECO ELC-12, manufactured by the Laboratory Equipment Co., have been found suitable. The ELC-12 provides better sensitivity for lo w-carbon values.

[22] LECO tin, Catalog No. 25705, has been found satisfactory for this use.

168.5 *Standard Fe-12Mn Tabs*, annealed, 5-mil thick by 1-in. wide by 1-in. long (0.13 by 25 by 25-mm).[23]

169. Calibration

169.1 Analyze four or five samples of NBS Type 335 steel. For each determination, use approximately 0.7 g of tin accelerator. Use the manufacturer's recommended procedure for the carbon analyzer used.

169.2 Prepare a calibration curve of instrument meter units versus micrograms of carbon.

170. Procedure

170.1 *Tab Preparation*:

170.1.1 Prepare tabs by cutting the standard Fe-12Mn strip stock into 1-in. (25-mm) long lengths.

170.1.2 Scribe or punch identifying numbers on each tab.

170.1.3 Hold a tab with clean dissecting forceps and carefully degrease it with acetone washes. After degreasing, the tab must be handled with degreased tools.

170.1.4 Degrease the sample holder by washing it with acetone.

170.1.5 Mount the tabs in the sample holder.

170.2 *Equilibration*:

170.2.1 Insert the sample holder into the sodium system.

170.2.2 After establishing sodium flow [minimum, 0.2 gpm (1.3×10^{-5} m^3/s)] through the equilibration device, equilibrate the tabs at 750 ± 2°C (1382 ± 4°F) for at least one day and for no more than seven days.

170.3 *Post-Exposure Treatment*:

170.3.1 Shut off sodium flow by closing inlet and outlet valves.

170.3.2 Pressurize the equilibration device with inert gas, open the drain valve, and drain sodium from the equilibration device. If drainage at 750°C (1382°F) is prohibited by local safety practices, cool the sodium in the device at a rate of 50°C (90°F)/min down to 500°C (932°F) before draining the sodium.

170.3.3 Cool the tabs by cooling the loop section containing the holder. Allow no more than an over-night cooling while maintaining a positive inert-gas pressure during this period.

170.3.4 Remove the sample holder from the equilibration module or device.

170.3.5 Dissolve the sodium adhering to the holder in approximately 1000 mL of technical-grade ethanol (The large volume of alcohol prevents excessive heating).

170.3.6 Rinse the holder and tabs with distilled water and then with reagent-grade absolute ethyl alcohol; allow the tabs and tab holder to dry.

170.3.7 Remove the tabs from the holder and place them in a clean, dry glass vial.

170.4 *Carbon Determination*:

170.4.1 Analyze approximately 0.5-g samples from a tab by following the manufacturer's recommended procedure for the carbon analyzer used.

NOTE 25—This procedure consists of burning the sample in oxygen, trapping the carbon dioxide formed on a cold molecular sieve column, flushing the sieve while hot with oxygen or helium, and measuring the carbon dioxide with a thermal conductivity detector.

170.4.2 From the calibration curve determine the micrograms of carbon in each sample.

171. Calculation

171.1 Calculate the micrograms per gram of carbon in the Fe-12Mn tab as follows:

$$A = B/C \tag{17}$$

where:

A = carbon in tab, µg/g,
B = carbon in sample, µg, and
C = weight of sample, g.

171.2 Using A from the above equation, calculate the active carbon concentration in the sodium as follows:

$$\text{Carbon, µg/g} = 0.0042A \tag{18}$$

NOTE 26—The factor (0.0042) assumes a saturated solubility of 75 µg/g at 750°C (1382°F).

172. Precision and Accuracy

172.1 *Precision*—For concentrations from 0.1 to 0.7 µg/g of carbon in sodium, one laboratory reported relative standard deviations ranging from 5 to 20 % for 12 sets of replicate determinations made over a period of several months. One other set had a relative standard deviation of 40 % and another set showed no variation between results.

172.2 *Accuracy*—No standards are available for accuracy assessment. The carbon analyzer is calibrated using NBS carbon standards in steel to eliminate bias in the measurement of carbon contained in the metal tabs.

HYDROGEN BY EQUILIBRATION METHOD

173. Scope

173.1 This method is applicable for determining hydrogen in sodium by equilibration using scandium tabs. This method, exclusive of equilibration, requires about 6 h.

173.2 This method is applicable for active hydrogen concentrations in sodium in the range 0.06 to 0.5 µg/g.

174. Summary of Method

174.1 A scandium tab is immersed in flowing sodium at 750°C (1382°F) until equilibrium with respect to hydrogen is reached. Subsequently, the hydrogen concentration in the tab is measured and the concentration of active hydrogen is calculated.

175. Apparatus

175.1 *Equilibration Module*—Fig. 22 is a schematic drawing of the specimen equilibration module for use on reactors and large sodium systems. Fig. 23 is a schematic drawing of a typical-specimen equilibration device for use on small experimental systems.

175.2 *Hydrogen-Determination Apparatus*, capable of determining 10 to 200 µg of hydrogen in 20 to 100 mg of

[23] Suitable 5-mil thick by 1-in. wide (0.13 × 25-mm) strip stock has been supplied by the Materials Research Corp.

scandium by vacuum or inert-gas fusion or by the hot-extraction technique.[24]

175.3 *Forceps*—Dissecting forceps.

176. Reagents and Materials

176.1 *Accelerator*, iron metal.[25]

176.2 *Ethanol*, absolute.

176.3 *Hydrogen Standard*. [26]

176.4 *Standard Scandium Tabs*, 10-mil thick by ⅛-in. wide by ¾-in. long (0.25 by 3.2 by 19-mm), prepared from 99.9 % scandium sheet.[27]

177. Calibration

177.1 Analyze one or two samples of the hydrogen standard. For each determination use approximately 0.5 g of accelerator. Use the manufacturer's recommended procedure for the hydrogen analyzer used.

177.2 Prepare a calibration curve of instrument meter units versus micrograms of hydrogen.

178. Procedure

178.1 *Tab Preparation*:

178.1.1 Store scandium stock in a plastic container or bag.

178.1.2 Handle stock material with degreased forceps.

178.1.3 Prepare tabs by cutting stock material into ¾-in. (19-mm) long by at least ⅛-in. (3.2-mm) wide strips.

178.1.4 Wrap strips in 1-mil (0.025-mm) nickel foil to completely enclose.

178.1.5 Place the tabs in the sample holder.

178.2 *Equilibration*:

178.2.1 Insert the sample holder into the sodium system.

178.2.2 After establishing sodium flow [0.1 gpm (6.3×10^{-6} m^3/s) minimum] through the equilibration device, equilibrate the tabs at 750 ± 2°C (1382 ± 4°F) for 24 h.

178.3 *Post-Exposure Treatment*:

178.3.1 Shut off sodium flow by closing inlet and outlet valves.

178.3.2 Pressurize the equilibration device with inert gas, open the drain valve, and drain the sodium from the equilibration device. If drainage at 750°C (1382°F) is prohibited by local safety practices, cool the sodium in the device at a rate of 50°C (90°F)/min down to 500°C (932°F) before draining the sodium.

178.3.3 Cool the tabs by cooling the loop section containing the holder. Allow no more than an overnight cooling while maintaining a positive inert-gas pressure during this period.

178.3.4 Remove the sample holder from the equilibration device and send it to the laboratory with minimum exposure to moist air.

178.3.5 Dissolve the sodium adhering to the holder and tabs in a large volume of ethanol to prevent heating.

178.3.6 Rinse the tab with water, then with ethanol.

178.3.7 Gently dry the tabs at 60°C (140°F) for 30 min.

178.4 *Hydrogen Determination*:

178.4.1 Analyze each tab individually. The tab may be bent or cut in two pieces in order to facilitate analysis.

178.4.2 Place the tab in the ignition boat.

178.4.3 Melt the scandium in a flowing argon stream.

178.4.4 Pass the hydrogen-argon mixture through a molecular sieve column and measure the hydrogen using a thermal-conductivity detector.

178.4.5 Alternately, a manometric hydrogen measurement may be used.

178.4.6 From the calibration curve, determine the micrograms of hydrogen in each sample.

179. Calculation

179.1 Calculate the micrograms per gram of hydrogen in the scandium as follows:

$$A = B/C \tag{19}$$

where:

A = hydrogen in tab, µg/g,
B = hydrogen in sample, µg, and
C = weight of sample, g.

179.2 Calculate the hydrogen concentration in the sodium as follows:

$$\text{µg/g Hydrogen} = 0.000156\ A\ (A \text{ from previous equation}). \tag{20}$$

180. Precision and Accuracy

180.1 *Precision*—For concentrations from 0.06 to 0.5 µg/g of hydrogen in sodium, one laboratory reported relative standard deviations ranging from 1 to 17 % for 8 sets of triplicate determinations made over a period of several months. One other set showed no variation between results.

180.2 *Accuracy*—No standards are available for accuracy assessment. The hydrogen analyzer is calibrated to eliminate bias in the measurement of hydrogen in the scandium metal.

SULFUR BY SPECTROPHOTOMETRY

181. Scope

181.1 This method is applicable for determining sulfur in sodium. This procedure requires 4 to 6 h.

181.2 The detection limit is 1 µg sulfur or 0.2 µg/g in a 5-g sample.

182. Summary of Method

182.1 Sodium metal is dissolved in an ethanol-water solution; the solution is acidified; the hydrogen sulfide is distilled into an alkaline trap and measured spectrophotometrically as methylene blue.

183. Apparatus

183.1 *Distillation Apparatus*—See Fig. 28.

183.2 *Argon Supply*—Purity 99.9 % at 1 to 2 psi (7 to 14 kPa). Helium or nitrogen may be substituted.

183.3 *Spectrophotometer*—The instrument shall be suitable for use with 40 or 50-mm cells.

183.4 *Inert-Atmosphere Glovebox*.

183.5 *Safety Shield*.

[24] The LECO RH-1 Hydrogen Determinator, manufactured by the Laboratory Equipment Co., has been found suitable.

[25] LECO Catalog No. 501-007 has been found satisfactory for this use.

[26] LECO Catalog No. 762-741 has been found suitable.

[27] Suitable 10-mil by 2 inch-wide (0.25 × 51-mm) sheet has been supplied by Research Chemicals, a Division of Nucor Corp.

