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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.

ϵ^1 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:

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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

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[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.

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[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·atm/s ($<1 \times 10^{-8}$ m^3·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·atm/s ($<1 \times 10^{-8}$ m^3·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.

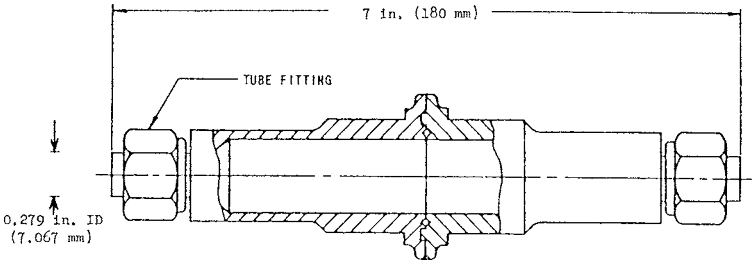

FIG. 1 Typical Sample Vessel

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

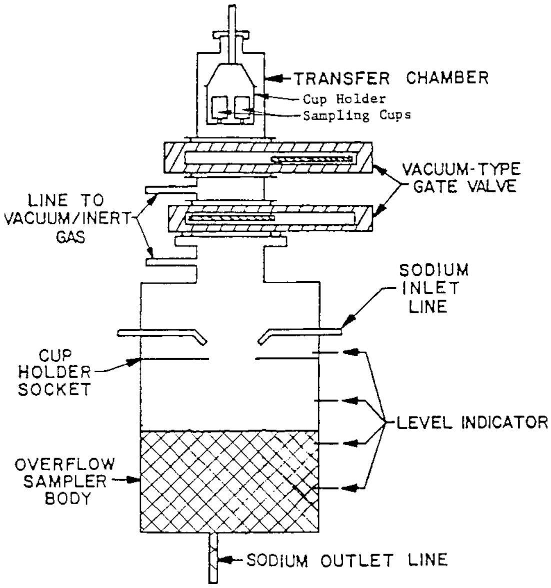

FIG. 2 Typical Overflow Sampler with Transfer Chamber Attached

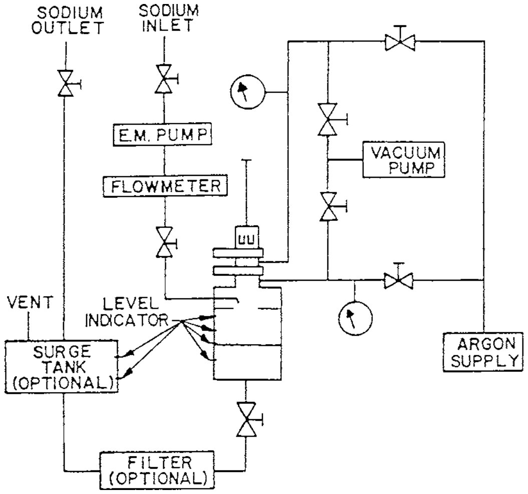

FIG. 3 Typical Sampling System

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,

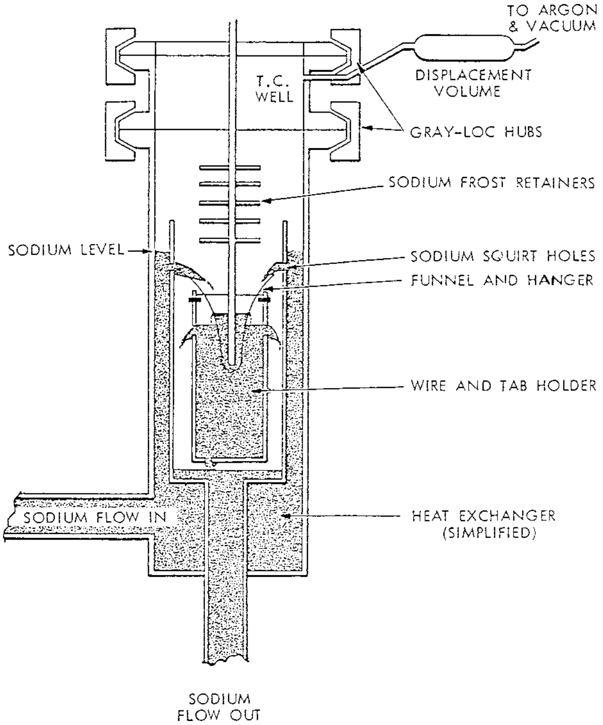

FIG. 4 Multipurpose Sampler

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.