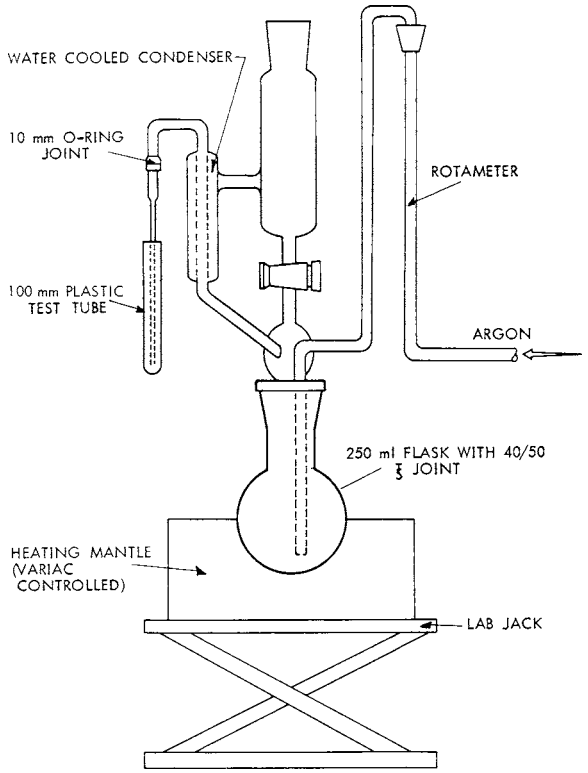

FIG. 28 Distillation Apparatus

184. Reagents and Materials

184.1 *Diamine Solution*—Dissolve 0.6 g of N,N-dimethyl-p-phenylene-diamine sulfate (Eastman #1333) in 200 mL of cool 2 + 1 sulfuric acid; add 1.1 g ferric chloride dissolved in 40 mL 1 + 1 hydrochloric acid, and dilute to 250 mL.

184.2 *Ethanol*, absolute.

184.3 *Hydrochloric Acid*, approximately 1 + 4.

184.4 *Methyl Orange*, 0.05 % in alcohol.

184.5 *Mixed Acid*, 250 mL of concentrated hydrochloric acid and 25 mL of concentrated phosphoric acid diluted to 500 mL.

184.6 *Sodium Hydroxide*, 0.1 *N*.

184.7 *Sulfide Standard*, *200 ppm*—Wash crystals of sodium sulfide ($Na_2S·9\ H_2O$) with water and blot dry. Dissolve 150 mg sodium sulfide in 100 mL of 0.1 *N* sodium hydroxide. This solution is unstable when exposed to air and must be stored under an inert atmosphere if it is to be kept more than one day.

185. Precautions

185.1 Every effort should be made to dissolve the sodium with a minimum of vigorous reaction and spray release. Yields are consistently higher when the sodium dissolves quietly and the reactants remain cool. A likely source of low recoveries is caustic spray carried into the condenser.

186. Calibration

186.1 Prepare standards by pipetting 0.10, 25, and 50 µL of sulfide standard into 5 mL of 0.1 *N* sodium hydroxide diluted to 15 mL and adding 3 mL of diamine slowly with stirring and reading as in step 187.11. Plot optical density against micrograms of sulfide.

187. Procedure

187.1 Working in the inert-atmosphere glovebox, place a weighed 1 to 5-g sodium sample into the dissolution flask. Cover the flask with aluminum foil or saran.

NOTE 27—If a section of bypass tubing is used, the tubing should have been recently cleaned with toluene or should have been cleaned by filing.

187.2 Prepare the apparatus by flushing thoroughly with dilute hydrochloric acid, water, and finally ethanol. Start the condenser cooling water and the argon purge. Place 25 to 75 mL (depending upon sample size) of ethanol in the reservoir.

187.3 Transfer the loaded flask from the glovebox to the apparatus quickly to minimize the air/sodium contact. Purge with argon for 5 min at 1 L/min.

187.4 Put the safety shield in place and place an ice bath under the dissolution flask. Adjust the argon purge to about 50 mL/min.

187.5 Slowly drain about three fourths of the alcohol from the reservoir onto the sodium. When the reaction slows, add 50 mL of water to the reservoir and drip this into the flask also.

187.6 Put 5 mL 0.1 *N* sodium hydroxide in a 10-mL plastic test tube and attach as a gas scrubber.

187.7 Put several drops of methyl orange and enough mixed acid to neutralize the sodium hydroxide (7.2 mL/g of sodium) plus 3 mL excess in the reservoir.

187.8 With the argon purge at 100 to 150 mL/min, drain the acid into the flask. The solution should be colored pink by the indicator. Add more acid if the solution is yellow.

187.9 Place a heating mantle under the flask and heat until the solution is refluxing at 1 to 2 drops per s. Turn off the heat and continue the argon purge for a total of 30 min.

187.10 Remove the scrubber and note the volume. If it is more than 6 mL, full-color development will not occur due to interference from ethanol. Excess alcohol distillation is caused by insufficient condenser cooling, or excessive heating or purging.

187.11 Dilute the scrub solution to 15 mL and add 3.0 mL of diamine slowly while stirring with a magnetic stirrer. After 15 min, read at 750 nm in 40 or 50-mm cells.

187.12 Determine the micrograms of sulfur present from the calibration curve.

188. Calculation

188.1 Calculate the sulfur concentrations as follows:

$$\text{Sulfur, } \mu g/g = A/B \times Y \qquad (21)$$

where:

A = µg of sulfur found,
B = g of sodium taken, and
Y = yield.

188.2 The typical yield is 0.9, but may be determined by the following procedure if enough sample is available.

188.2.1 Prepare a sample as in step 187.1.

188.2.2 Prepare the apparatus as in step 187.2 but do not put ethanol in the reservoir.

188.2.3 Put 2 mL of ethanol in a 5-mL beaker and add 25 µL of sulfide standard.

188.2.4 Wash this into the reservoir with a few millilitres of ethanol.

188.2.5 Drain the ethanol sulfide onto the sodium.

188.2.6 Add 25 to 75 mL of ethanol to the reservoir and continue the analysis.

188.2.7 By comparison with the standard plot, determine the micrograms of sulfide recovered and calculate the yield.

189. Precision and Accuracy

189.1 *Precision*—No data are available to provide information about precision.

189.2 *Accuracy*—No standards are available for accuracy assessment. The instrument is calibrated to eliminate bias from the measurement of sulfur in the sample solutions.

SODIUM PURITY BY TITRATION

190. Scope

190.1 This method is applicable for the sodium concentration (or purity) in a sodium sample using an acid-base titration.

191. Summary of Method

191.1 Sodium is converted to sodium hydroxide by hydrolysis and determined by weight titration with a slight excess of hydrochloric acid, followed by a back titration of the excess acid with sodium hydroxide.

192. Interferences

192.1 Tris (see 194.5) is a weak base and for that reason it is not an ideal primary standard for highly accurate work. The pH changes only gradually at the equivalence point and, therefore, a pH meter must be used for an accuracy better than about 0.1 %. Because the pH at the equivalence point is a function of the salt concentration, the prescribed quantities of reagents and water should be closely adhered to.

193. Apparatus

193.1 *Inert-Atmosphere Glovebox*, shall be maintained at less than 2 µL/L of oxygen and moisture.

193.2 *Two Single-Pan Analytical Balances*—Weights shall be within Class S tolerances. The weights should have a density of 7.8 g/cm^3 (7800 kg/m^3) (stainless steel). All weighings should be to the nearest 0.1 mg.

193.3 *Dissolution Vessel*, made from a 500-mL cylindrical polyethylene narrow-mouth bottle. Cut off the top of the bottle cleanly about 20 mm below the shoulder. Invert the cut-off top to serve as a funnel to allow addition of methanol or water and the escape of hydrogen.

193.4 *Acid-Weight Buret*—A 125-mL polyethylene wash bottle is used.

193.5 *Buret, 10-mL*—The buret shall have a reservoir protected from atmospheric carbon dioxide.

193.6 *Glass Wool*—Prepare by washing with acetone, soaking 1 to 2 min in 0.001 *M* hydrochloric acid, rinsing with water, and drying at 120 to 150°C.

193.7 *Magnetic Stirrer*, with stirring bars.

193.8 *pH Meter*.

193.9 *Jar (optional)*, screw-capped, gas-tight jar. Size should be just sufficient to contain the sample.

193.10 *Safety Shield*, for use during dissolution of sodium.

194. Reagents and Materials

194.1 *Ethanol*, neutral, acetone-free.

194.2 *Ethyl Red-Indicator Solution*—Dissolve 0.1 g of ethyl red indicator (formula weight 454.36) in 100 mL of ethanol.[28]

194.3 *Hydrochloric Acid*—Dilute 1150 mL of concentrated hydrochloric acid to 4 L with water.

194.3.1 Standardize the acid as follows:

194.3.1.1 Fill the weight buret with hydrochloric acid and weigh it.

194.3.1.2 Weigh a 250-mL beaker and then add 10 to 11 g of Tris.

194.3.1.3 Reweigh the beaker and Tris.

194.3.1.4 Add 150 mL of water, a stirring bar, and a drop of ethyl red-indicator solution to the beaker.

194.3.1.5 Titrate with hydrochloric acid from the weight buret until the red color of the indicator has completely faded (pH 3 to 4), but avoid an excess of more than one drop of acid.

194.3.1.6 Wash down the beaker walls with water.

194.3.1.7 Reweigh the acid weight buret.

194.3.1.8 Insert the pH electrodes into the beaker and back titrate with standard sodium hydroxide to a pH of 4.2.

194.3.1.9 Practice with commercial Tris before using the expensive NBS standard material.

194.3.2 Store the standardized acid in well-capped bottles. Reconfirm the titer of the acid monthly.

194.4 *Methanol*, neutral, acetone-free.

194.5 *Sodium Hydroxide*—Dilute 8 mL of saturated sodium hydroxide to 4 L with water. Standardize against high purity sulfamic acid, potassium acid phthalate, or hydrochloric acid. Store in a polyethylene bottle protected from carbon dioxide.

194.6 *Sulfamic Acid or Potassium Acid Phthalate*, primary standard. Dry at 110 to 120°C before use.

194.7 *Tris*—Dry NBS Standard Reference Material 723, tris-(hydroxymethyl)-aminomethane, or equivalent under vacuum for 24 h at 70°C, and then store it in a desiccator over magnesium perchlorate.

194.8 *Water*—Boil double deionized water for 5 min; transfer it to covered storage bottles while still hot. Freshly prepare for each use.

195. Precautions

195.1 The dissolution of sodium presents the possibility of a hydrogen explosion. This operation must be carried on behind a safety shield and preferably in a metal hood.

196. Calibration

196.1 Calibration consists of standardizing the hydrochloric acid used to titrate the sodium in solution as the hydroxide (see 194.3.1).

197. Procedure

197.1 *Sample Preparation*:

197.1.1 *Bypass Sample*:

[28] Eastman Organic Chemicals, No. 2155, Ethyl Red has been found suitable for this purpose. At least one other compound (of formula weight 297.36) has the accepted commercial designation of Ethyl Red, but its behavior as an acid-base indicator makes it unsuitable for use in this method.

197.1.1.1 Obtain a sodium sample in a stainless-steel bypass tube by the Bypass Sampling Procedure.

197.1.1.2 Rinse the exterior of the tube with water and methanol.

197.1.1.3 Dry the tube and transfer it into an inert-atmosphere box.

197.1.1.4 Cut off at least a 1-in. (25-mm) section from the end of the tube with a tubing cutter. Discard the end section.

197.1.1.5 Cut off and weigh a section containing 5 to 6 g of sodium.

197.1.1.6 Proceed to 197.2.

197.1.2 *Overflow-Cup Sample*:

197.1.2.1 Obtain a sodium sample weighing 5 to 6 g in a nickel, stainless steel, tantalum, or glass overflow cup.

197.1.2.2 Open the overflow sampling device in the inert-atmosphere box and remove the cup.

197.1.2.3 Weigh the cup plus sample and record the weight.

197.1.2.4 Proceed to 197.2.

197.1.3 *Sample Weighing*:

197.1.3.1 Accurate weighing in some gloveboxes can present problems. For bypass samples, it is possible to protect the open ends of a section of sample tubing long enough to bring it out in the air for weighing. Polyethylene end caps are satisfactory for this, but care must be taken to minimize the gas trapped in the caps since each millilitre of argon, for example, will increase the apparent sample weight by approximately 0.4 mg.

197.1.3.2 If an analytical balance with a capacity of at least 500 g is available in the laboratory, no weighings need to be made in the inert-atmosphere box. Instead, transfer the sodium-filled cup or tube to a jar in the inert-atmosphere box. Remove the closed, inert-gas filled jar and weigh it promptly in the laboratory. Later, return the same jar and the empty cup or tube to the inert-atmosphere box, seal the cup or tube in the jar, remove the gas-filled jar, and weigh. The apparent loss in weight of the jar is taken as the uncorrected weight of the sodium sample. For weighings made this way, the buoyancy correction factor for sodium is 1.00157 if an argon filled box is used; or it is 1.00002 if a helium filled box is used; and it is 1.00105 if a nitrogen filled box is used. In calculating these factors, it was assumed that the balance weights were stainless steel of density 7.8 g/cm^3 (7800 kg/m^3).

197.2 *Analysis*:

197.2.1 Place a loose plug of glass wool in the neck opening of the top of the dissolution vessel.

197.2.2 Take the sample from the inert-atmosphere box and slide it into 100 mL of cold methanol in the bottom of the dissolution vessel. Place the top on the vessel, with the neck down, and press the top into place. Cool the vessel in a suitable bath to keep the reaction under control and to minimize spray.

197.2.3 After all the sodium is in solution, rinse back into the dissolution vessel any spray trapped by the glass wool and on the underside of the vessel top. Use a total of 100 to 150 mL of water for the rinses and the transfer in this and the next two steps. Discard the glass wool.

197.2.4 Remove the sample container from the vessel, using appropriate rinses to retain all the sample in the dissolution vessel.

197.2.5 Quantitatively transfer the sample solution to a 400-mL beaker.

197.2.6 Fill the acid weight buret with the standardized hydrochloric acid and weigh it.

197.2.7 Add a drop of ethyl red-indicator solution and a stirring bar to the sample; then add acid from the weight buret until the indicator fades to just colorless. Do not allow any material to adhere to the buret. The end point appears suddenly in the absence of large amounts of carbonate. Since a large excess of acid is undesirable, the use of a titration thief is recommended to avoid overrunning the endpoint.

197.2.8 Reweigh the acid weight buret while heating the sample to boiling on a hot plate. After boiling the acidified sample briefly, cool to 40 to 60°C and titrate with sodium hydroxide until the maximum pink color is reached (pH 6 to 7). Boiling and back titration are used to avoid errors due to the absorption of carbon dioxide during the dissolution of the sample. It would be very difficult to protect the sample completely from atmospheric carbon dioxide during the dissolution and still retain all of the spray.

NOTE 28—A pH meter may be used for the titration and the back titration, although the use of an indicator is satisfactory, particularly if a comparison solution is used.

197.2.9 Dry the sample tube or cup and weigh it in the inert-atmosphere box.

198. Calculation

198.1 *Standardization of Acid*—The grams (in air) of hydrochloric acid equivalent to 1 g (in vacuum) of sodium is obtained using the following equation:

$$\text{g hydrochloric acid/g sodium} = [(A/B)/((C)(D)(E)/F) + ((G)(H)/1000)] \quad (22)$$

where:

A = weight of hydrochloric acid, g,
B = equivalent weight of sodium (22.9898),
C = weight of Tris, g,
D = purity of Tris,
E = buoyancy correction factor for Tris in air, (1.00075),
F = equivalent weight of Tris (121.137),
G = volume of sodium hydroxide, mL, and
H = normality of sodium hydroxide.

NOTE 29—For Tris weighed in air, the buoyancy correction factor is 1.00075 based on:
(1) density of air = 0.0012 g/cm^3,
(2) density of Tris = 1.35 g/cm^3, and
(3) density of stainless weights = 7.8 g/cm^3.

198.2 *Uncorrected Percent Sodium*—Calculate the purity as percent of sodium in the sample uncorrected for potassium as follows:

$$\text{Purity, percent sodium uncorrected for potassium} = (A/I) - ((G)(H)(B)/1000)/((J)(C)(0.01)) \quad (23)$$

where:

A = weight of hydrochloric acid, g
B = equivalent weight of sodium (22.9898),
C = buoyancy correction factor for sodium (1.0015 if weighed in argon; 1.00016 if weighed in helium),
G = volume of sodium hydroxide, mL,

H = normality of sodium hydroxide,
I = concentration of hydrochloric acid, g of hydrochloric acid/g of sodium, and
J = uncorrected weight of sodium, g.

NOTE 30—For sodium weighed in argon, the buoyancy correction factor is 1.00151, based on:
(1) density of argon = 0.00166 g/cm^3,
(2) density of sodium = 0.9684 g/cm^3, and
(3) density of stainless weights = 7.8 g/cm^3.
For sodium weighed in helium, the buoyancy correction factor is 1.00016 based on:
(1) density of helium = 0.0001635 g/cm^3,
(2) density of sodium = 0.9684 g/cm^3, and
(3) density of stainless weights = 7.8 g/cm^3.

NOTE 31—Although a buoyance correction is required in the calculation of sodium weight, no correction is needed for the stainless-steel sample containers because the density is the same (7.8) as that of the balance weights. If a sample of sodium is assayed from a container of another density, such as glass or tantalum, the empty container should be reweighed in the inert atmosphere to avoid complex buoyancy calculations.

198.3 *Corrected Percent Sodium*—Correct for the higher equivalent weight of potassium as follows:

$$\text{Purity, percent sodium plus potassium} = K(4 \times 10^{-5}) + L \quad (24)$$

where:
K = amount of potassium known to be in the sodium, µg/g, and
L = percent sodium uncorrected for potassium.

198.4 *Buoyancy Corrections*—Reduction of weights to vacuum is accomplished by using the following equation:

$$W_o = W_a(1 + 1.2 \times 10^{-5})(1 - d_A/d_w)(1 - d_A/d_s)^{-1} \quad (25)$$

where:
W_o = weight of the sample in vacuum,
W_a = apparent weight of the sample in an atmosphere,
d_A = density of the sample, g/cm^3, (1 g/cm^3 = 1000 kg/m^3)
d_s = density of the sample, g/cm^3, and
d_w = density of the weights, g/cm^3.

NOTE 32—The constant, 1.2×10^{-5}, is included because of the convention that stainless-steel weights are adjusted to balance brass weights (of density 8.4) of the correct mass, when the two types of weights are intercompared in air of density 0.0012 g/cm^3.

199. Precision and Accuracy

199.1 *Precision*—Limited data indicate that the difference between duplicate analyses should be no greater than 0.01 % (absolute).

199.2 *Accuracy*—No standards are available for accuracy assessment. The hydrochloric acid and sodium hydroxide solutions used to titrate the solutions of sodium are standardized against NBS standards to eliminate bias from the titrations.

PLUTONIUM BY ALPHA ASSAY

200. Scope

200.1 This method is applicable for determining plutonium in a sodium sample. This entire procedure, exclusive of sampling and distillation, requires 5 to 8 h. The gross alpha count requires about 1 h. An additional hour is required for the plutonium extraction and counting.

200.2 The detection limit is about 0.03 µg/kg for Pu 239 under the conditions of this procedure.

201. Summary of Method

201.1 The residue from vacuum distillation of a sodium sample is dissolved in concentrated nitric acid and the analysis completed by one or more of three different methods: (1) gross alpha assay of an aliquot of the solution to establish an upper limit of plutonium content; (2) separation of plutonium by extraction prior to alpha assay; or (3) separation of plutonium by electrodeposition for alpha spectrometry.

202. Interferences

202.1 The gross alpha assay (207.1) is not specific for plutonium. Neptunium is the only known interference in the plutonium assay (207.2).

202.2 The gross alpha count should not be used in instances where the residue weight indicates that the amount of solid on the planchet would significantly attenuate the alpha particles. The comment given in step 207.1.2 is based on the assumption that the planchet is approximately 1 in. (25 mm) in diameter and that the bulk composition of the solids is sodium nitrate.

203. Apparatus

203.1 *Alpha Counter*—This instrument consists of a counting chamber through which a suitable counting gas is passed, a high voltage supply, and associated electronics for registering the alpha counts.

203.2 *Alpha Spectrometer*—This instrument consists of a solid-state detector mounted in an evacuable chamber, a bias amplifier, a multichannel analyzer, and associated electronics. The alpha spectrometers must be capable of recording and analyzing energy pulses in the 4.5 to 5.5 MeV range.

203.3 *Planchets*—Stainless-steel planchets adaptable to the alpha counter and alpha spectrometer should be used.

203.4 *Electrodeposition Cell*—See Figs. 28-31 for a typical cell.

203.5 *Separatory Funnels*, 60 mL.

204. Reagents and Materials

204.1 *Ammonium Citrate Solution*, 20 % aqueous solution.

204.2 *Ascorbic Acid Solution*, 5 % aqueous solution.

204.3 *Benzene*.

204.4 *N-benzoyl-N-phenylhydroxylamine (BPHA) Solution*—Dissolve 4 g BPHA in 100 mL of ethanol.

204.5 *Nitric Acid*, concentrated.

204.6 *Nitric Acid, 2 N*—Add 130 mL of concentrated nitric acid to 500 mL of water and dilute to 1 L.

204.7 *Perchloric Acid*, 70 to 72 %.

204.8 *Potassium Cyanide Solution*, 5 % aqueous solution.

204.9 *Sodium Bicarbonate Solution*, saturated aqueous solution.