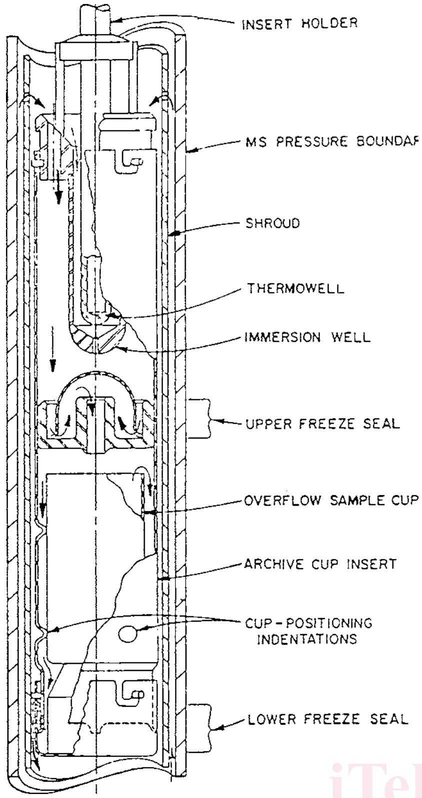

FIG. 5 Overflow Insert for Multipurpose Sampler

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.

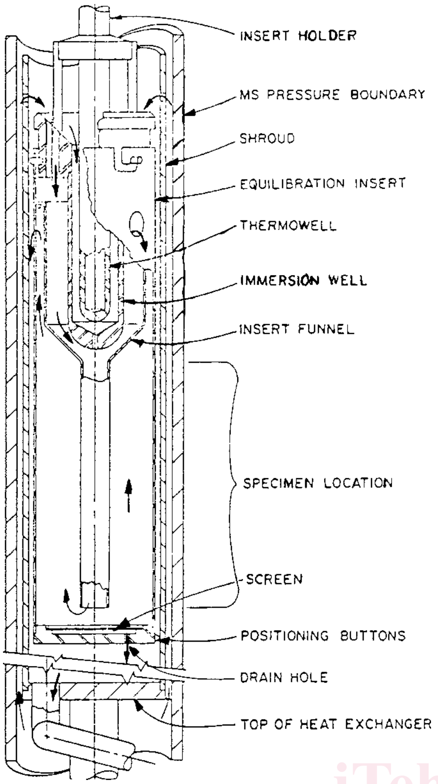

FIG. 6 Equilibrium Insert for MPS

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*.

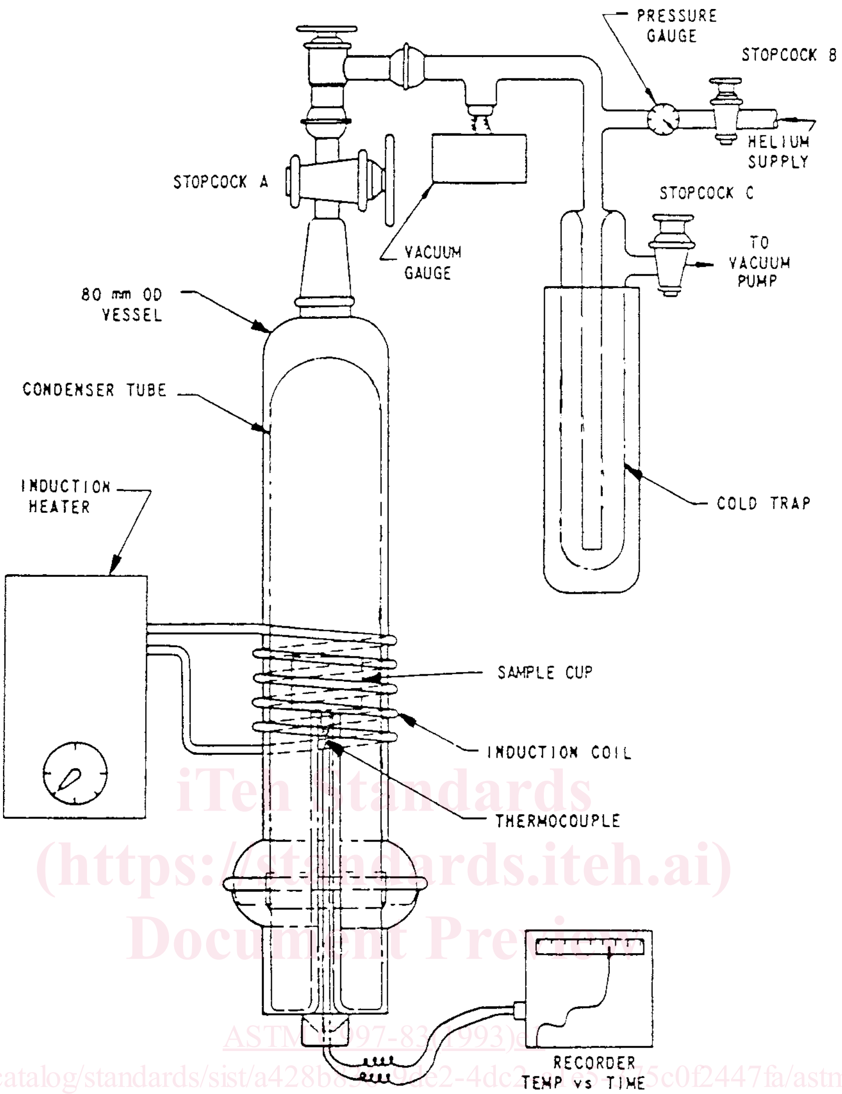

FIG. 7 Typical Vacuum Distillation Assembly

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.