204.10 *Sodium Hydroxide*, 2 *N* aqueous solution.

204.11 *Sodium Hypochlorite Solution*, 5 % aqueous solution.

204.12 *Thioglycolic Acid (TGA) Solution*, 16 % aqueous solution.

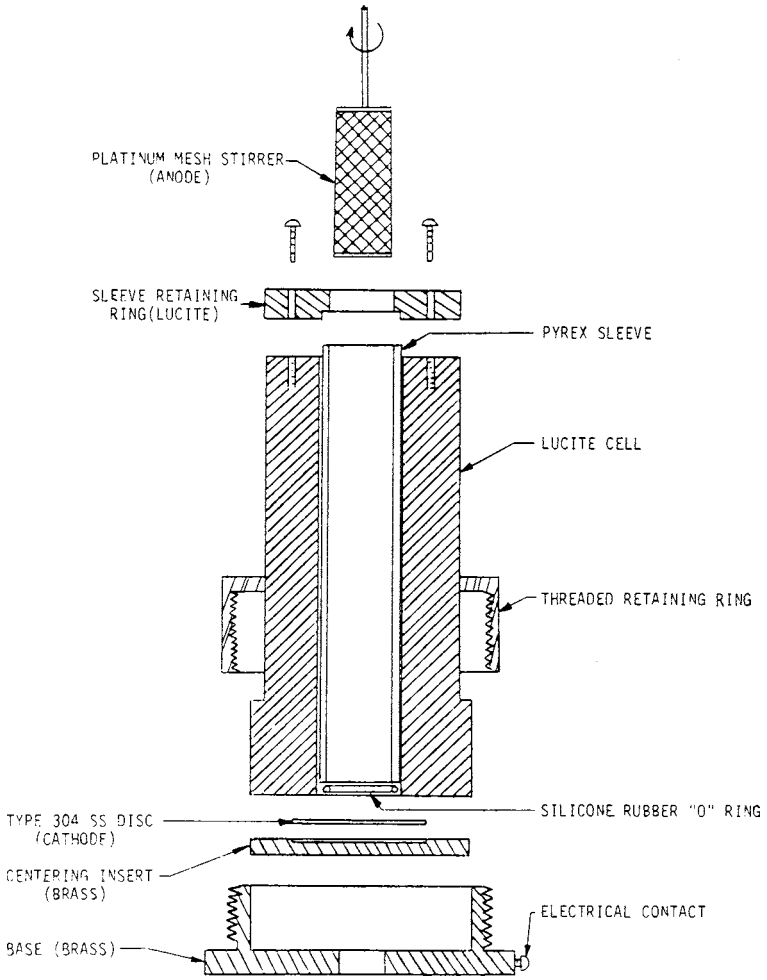

FIG. 29 Typical Electrodeposition Cell for Plutonium

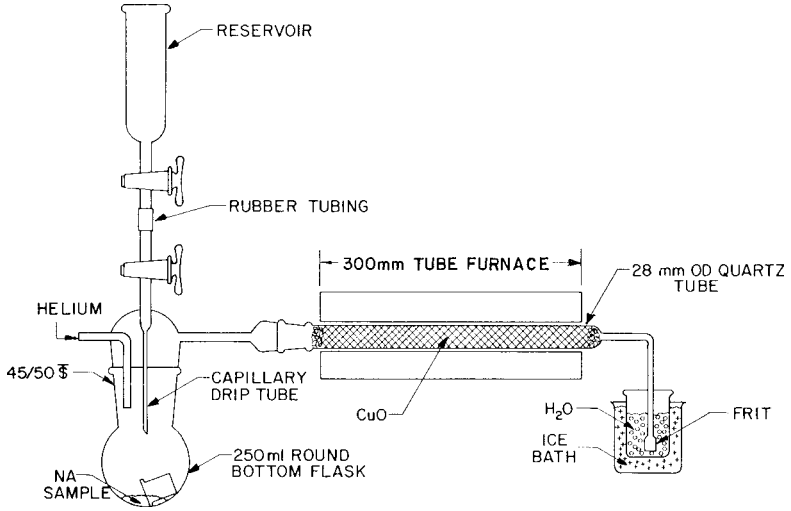

FIG. 30 Typical Sodium Dissolution Flask and Copper Oxide Train

205. Precautions

205.1 Hot concentrated perchloric acid in contact with organic materials can lead to explosive reactions. The amount of nitric acid added prior to the perchloric acid evaporation is sufficient to oxidize the small amounts of organic material that will be present if good phase separations are achieved.

205.2 Cyanide poisoning can occur from ingestion or skin absorption of cyanide salts or from inhalation of hydrogen cyanide gas that forms when even the weakest acids contact cyanide solutions. Handle solid potassium cyanide with respect. Dispose of cyanide residues in compliance with local safety practices.

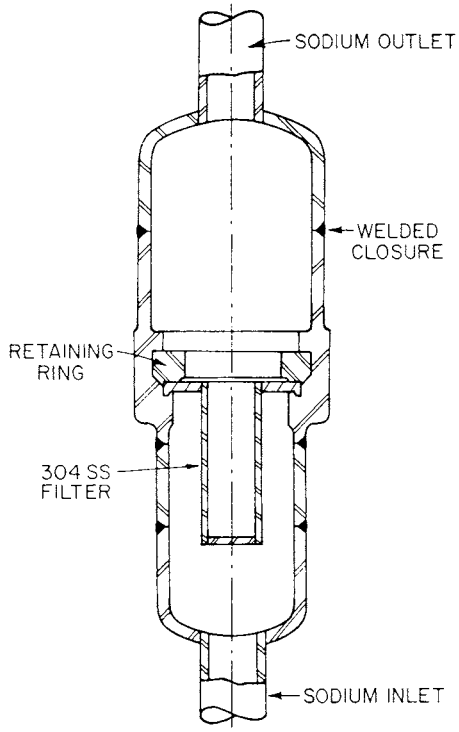

FIG. 31 Typical Welded Filter Cartridge

206. Calibration

206.1 Count the calibration standard and then take a background count. Convert both counts to counts per minute (cpm) and obtain net counts per minute for standard by subtracting background from standard.

206.2 Determine the geometry factor by dividing net counts per minute by disintegrations per minute established for the calibration standard. This geometry factor is *G* in 208.1.

206.3 The calibration standard is a disk containing alpha activity of a known disintegration rate. The standard must be handled carefully to avoid changing its disintegration rate through contamination or loss of alpha source from the disk.

207. Procedure

207.1 *Gross Alpha Assay*:

207.1.1 Obtain a distillation residue from approximately 50 g of sodium as described in the Laboratory Distillation Procedure. Use a tantalum cup. Record the weights given on the transfer container.

207.1.2 Remove the distillation cup from the container and weigh it. Calculate the residue weight by subtracting the weight of the empty cup from this weight. If the residue weight is >10 mg, omit steps 207.1.7-207.1.10 and step 207.2.1.

207.1.3 Add 5 mL of concentrated nitric acid to the distillation residue in the distillation cup. Tilt and rotate the cup to moisten the inner surface.

207.1.4 Carefully heat the cup in a simmering water bath for 20 min to dissolve any plutonium dioxide in the residue.

207.1.5 Transfer the solution to a 30-mL beaker. Rinse the cup with concentrated nitric acid and combine the rinsings with the solution.

207.1.6 Evaporate the solution to 1 mL and cool. Proceed to step 207.2.2 if steps 207.1.7-207.1.10 are to be omitted.

207.1.7 Transfer the solution quantitatively to a 10-mL volumetric flask and dilute to volume with 2 *N* nitric acid.

207.1.8 Pipet a 1-mL aliquot of the above solution onto a stainless-steel planchet and carefully evaporate under a heat lamp. Reserve the remaining solution for 207.2.

207.1.9 Carefully flame the planchet to dull red heat over a gas burner.

207.1.10 Alpha count the planchet in a calibrated alpha counter and calculate the alpha activity. If the alpha count obtained is significant, proceed to 207.2.

207.2 *Plutonium Extraction and Alpha Assay*:

207.2.1 Transfer the solution remaining from step 207.1.8 into a 30-mL beaker, evaporate to approximately 1 mL, and cool.

207.2.2 To the solution from step 207.1.6 or 207.2.1, add 2 mL of 5 % ascorbic acid solution and mix. Next, add 1 mL of 20 % ammonium citrate solution and mix. Add 1 mL of 16 % TGA solution, mix, and then make the solution basic (pH 6.9 to 7.5) by adding an excess of saturated sodium bicarbonate solution. Next, add 1 mL of 5 % potassium cyanide solution and 1 mL of 4 % BPHA in ethanol. Mix and allow the solution to stand for 5 min.

NOTE 33—The order of addition of the reagents is important. Follow the above directions exactly.

207.2.3 Transfer the solution into a 60-mL separatory funnel, add 10 mL of benzene, and extract the plutonium-BPHA complex into the benzene phase by shaking for 2 min.

207.2.4 Transfer a 1-mL aliquot of the benzene phase to a stainless-steel planchet, dry under a heat lamp, and flame the planchet to dull red heat over a burner. Alpha count in a calibrated counter and calculate the plutonium activity. If the alpha count indicates a significant amount of plutonium activity, proceed to 207.3.

NOTE 34—The results obtained from the alpha counting (207.1 and 207.2) should be used to determine whether or not further characterization is necessary. For example, should the alpha counting indicate an insignificant amount of alpha activity, no electroplating is necessary.

207.3 *Plutonium Separation by Electrodeposition and Assay by Alpha Spectrometry*:

207.3.1 Back extract the plutonium from the benzene phase into 5 mL of 0.5 *N* nitric acid. Drain the aqueous phase into a 30-mL beaker. Wash the benzene with approximately 5 mL of 0.5 *N* nitric acid and add the washings to the 30-mL beaker.

207.3.2 Add 1 mL of perchloric acid to the solution in the 30-mL beaker and evaporate the solution to approximately 0.5 mL. Fuming with perchloric acid will remove any organic material and oxidize all plutonium to Pu (VI).

207.3.3 During evaporation of the solution, prepare the electrodeposition cell. Clean the 304 stainless-steel plate in warm chromic-acid cleaning solution, rinse it with water, and assemble the cell as indicated in Fig. 31 (Handle the plate with tweezers during this operation; do not touch it with fingers). Immediately fill the cell with 2 *N* sodium hydroxide and set it aside until ready to continue with the electrodeposition.

207.3.4 Add approximately 2 mL of water, 8 mL of 2 *N* sodium hydroxide, and 1 mL of 5 % sodium hypochlorite solution to the 0.5 mL of perchloric acid from step 207.3.2.

207.3.5 Discard the 2 *N* sodium hydroxide in the cell and transfer the solution from step 207.4 into the cell. Wash the beaker with 2 mL of water and add the washings to the cell.