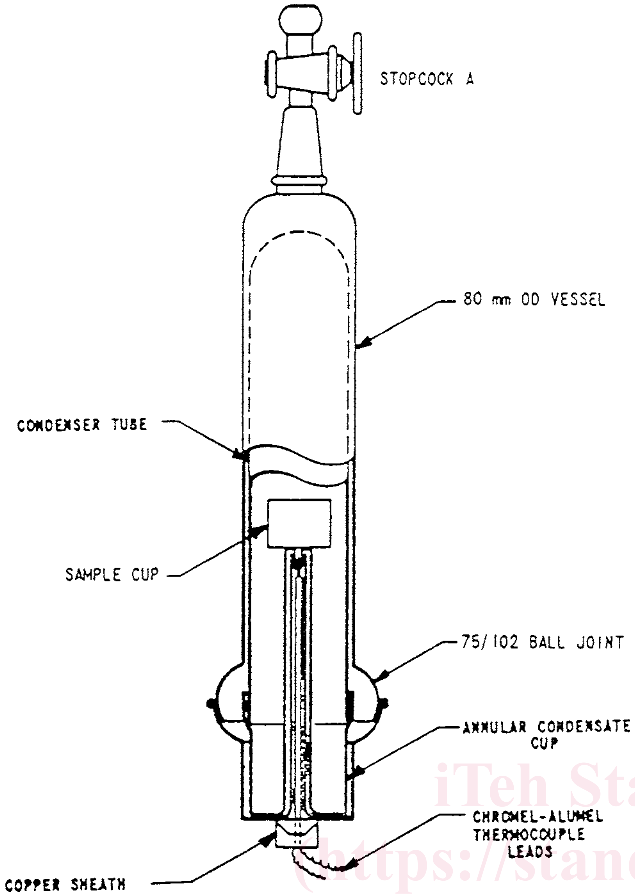

FIG. 8 Typical Sodium Distillation Unit

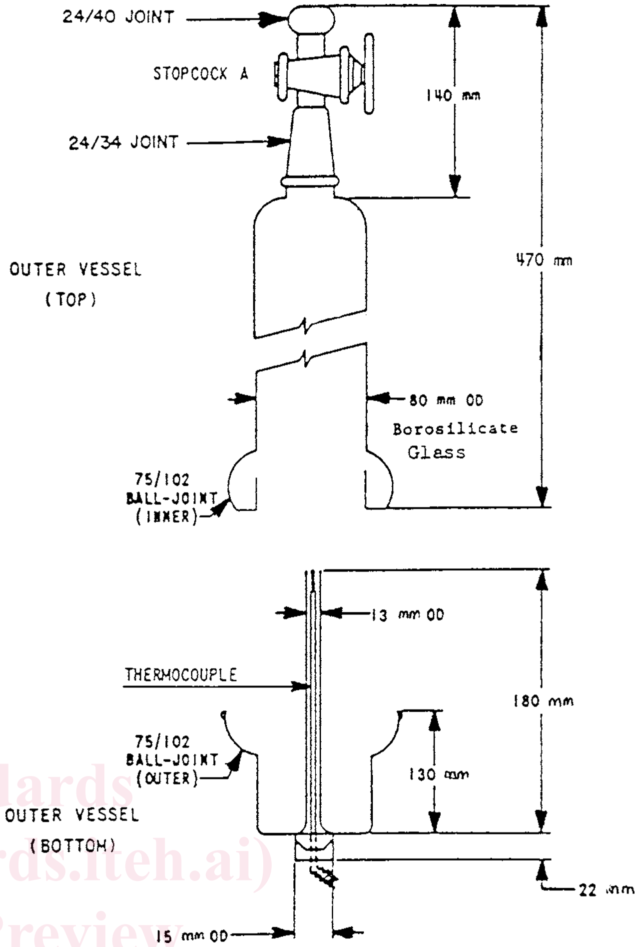

FIG. 9 Dimensions of a Typical Distillation Unit Shell

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.

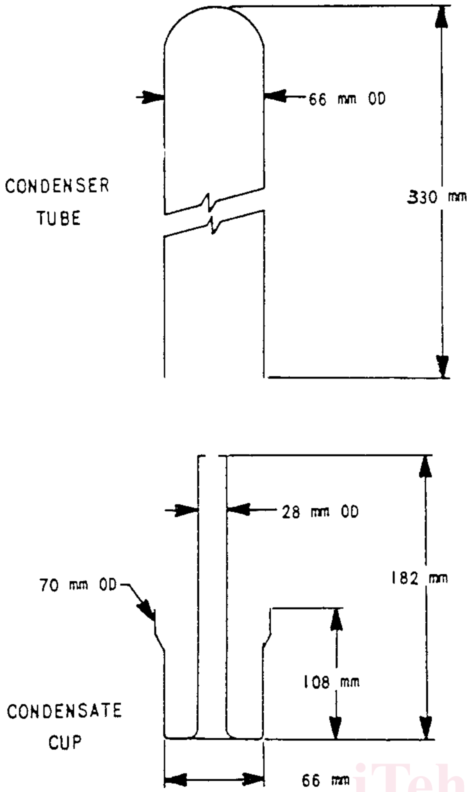

FIG. 10 Dimensions of a Typical Condenser System

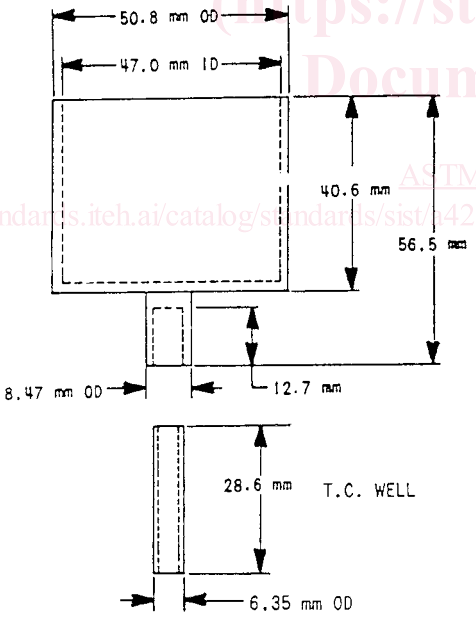

FIG. 11 Typical Sample Cup with Thermocouple Well

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.

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

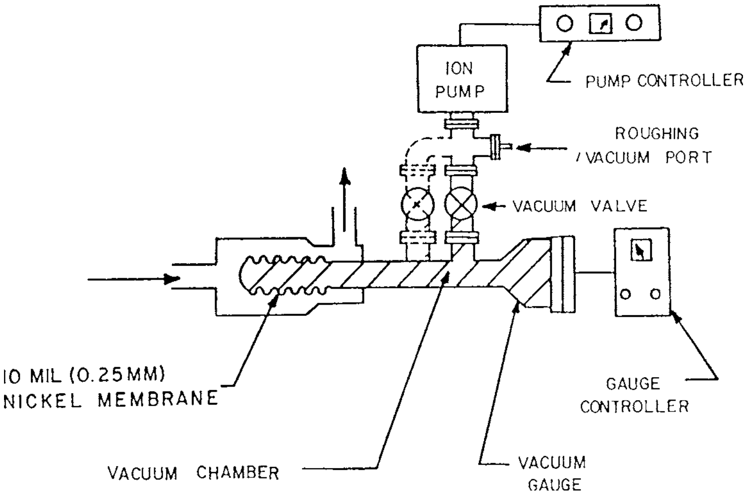

FIG. 12 Schematic Representation of a Typical Hydrogen Meter

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:

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

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

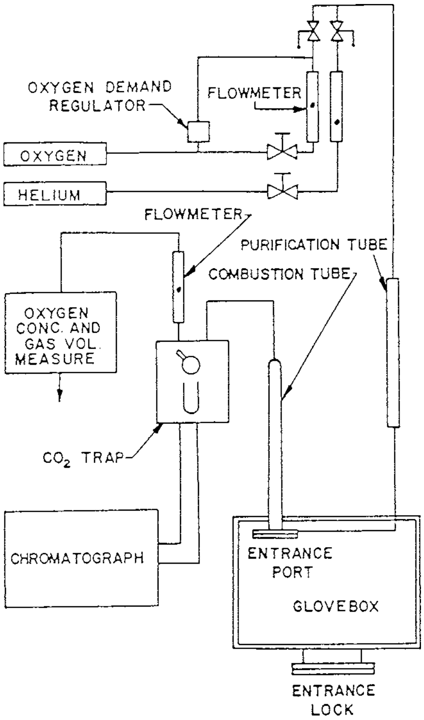

FIG. 13 Block Diagram of Analytical System

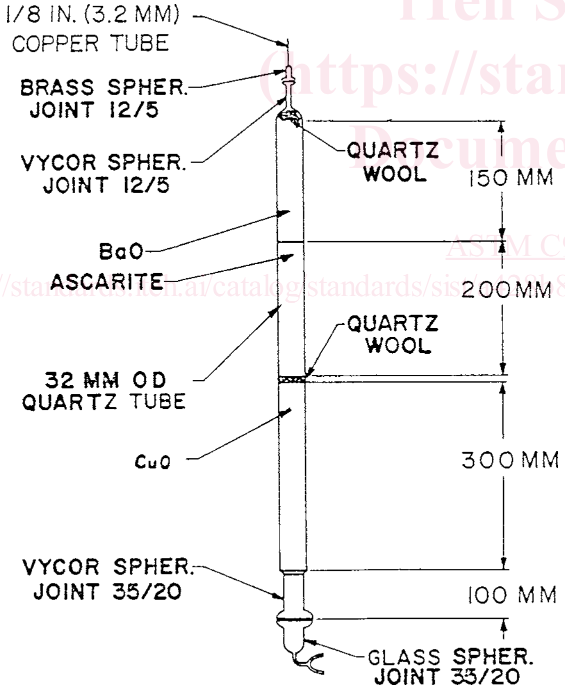

FIG. 14 Typical Gas Purification Tube

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.