207.3.6 Place the cell in a water bath maintained at approximately 70°C and position the cell so that the bottom of the platinum mesh stirrer is 10 to 15 mm above the stainless-steel plate. Connect the cell to a direct-current power source with the stirrer as the anode and the stainless-steel plate as the cathode. Electrodeposit the plutonium at approximately 70°C for 3 h at 150 mA while stirring at about 100 rpm.

207.3.7 Disconnect the power source at the end of the 3 h plating period and immediately discard the residual solution. Rinse the cell with water and disassemble the cell. Rinse the stainless-steel plate with acetone, air dry it, and flame the plate to dull red heat over a burner.

207.3.8 Identify the isotopes present in the electrodeposited plutonium by alpha spectrometry. The yield under the above conditions is 95 to 100 %.

208. Calculation

208.1 Calculate the gross-alpha or plutonium-alpha activity as disintegrations per minute per gram (d/m/g) by using the following equation:

$$\text{Activity, d/m/g} = R \times F/A \times G \quad (26)$$

where:

R = net count rate, counts per minute,
F = total volume of sample solution divided by volume of aliquot,
G = geometry factor of counter (see 206.2), and
A = weight of sodium, g.

209. Precision and Accuracy

209.1 Data are not available to provide information about precision and accuracy. Sampling is probably the most significant source of bias in the analysis.

GAMMA ASSAY OF DISTILLATION RESIDUE

210. Scope

210.1 This method is applicable for determining the gamma-emitting radionuclides in the residue after distilling a sodium sample. This procedure, exclusive of sampling and distillation, requires about 0.5 h.

210.2 The sensitivity will vary with the branching ratio of the particular isotope being determined and with the activity levels of other isotopes present. Detection limits of the order of 10 pCi/g of sodium for isotopes with favorable branching ratios, (for example, manganese-54, antimony-125) have been obtained in sodium.

211. Summary of Method

211.1 A distillation residue of a sodium sample is dissolved and the radioisotopic content of the sample is determined by standard gamma-spectrometric techniques applied to an aliquot of the solution.

212. Apparatus

212.1 *Multichannel Analyzer System*, consists of a gamma detector and associated electronics. The degree of sophistication of the detector and the electronics will depend on the purpose for which the assay is used. The preferred system is one using a Ge(Li) detector and electronics suitable for covering the range 0 to 2 MeV with a channel width of 0.5 keV or less.

212.2 *Counting Vials*—The vials must be calibrated to contain a standard volume.

213. Reagents and Materials

213.1 *Aqua Regia*—Prepare fresh by mixing 1 part of concentrated nitric acid with 3 parts of concentrated hydrochloric acid.

214. Calibration

214.1 The system must be calibrated for both efficiency and geometry by standard gamma spectrometric techniques. These techniques are given by J. E. Cline and by R. L. Health **(3, 4).**

215. Procedure

215.1 Obtain a distillation residue from approximately 50 g of sodium in either a tantalum or titanium cup in accordance with the Laboratory Distillation Procedure. Record the weights given on the sample container.

215.2 Add 5 mL of aqua regia to the distillation cup. Swirl to dissolve the residue.

215.3 Transfer the solution quantitatively to a counting vial and dilute to volume.

215.4 Check the cup for residual activity. If activity is detected, repeat steps 215.2 and 215.3.

215.5 Obtain a gamma spectrum under previously established standard conditions.

216. Calculation

216.1 Calculate the gamma activity of each isotope identified as follows:

$$\text{Activity, pCi/g Na} = R/A \times B \times E \times 2.2 \quad (27)$$

where:

A = weight of sodium, g,
R = net count rate, counts per minute,
B = fraction of total disintegrations emitting measured energy, and
E = efficiency of counting system, counts per gamma emitted at the energy used.

217. Precision and Accuracy

217.1 Data are not available to provide information about precision and accuracy.

GAMMA ASSAY OF SODIUM SOLUTION

218. Scope

218.1 This method is applicable for determining the gamma emitting radionuclides in a solution of a sodium sample. This procedure, exclusive of sampling, requires 1 h.

218.2 This assay is useful in determining only the more abundant gamma energies emitted by radioisotopes in a sodium sample. Thus, the radiation level of the more abundant activities will dictate the sensitivities achievable by this procedure.

218.3 This procedure should be applied only to isotopes soluble in basic solution unless the sample is acidified after dissolution in methanol water.

219. Summary of Method

219.1 A sodium sample is dissolved in a methanol-water mixture and the isotopes present are determined by standard techniques of gamma spectrometry.

220. Apparatus

220.1 *Multichannel Analyzer System*, consists of a gamma-ray detector and associated electronics. The degree of sophistication in detectors and electronics needed for this assay will depend on the complexity of the gamma spectrum and on the purpose for which the analysis is being performed. The preferred system is one having a Ge(Li) detector and electronics capable of covering the energy range 0 to 2 MeV with a channel width of 0.5 keV or less.

220.2 *Separatory Funnel*, 125 mL.

220.3 *Safety Shield*, for use during dissolution of sodium.

221. Reagents and Materials

221.1 *Aqua Regia*—Freshly prepare by mixing 1 part concentrated nitric acid with 3 parts concentrated hydrochloric acid.

221.2 *Demineralized Water*—Pass distilled water through a high-quality commercial mixed-bed ion exchange column. Store in polyethylene bottles.

221.3 *Methanol*, anhydrous, reagent grade.

222. Precautions

222.1 The dissolution of sodium in methanol water could become vigorous enough to ignite the hydrogen and methanol vapors. The dissolution must be carried out in a beaker. A flask or bottle that could permit an explosive atmosphere to build up shall never be used. The dissolution beaker shall be contained in a metal tray or pan to retain any spilled alcohol.

223. Calibration

223.1 The system must be calibrated for both counting efficiency and geometry in accordance with conventional gamma spectrometric techniques. These techniques are described by J. E. Cline and by R. L. Heath (**3**, **4**).

224. Procedure

224.1 Obtain a sample of sodium (approximately 10 g) either as a section of tubing from the Bypass Sampling Procedure or in a quartz, tantalum, or titanium cup obtained by the Overflow Sampling Procedure. For most samples, it will be necessary to allow the sodium-24 activity to decay to a safe level before the sample is handled.

224.2 Weigh the sample plus the container.

224.3 Place the sample and its container in a 250-mL beaker.

224.4 Dissolve the sodium by dropping 120 mL of a water-methanol mixture (1 volume of water + 3 volumes of methanol) from a separatory funnel onto the sodium surface at a rate of 30 to 60 drops per min.

224.5 Quantitatively transfer the sodium solution to a 100-mL volumetric flask, dilute to volume with water, and mix thoroughly.

224.6 Transfer an appropriate aliquot of the solution to a counting vessel and obtain the gamma spectrum under standardized counting conditions.

224.7 Gamma scan the crucible for residual activity. If activity is detected, rinse the crucible with 5 mL of aqua regia. Swirl to dissolve residual activity.

224.8 Transfer the solution quantitatively to a counting vial and dilute to volume.

224.9 Check the crucible for residual activity. Repeat steps 224.6 and 224.7 until no activity is detected.

224.10 Obtain a gamma spectrum under previously established standard conditions.

224.11 Dry and weigh the empty sample container.

225. Calculation

225.1 Calculate the gamma activity of each basic and acidic aliquot as follows:

$$\text{Activity, pCi/g Na} = R \times F/A \times B \times E \times 2.2 \quad (28)$$

where:

A = weight of sodium, g,
R = net count rate, counts per minute,
F = aliquot factor,
B = fraction of total disintegrations emitting measured energy, and
E = efficiency of counting system.

225.2 Add the activities of each aliquot to determine the total gamma activity of the sodium.

226. Precision and Accuracy

226.1 Data are not available to provide information about precision and accuracy.

RADIOACTIVE IODINE BY GAMMA COUNTING

227. Scope

227.1 This method is applicable for determining radioactive iodine in a sodium sample after dissolution of the sodium. This procedure, exclusive of sampling, requires 2 to 3 h.

227.2 The sensitivity will depend on the type of detector used. A detection limit of approximately 10 pCi/g should be obtainable using a sodium-iodide detector in conjunction with a multichannel analyzer.

228. Summary of Method

228.1 A sodium sample is dissolved in a water-methanol mixture. The radioisotopes of iodine in the sample are isotopically exchanged with carrier iodine and separated from other radioactivity by a series of solvent extraction and precipitation steps. The iodine activity is then determined by standard radiochemical techniques.

229. Apparatus

229.1 *Multichannel-Analyzer System*, consists of a gamma detector and associated electronics. The preferred system is one using either a sodium iodide or a Ge(Li) detector and a multichannel analyzer. The detector used will dictate the degree of sophistication (number of channels) required in the multichannel analyzer.

229.2 *Counting Vials*—The vials must be calibrated to contain a standard volume.

229.3 *Separatory Funnel*, 125 mL.

229.4 *Safety Shield*, for use during dissolution of sodium.

230. Reagents and Materials

230.1 *Carbon Tetrachloride*.

230.2 *Demineralized Water*—Pass distilled water through a high-quality commercial mixed-bed ion exchange column. Store in a polyethylene bottle.

230.3 *Filter Paper*, 24-mm glass fiber.[29]

230.4 *Hydrochloric acid*, 12 *N* and 1 *N*.

230.5 *Methanol*, anhydrous.

230.6 *Palladium Chloride, 20 mg Pd/mL*—Dissolve 3.34 g palladium chloride in 50 mL of 6 *N* hydrochloric acid and dilute to 100 mL with water.

230.7 *Sodium Hydroxide*, 10 *M* aqueous solution.

230.8 *Sodium Iodide*.

230.9 *Sodium Nitrite*, 1 *M* aqueous solution.

230.10 *Sodium Sulfite*, 1 *M* aqueous solution.

230.11 *Sulfuric Acid*, 9 *N* and 3 *N*.

231. Precautions

231.1 The dissolution of sodium in methanol could become vigorous enough to ignite the hydrogen and methanol vapors. The dissolution must be carried out in a beaker. A flask or bottle that could permit an explosive atmosphere to build up shall never be used. The dissolution beaker should be contained in a metal tray or pan to retain any spilled alcohol.

232. Calibration

232.1 The system must be calibrated for both efficiency and geometry by standard gamma-spectrometric techniques. The techniques are described by J. E. Cline and by R. L. Heath (**3**, **4**).

233. Procedure

233.1 Obtain a 10 to 15-g sample of sodium by the Overflow Sampling Procedure. Borosilicate-glass or quartz beakers have been found suitable.

233.2 Weigh the sample plus the container.

233.3 Place the sample and container in a 250-mL Pyrex beaker.

233.4 Dissolve the sodium by dripping 120 mL of a water-methanol mixture (1 volume of water + 3 volumes of methanol) containing 10 mg of iodine carrier (sodium iodide) from a separatory funnel onto the sodium surface at 30 to 60 drops per min. The volume at the completion of this step is expected to be 100 mL because some of the alcohol evaporates in the process.

233.5 Quantitatively transfer the sodium solution to a 100-mL volumetric flask, dilute to volume, and mix thoroughly.

233.6 Weigh the empty sample container. If the iodine level is known to be high enough, omit extraction steps 233.7-233.18 and go directly to step 233.19.

233.7 Transfer a 50-mL aliquot of the sodium solution to a 200-mL beaker.

233.8 Add 9 *N* sulfuric acid (25 to 30 mL) to make the solution slightly acid. Cool in an ice bath.

233.9 Add 5 mL of excess 9 *N* sulfuric acid and transfer the solution quantitatively to a 125-mL separatory funnel.

233.10 Add 15 mL of carbon tetrachloride to the separatory funnel.

233.11 Add 5 to 10 drops of 1 *M* sodium sulfite to reduce all iodine to iodide.

233.12 Add enough 1 *M* sodium nitrite to oxidize all iodide to free iodine.

233.13 Extract the iodine into the carbon tetrachloride.

233.14 Transfer the carbon tetrachloride to a secondary separatory funnel and repeat steps 233.10-233.13 until no iodine color remains in the aqueous solution.

233.15 Combine all carbon tetrachloride extracts.

233.16 Wash the carbon tetrachloride extracts with 15 mL of 3 *N* sulfuric acid containing a few drops of sodium nitrite.

233.17 Discard the wash solution.

233.18 Extract the iodine from the carbon tetrachloride into 15 mL of water containing 1 mL of 1 *M* sodium sulfite and 4 to 5 drops of 10 *M* sodium hydroxide.

233.19 Transfer the aqueous solution from the previous step, or an aliquot from step 233.5 to a counting vial, dilute to volume with water, and gamma count under standard counting conditions.

NOTE 35—For low-level radioiodine concentrations, it may be preferable to separate the iodine by precipitation to provide a better counting geometry and to remove background interference. Proceed to steps 233.20-233.24 for the precipitation method.

233.20 Transfer the 15-mL extraction solution from step 233.18 to a 40-mL centrifuge cone and add 2 mL of concentrated hydrochloric acid. Gently heat the solution to remove any sulfur dioxide which may be present.

233.21 Dilute to approximately 25 mL with deionized water.

233.22 Add 1 mL of the palladium chloride solution and swirl for approximately 15 s every 1 to 2 min until the palladium iodine precipitate coagulates (about 5 min).

233.23 Filter the precipitate onto a 24-mm glass-fiber filter paper and wash the centrifuge cone onto the filtered precipitate with 20 mL of 1 *N* hydrochloric acid.

233.24 Mount the filter paper for counting and count under standard geometry.

234. Calculation

234.1 Calculate the activity of each iodine isotope in sodium as follows:

[29] Reeve-Angel 934 AH has been found satisfactory.

$$\text{Activity, pCi/g Na} = R \times F/A \times B \times E \times 2.2 \quad (29)$$

where:
A = weight of sodium, g,
B = count rate, counts per minute,
F = aliquot factor,
B = fraction of total disintegrations emitting measured energy, and
E = efficiency of analyzer system for gamma energy used.

234.2 No yield correction is required; the recovery is > 95 %.

235. Precision and Accuracy

235.1 Data are not available to provide information about precision and accuracy.

TRITIUM BY LIQUID-SCINTILLATION COUNTING

236. Scope

236.1 This method is applicable for determining tritium in a sodium sample by liquid-scintillation counting. This procedure, exclusive of sampling, requires about 4 h.

236.2 The detection limit is $<1 \times 10^3$ pCi/g of sodium.

237. Summary of Method

237.1 A sodium sample is dissolved carefully in water, producing tritiated hydrogen gas and a tritiated aqueous solution of sodium hydroxide. The tritium in the gas is oxidized over hot copper oxide and trapped as tritiated water. Tritium in the solution is distilled, after careful neutralization, and collected as tritiated water. The two condensates are combined, diluted to volume, and analyzed for tritium by liquid-scintillation counting.

238. Interferences

238.1 Because of the known segregation of tritium in frozen sodium samples, all tritium determinations are made on a total sodium sample collected by overflow sampling.

239. Apparatus

239.1 *Sodium Dissolution Flask and Copper Oxide Train*—See Fig. 30. The dissolution flask must be round bottomed to provide immediate and intimate contact of the added water with the sodium sample. Prepare the copper oxide train as follows:

239.1.1 Pack the quartz tube with copper turnings,

239.1.2 Heat the tube to 600°C,

239.1.3 Pass oxygen over the heated copper at a flow rate of 25 to 50 mL/min until the packing is completely black, and

239.1.4 Continue heating and passing oxygen over the copper oxide for 3 to 4 h longer.

239.2 *Liquid - Scintillation Counter*—Any commercially available low-noise liquid-scintillation counter is adequate for counting tritium.

239.3 *Water-Cooled Condenser*—The condenser must be equipped with a 45/50 standard taper joint to fit the dissolution flask.

239.4 *Heat Gun*.

240. Reagents and Materials

240.1 *Hydrochloric Acid*, concentrated.

240.2 *Liquid - Scintillation Solution*—Any scintillation solution in which water is soluble and in which water will not cause appreciable quenching is adequate; for example, a mixture of 0.5 g dimethyl POPOP (1,4-bis-2-(4-methyl-5-phenyloxazolyl)-benzene), 6.9 g PPO (2,5-diphenyloxazole), 98 g naphathalene, and 980 mL p-dioxane.

240.3 *Phenolphthalein Indicator*—Dissolve 0.1 g of phenolphthalein in 50 mL of ethanol and add 50 mL of water.

240.4 *Tritiated Water Standards*.

241. Precautions

241.1 Molten sodium in contact with air or moisture is extremely dangerous. Therefore, it is absolutely necessary that the dissolution flask be dry and completely purged of air before the sodium sample is melted out of its container into the flask. In addition, this step of the procedure shall never be attempted without a safety shield between the operator and the apparatus.

242. Calibration

242.1 Calibration is done by counting tritium standards along with samples. See step 243.18.

243. Procedure

243.1 Bring the copper oxide train to operating temperature, 600°C.

243.2 Add 75 mL of water to the reservoir of the dissolution apparatus, open the upper stopcock in the reservoir, and establish a drip rate of 1 drop every 10 to 12 s by adjusting the lower stopcock. Close the upper stopcock.

243.3 Obtain a 2 to 4-g sample of sodium by the Overflow Sampling Procedure. Borosilicate-glass or quartz beakers have been found suitable.

243.4 Transfer the protected sample into an inert-atmosphere glovebox, weigh it, and introduce it into the cleaned and dried dissolution flask. Make certain that the cup is lying on its side. Cap the dissolution flask with a standard taper plug and remove the flask from the glovebox.

243.5 Remove the plug from the dissolution flask and quickly connect the flask to the train at the inner 45/50 standard taper joint.

243.6 Start helium flowing through the flask and train at the rate of 80 to 100 mL/min and maintain this flow rate throughout the dissolution.

243.7 Continue to purge with helium for 10 min to make certain that any oxygen in the system has been completely removed before beginning the next step.

243.8 Place a safety shield between the flask and the operator, and then heat the sample in the dissolution flask with a heat gun to melt the sodium from the sample cup; allow it to spread over the bottom of the flask.

243.9 Allow the flask to cool.

243.10 Open the upper stopcock on the water reservoir to begin the dissolution of the sample. Continue the water addition at the previously established rate until the sodium is completely dissolved, including any sodium left inside the sample cup.

243.11 With the helium still flowing, gently warm with a heat gun first the inlet tube and then the outlet tube of the copper oxide train to drive any water that may have condensed at these points into the water trap.

243.12 Shut off the helium flow and remove the dissolution flask at 45/50 standard taper joint.

243.13 Carefully withdraw the sample cup into the mouth of the dissolution flask with a pair of tweezers.

243.14 Using a minimum amount of water, wash the inside and outside of the cup and the tweezer ends, making certain that all washings are introduced into the dissolution flask.

243.15 Dry and weigh the empty sample cup.

243.16 Cool the flask in an ice bath and carefully neutralize the sodium hydroxide solution to the phenolphthalein end point by addition of concentrated hydrochloric acid. Do not add any excess acid.

243.17 Connect a water-cooled condenser to the dissolution flask and distill all water from the flask. Combine this distillate with water from the trap on the copper oxide train. Dilute the solution to a known volume.

243.18 Pipet a suitable aliquot of the solution into liquid-scintillator solution, and count the sample on the liquid-scintillation counter. Count a suitable aliquot of the tritiated water standard under the same conditions. The maximum aliquot size that can be used will be dictated by the amount and type of liquid scintillation solution used. The volume of the counting vial will, in turn, dictate the volume of scintillation solution required. In general, the amount of aqueous sample must be < 20 % of the total volume.

244. Calculation

244.1 Calculate the activity of tritium in sodium as follows:

$$\text{Activity, pCi/g Na} = D_s \times R_u/R_s \times V \times A_s/B \times A_u \times 2.22 \quad (30)$$

where:

D_s = disintegration rate of standard, disintegrations per min/mL,
R_u = count rate of sample aliquot, counts per minute (cpm),
R_s = count rate of standard, cpm,
V = volume of sample solution, mL,
A_s = volume of aliquot used for standard, mL,
A_u = volume of aliquot used for sample, mL, and
B = weight of sodium g.

245. Precision and Accuracy

245.1 Data are not available to provide information about precision and accuracy.

PARTICLES BY FILTRATION

246. Scope

246.1 This method is applicable for determining particles of solids in a sodium sample. This procedure, exclusive of sampling, requires about three days.

247. Summary of Method

247.1 Particulates in sodium are collected by passing the molten sodium through a stainless-steel filter. After removal of the filter cartridge from the system, sodium is melted and drained from the cartridge, and residual sodium is removed by vacuum distillation. Particulates are separated from the stainless-steel filter by ultrasonic cleaning in xylene and then in water. The particulates are collected on membrane filters.

248. Apparatus

248.1 *Filter Element*—A stainless-steel filter with nominal 10-µm filter rating. This rating implies that the filter will remove 98 % of the particles presented to it that are 10 µm and larger.[30] Before it is installed, the filter element should be ultrasonically precleaned as specified in Section 250.

248.2 *Filter Cartridge*—A stainless-steel holder for the replaceable filter element. The cartridge, which is reusable, is an all-welded design for high-temperature systems (>400°C), or it may be a flanged-type for low-temperature use. See Fig. 31 and Fig. 32 for typical designs.