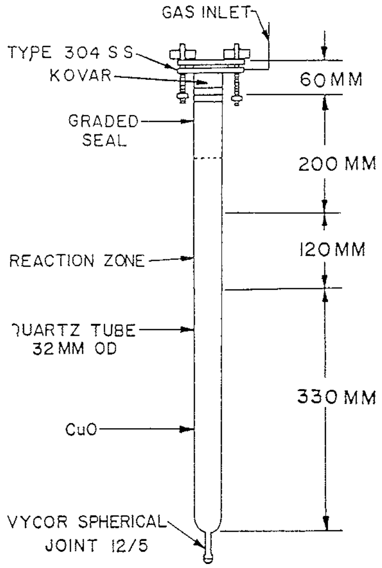

FIG. 15 Typical Combustion Tube

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.

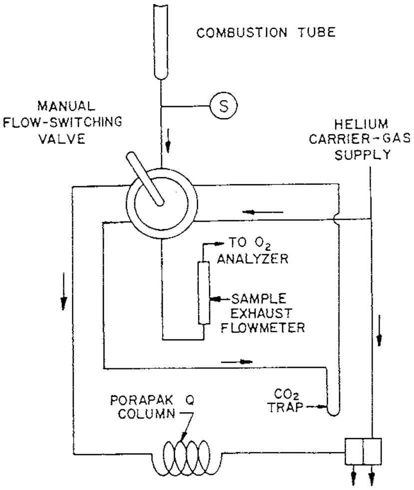

FIG. 16 Carbon Dioxide Measurement System

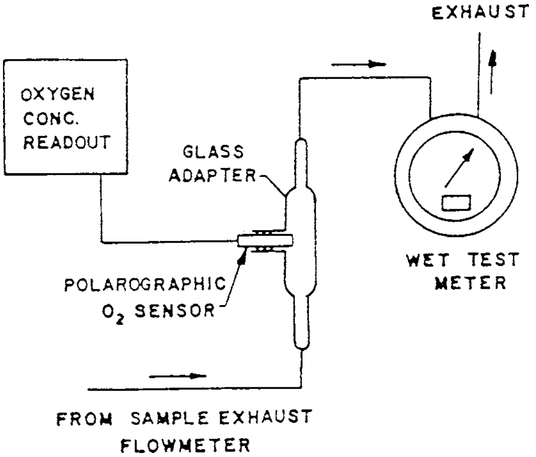

FIG. 17 Train Gas Composition and Volume Measurement

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 $\frac{1}{8}$-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

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[9] The SKC, Inc. Model 215 Component Concentrator has been found suitable for this application. A $\frac{3}{16}$-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 $\frac{1}{4}$-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.

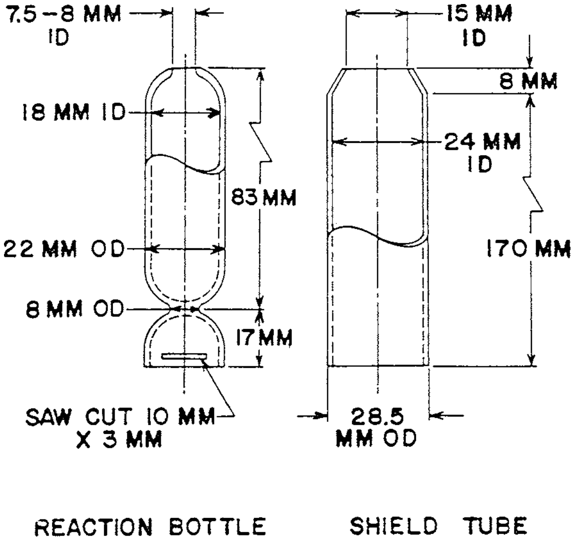

FIG. 18 Typical Reaction Bottle and Shield Tube

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.