248.3 *Distillation Assembly*—An evacuable glass assembly in which the residual sodium is removed from the filter element by distillation at 400°C.

248.4 *Membrane-Filter Holder*. [31]

248.5 *Membrane Filters*, 25-mm diameter and with a pore size of 1.2 µm are required.[32]

248.6 *Ultrasonic Cleaner*—A small 80-W bath-type ultrasonic cleaner is used for removing particulates from the stainless-steel filter.

[30] Sintered metal powder elements manufactured by the Mott Metallurgical Corp., sintered metal felt elements manufactured by Fluid Dynamics, Inc., and woven elements manufactured by the Wintec Corp. have been found suitable for this a pplication.

[31] Holders for 25-mm filters, as manufactured by the Millipore Corp., have been found satisfactory for this use.

[32] Filters produced by the Millipore Corp. have been found suitable for this purpose.

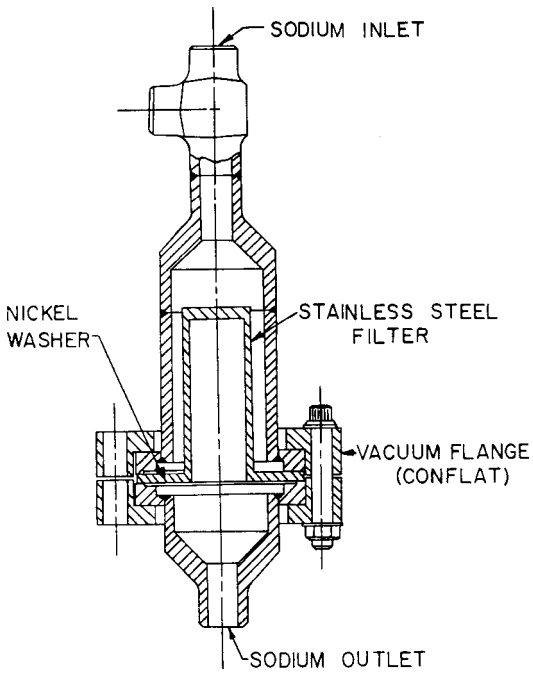

FIG. 32 Typical Flanged Filter Cartridge

248.7 *Balance*—A standard analytical balance capable of reading to the nearest 0.2 mg.

248.8 *Microscopes, (Optional)*—A low-power stereomicroscope for preliminary examination of collected particles and a petrographic microscope for particle counting and identification.

249. Reagents and Materials

249.1 *Water*—Pass distilled water through a high-quality commercial mixed-bed ion exchange column. Store in a polyethylene bottle.

249.2 *Xylene*—Store xylene over sodium, used as a drying agent, in a glass-stoppered bottle.

250. Precleaning and Testing

250.1 Ultrasonically clean the filter element in a bath of prefiltered xylene for 30 min.

250.2 Filter the bath xylene through a 1.2-μm porosity membrane filter.

250.3 Dry the membrane filter and weigh it.

250.4 Repeat steps 250.1, 250.2, and 250.3 with a new membrane filter until the weight gain is negligible (<1 mg).

250.5 Assemble the filter element in the cartridge either by bolting or welding.

250.6 Helium leak test the filter cartridge. If it is not leak tight, repair or reject the cartridge.

251. Sampling

251.1 Attach a tested and leak-tight cartridge to the system in a bypass arrangement upstream from the cold trap. Take care to avoid introduction of particulates during attachment.

251.2 Evacuate the filter cartridge (This avoids gas-bubble blockage of sodium flow).

251.3 Heat the filter cartridge and connecting lines, and then establish sodium flow.

251.4 Monitor the rate of flow through the filter to determine the volume of sodium sampled.

251.4.1 For systems <100 gal (<0.38 m^3), a volume equal to the entire sodium inventory must be passed through a filter. For systems >100 gal (>0.38 m^3), filter 100 gal (0.38 × m^3) or at least 1 % of the total inventory, whichever is greater.

251.5 Cool the cartridge and freeze the sodium.

251.6 Remove the filter cartridge from the system.

252. Procedure

252.1 In an inert-atmosphere box, scoop out some sodium at the inlet end to remove particles that may result during disconnect from the system; wrap the cartridge with heating tape and heat to approximately 125°C.

252.2 Drain the molten sodium from the filter cartridge in the direction of flow used in sampling. A small pressure, as from a rubber bulb attached to one end, will usually force the sodium out of the assembly.

252.3 Disassemble the cartridge either by removing the bolts from the flanged type or by cutting the welded type with a pipe cutter at the upstream side of the filter element.

252.4 Remove the filter element from the disassembled cartridge. This may require reheating.

252.5 Place the filter element in a glass-distillation assembly and remove it from the inert-atmosphere box.

252.6 Distill the residual sodium from the filter element at 400°C in vacuum. This may be done in a glovebox if one with the proper facilities is available.

252.7 Remove the filter element from the distillation assembly.

252.8 Ultrasonically agitate the filter element for 30 min in dry xylene that has been freshly filtered through a membrane filter of 1.2-μm porosity.

252.9 Pass the bath xylene through a 1.2-μm porosity membrane filter.

252.10 Dry the filter quickly and weigh it.

252.11 Repeat steps 252.8, 252.9, and 252.10 with new membrane filters until the weight gain is <1 mg.

252.12 Ultrasonically agitate the filter element in prefiltered water.

252.13 Filter the water through a 1.2-μm porosity membrane filter.

252.14 Dry the filter and weigh it.

252.15 If the weight of particulates on a filter exceeds 1 mg, repeat steps 252.12, 252.13, and 252.14 until the weight gain of a membrane is < 1 mg.

252.16 Calculate the concentration of particulates in the sodium.

252.17 (Optional) Perform microscopic examinations of the material collected on the membrane filters to determine particle-size distributions, to identify particles, etc.

253. Calculation

253.1 The concentration of particulates is calculated as follows:

$$\text{Particulates, } \mu g/g = (W_1 + W_2 + \ldots W_n)/S \quad (31)$$

where:

W_1 (etc.) = net weight of particulate material collected on a membrane filter, mg, and

S = weight of sodium passed through stainless-steel filter, kg.

NOTE 36—This weight may not exceed the system inventory, that is, if the total system sodium is passed through the filter more than one time, this weight is that of a single sodium inventory.

254. Precision and Accuracy

254.1 A precision and accuracy statement is not applicable to this procedure.

GASEOUS IMPURITIES IN COVER GAS BY GAS CHROMATOGRAPHY

255. Scope

255.1 The method is applicable for determining impurity gases in the cover gas using gas chromatography. A complete analysis requires two to three days.

255.2 Typical detection limits for various impurity gases are given in Table 7. This procedure is designed as a guide, in that the conditions of analysis given have been found satisfactory to achieve detection limits listed in Table 7. These conditions, however, should not be taken as the only ones that will give satisfactory results or optimum detection limits.

256. Summary of Method

256.1 Impurity gases are separated from the cover gas and determined by gas chromatography using various detector systems.

257. Apparatus

257.1 *Gas Chromatograph*—A high-quality, versatile chromatographic system is required. The wide applicability and simplicity of operation of thermal conductivity detectors makes their general use preferable for relatively high levels of most impurities. However, it will be necessary to resort to the use of helium or flame-ionization detectors to measure impurities at a level of less than a few microlitres per litre. Thermal-conductivity and flame-ionization detectors are required for the complete analysis of all cover gases, and helium-ionization detectors are required for the determination of hydrogen in helium. The variety of detectors and columns may make it practical to have two or more chromatographs set up to avoid time lost to extensive modifications. Signals from the chromatograph should be recorded with a potentiometric-type strip chart recorder with a full scale span of 1 mV or less.

257.2 *Helium Purifier*—Helium carrier gas used with the ionization detectors should be further purified by a quartz diffusion apparatus or by passage through 40 to 80-mesh 5A molecular sieve at liquid-nitrogen temperature.[33]

257.3 *Gas Handling System*—An apparatus suitable for preparing known dilutions of standard gas mixtures is desirable. A typical set up is shown in Fig. 21. Alternately, commercially prepared and analyzed gas mixtures may be used.

257.4 *Gas Sampling Loops*—Loops should be made from stainless-steel tubing and contain known volumes, typically 10 to 100 µL, and be detachable.

257.5 *Sample Trapping Systems*—The trap (Fig. 35) consists of an electrically isolated, 5 by 300 mm, thin-wall, low-carbon stainless-steel tube formed into a U. It contains sufficient 60 to 80-mesh molecular sieve 5A to fill 60 to 80 mm of tube at the bottom of the U. Provisions are made to rapidly heat the tube by direct application of low voltage, high amperage current. A combination of valves is used to move the sample onto the trap and then onto the chromatograph.[34]

257.6 *Regulators*—Metal diaphragm regulators, which may be evacuated without damage, should be used to avoid contaminating gases.[35]

257.7 *Electrolytic Oxygen Analyzer*—This type of instrument ordinarily uses a silver cathode and a lead or cadmium anode in an alkaline electrolyte.[36]

257.8 *Hygrometers*—Two hygrometers that have been calibrated by the manufacturer are required. It is convenient to connect strip chart recorders to the hygrometer. Suitable instruments operate on one of the following principals:

257.8.1 Measurement of the electrolysis current due to water absorbed in a film of phosphorous pentoxide deposited between a pair of electrodes.[37]

[33] The Electron Technology, Inc. Model SLM-1 quartz diffusion apparatus has been found satisfactory.

[34] These functions have been combined in the Model 215 Component Concentrator manufactured by SKC. Inc., Pittsburgh, PA.

[35] The Matheson Gas Products Model 3104 has been found satisfactory.

[36] Instruments manufactured by Beckman Instruments, Inc., by the Manufacturers Engineering and Equipment Co., and by Lockwood and McLorie, Inc. have been found satisfactory.

[37] Instruments manufactured by Beckman Instruments, Inc. and E. I. du Pont de Nemours and Co., Inc., have been found suitable.

TABLE 7 Typical Analytical Parameters for Determining Impurities in Cover Gas

Impurity	Sample Matrix	Column			Carrier Identity	Flow, mL/min	Detection Limit, µL/L	Detector[A]
		Packing	Dimensions, m × mm	°C				
Neon	He, Ar, N_2	5A	6.1 × 3.2	25	He	40	20	TC
							0.5	HI
Krypton	He, Ar	5A	1.8 × 6.4	50	He	40	20	TC
							0.1	HI
Krypton	N_2	5A	1.8 × 6.4	25	He	20	100	TC
							1.0	HI
Xenon	He, Ar, N_2	5A	0.9 × 6.4	100	He	40	5[B]	TC
							0.05[B]	HI
Hydrogen	He, Ar, N_2	5A	1.8 × 6.4	25	He	20	1000	TC
							0.1	HI
Hydrogen	Ar, N_2	5A	1.8 × 6.4	25	Ar	20	5	TC
Nitrogen	He, Ar	5A	1.8 × 6.4	50	He	40	20	TC
							0.1	HI
Oxygen	He, Ar, N_2	5A	1.8 × 6.4	50	He	40	10	TC
							0.1	HI
Oxygen	He, Ar, N_2	...	...	25	...	100	0.5	E
Water	He, Ar, N_2	...	...	25	...	200	1.0	H
Carbon Monoxide	He, Ar, N_2	Porapak Q	3.7 × 3.2	55	He	20	5[B]	TC
							0.1[B]	FI
Carbon Dioxide	He, Ar, N_2	Porapak Q	3.7 × 3.2	55	He	20	10	TC
							0.1	FI
Methane	He, Ar, N_2	Porapak Q	3.7 × 3.2	55	He	20	5	TC
							0.1	FI
Total Hydrocarbons	He, Ar, N_2	None	0.3 × 3.2	25	He	20	1.0	FI

[A] Detectors: TC = Thermal Conductivity, HI = Helium Ionization, FI = Flame Ionization, E = Electrolytic, H = Hygrometer.
[B] Based on concentrating impurity from 100-mL sample by cold trapping. Detection limit can be decreased by use of lar ger samples.

257.8.2 Measurement of capacitance, which varies with water absorbed by an aluminum-aluminum oxide-gold capacitor.[38]

258. Reagents and Materials

258.1 *Carrier Gases*:

258.1.1 *Argon*, ≥99.998 % for carrier gas.

258.1.2 *Helium*, ≥99.995 % for carrier gas. Further purification is necessary for use with ionization detectors.

258.1.3 *Hydrogen*, ≥99.95 % for flame-ionization detector.

258.2 *Methanation Catalyst*—A 60 to 80-mesh mixed-oxide catalyst.[39]

258.3 *Standard Gases*:

258.3.1 *Argon* ≥99.9999 %.

258.3.2 *Carbon dioxide*, ≥99.96 %.

258.3.3 *Carbon monoxide*, ≥99.5 %.

258.3.4 *Helium*, ≥99.9999 %.

258.3.5 *Hydrogen*, ≥99.9 %.

258.3.6 *Krypton*, ≥99.9 %.

258.3.7 *Methane*, ≥99.9 %.

258.3.8 *Neon*, ≥99.9 %.

258.3.9 *Nitrogen*, ≥99.9999 %.

258.3.10 *Xenon*, ≥99.9 %.

NOTE 37—See 257.3 and Fig. 19 regarding blending the above gases to prepare standard gas mixtures.

259. Precautions

259.1 The usual safety precautions should be followed for handling evaluated and pressurized glassware, compressed gases in cylinders, liquified cryogenic gases, catalysts in the reduced (pyrophoric) state, and catalyst dust containing chromia.

260. Calibration

260.1 Establish the analytical parameters for the required analysis using Table 7 for guidance.

260.2 Bring the chromatograph to stable operating conditions with suitably conditioned columns. Condition columns by the procedure recommended by the packing manufacturer.

260.3 Elute a series of standards throughout the chromatograph and plot calibration curves of peak height versus microlitres at NTP of impurity for each impurity to be measured.[40]

NOTE 38—The standards used will depend on the impurities determined.

261. Procedure

261.1 *General Procedure*:

261.1.1 Follow steps 260.1 and 260.2.

261.1.2 Elute known volumes of the sample at NTP through the chromatograph under the same conditions as used for the standards.

261.1.3 Identify the impurities by their retention times and determine the microlitres of each impurity in the sample by relating the peak heights to the appropriate calibration curves.

NOTE 39—The following comments are given to aid in selecting operating procedures and in interpreting chromatograms.

(1) The elution order on molecular sieve columns at 25°C is: H_2 + He, Ar + O_2, N_2, Kr, CH_4, Xe, and CO.

(2) The elution order on Porapak Q columns at 25°C is: H_2 + Ne + Ar + O_2 + N_2 + CO, CH_4 + Kr, CO_2, and Xe.

(3) The elution order on silica gel columns at 25°C is: H_2 + He + Ne + Ar + O_2 + N_2, CO, CH_4, Kr, and Xe.

(4) Longer columns and lower temperatures improve separations, but decrease sensitivity.

(5) Although peak height measurements are mentioned as the only indication of detector response, in certain cases (particularly for large retention times and broad peaks) the measurement of peak area may be a more suitable choice.

261.2 *Procedure for Methane, Carbon Monoxide, and Carbon Dioxide Using Cold Trapping and Flame-Ionization Detection*:

261.2.1 Establish the analytical parameters from Table 7 and the apparatus from Fig. 33.

261.2.2 Bring the chromatograph to stable operation. The sensitivity of the flame ionization detector may require the use of stainless-steel columns cleaned with 2 *M*-nitric/7 *M*-hydrofluoric acid and tightly packed with Porapak Q which has been dried overnight at 200°C. The packed column should be conditioned in the chromatography by purging with carrier gas for an hour at 200°C.

261.2.3 Activate the catalyst by the manufacturer's procedure. Typically this consists of slowly heating the material to 350 to 400°C in a reducing atmosphere.

261.2.4 Chill the trap with partially frozen acetone and flush a known amount of standard into the trap with carrier gas.

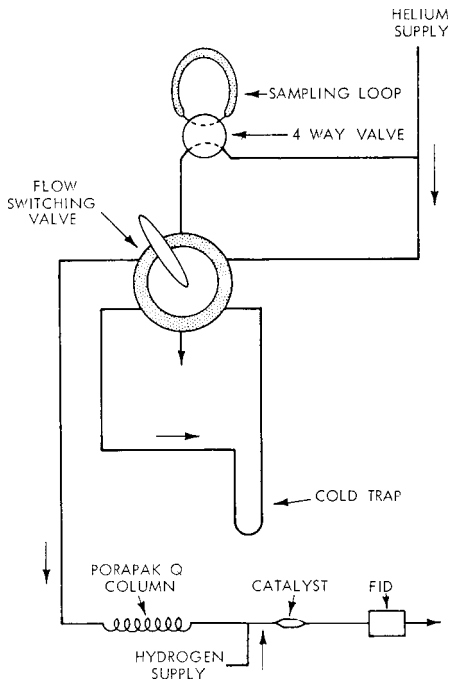

FIG. 33 Typical Apparatus for Determining Carboniferous Cover Gas Impurities

[38] Instruments manufactured by Panametrics, Inc. have been found suitable.

[39] Katalco 11-2, a product of Katalco Corp., 180 N. Michigan Avenue, Chicago, IL, has been found suitable for this purpose.

[40] NTP is an abbreviation for "normal temperature and pressure" (for example, 25°C and 750 mm Hg) to which all gas samples are adjusted.

Switch the trap into the chromatograph stream. Remove the ethanol and heat the trap to 280°C in less than 15 s. Record the chromatogram.

261.2.5 Trap and elute known volumes of sample at NTP through the chromatograph under the same conditions used for the standards. Identify impurities by their retention times and determine microlitres of each impurity by relating peak heights to the appropriate calibration curves.

NOTE 40—Liquid argon may be substituted for partially frozen acetone if the sample matrix is helium or nitrogen, and liquid nitrogen may be substituted if the sample matrix is helium. If liquid argon or nitrogen is used, Porapak Q may be substituted for the molecular sieve trap packing. Release of the trapped gases is then accomplished by heating the trap to 90°C with hot water.

261.3 *Procedure for Xenon Using Cold Trapping*:

261.3.1 Establish the analytical parameters from Table 7. Connect the sample trapping system (Fig. 35) to a chromatograph using thermal conductivity or helium ionization detectors.

261.3.2 Bring the chromatograph to stable operating conditions with suitably conditioned columns. Condition the columns as recommended by the packing manufacturer.

261.3.3 Chill the trap with dry ice-alcohol mixture and flush a known amount of xenon into the trap with carrier gas. Switch the trap into the chromatograph stream. Remove the coolant and heat the trap to 200°C in less than 15 s. Record the chromatogram.

261.3.4 Trap and elute known volumes of sample, at NTP, through the chromatograph under the same conditions as used for the standards. Determine microlitres of xenon in the sample by relating peak height to the calibration curve.

261.4 *Procedure for Water Using Hygrometers*:

261.4.1 Simultaneously expose the detectors of two hygrometers to the sample gas flowing at 100 to 500 mL/min at NTP through a small chamber. Operate the hygrometers in accordance with the manufacturer's instructions.

261.4.2 When both hygrometers readings have stabilized, record the water content of the sample.

261.4.3 If the two readings are spread by less than 10 % or not more than 2 μL/L, report the average as the water content of the gas sample. Otherwise repeat the reading with a third hygrometer that has recently been calibrated or hold the sample until the hygrometers can be returned to the manufacturer for recalibration.

261.5 *Procedure for Oxygen Using an Electrolytic Analyzer*:

261.5.1 Alternately pass high-purity helium and a standard mixture of oxygen in helium through the oxygen analyzer to verify the calibration.

261.5.2 Pass the sample gas through the analyzer and record the indicated oxygen concentration of the sample.

262. Calculation

262.1 Calculate the concentration in microlitres per litre of each impurity using the following equation:

$$\text{Impurity } (\mu L/L) = A \times 1000/B \quad (32)$$

where:

A = volume of impurity in sample, μL, and
B = volume of sample, mL.

263. Precision and Accuracy

263.1 *Precision*—When concentrations are 10 times the detection limit, limited data indicate that the range of replicate determinations made from the same should be no greater than 20 % (relative).

263.2 *Accuracy*—No standards are available for accuracy assessment. The gas chromatograph is calibrated with known quantities of given gases to eliminate bias in the measurements.

264. Keywords

264.1 breeder reactors; cover gas; reactor coolant; sodium metal

REFERENCES

(1) Takaishi and Sensui, "Thermal Transpiration Effect of Hydrogen, Rare Gases and Methane," *Trans. Faraday Soc. 59,* 1963, pp. 2503–2514.
(2) J. Van R. Smit, et al, "Cation Exchange Properties of the Ammonium Heteropoly Acid Salts," *J. Inorganic and Nuclear Chem. 12,* 1959, p. 95.
(3) J. E. Cline, "Studies of Detection Efficiencies and Operating Characteristics of Ge(Li) Detectors," *IEEE Trans. on Nuclear Science,* Vol. NS15, No. 3, 1968, pp. 198–213.
(4) R. L. Heath, "Scintillation Spectrometry Gamma-Ray Catalogue," 2nd Edition, *USAEC Report IDO-16880,* 1964.