RDT Standard

METHODS FOR THE ANALYSIS OF SODIUM
AND COVER GAS

JANUARY 1973

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METHODS FOR THE ANALYSIS OF SODIUM AND COVER GAS

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1. SCOPE

This standard provides the sampling and analytical procedures that are to be used in implementing operating and purchase purity specifications for sodium and cover gas. It provides procedures for the following:

1. Analysis of sodium and cover gas from reactor primary, secondary, and auxiliary loop systems and from large and small test and experimental systems.
2. Analysis of purchased sodium.
3. Analysis of purchased cover gas.
4. Treatment of data.
5. Packaging of samples for shipment or storage.

2. APPLICABLE DOCUMENTS

The following documents are a part of this standard to the extent specified herein. The issue of a document in effect on the date of invitation to bid, including any amendments also in effect on that date, shall apply unless otherwise specified. Where this standard appears to conflict with the requirements of a referenced document, such conflict shall be brought to the attention of the purchaser for resolution.

2.1 RDT STANDARDS

RDT C 8-6T - Hydrogen Meter for Service in Liquid Sodium.

RDT C 8-8T - Specimen Equilibration Device for the Analysis of Nonmetals in Liquid Sodium.

RDT F 7-2T - Preparations for Sealing, Packaging, Packing, and Marking of Components for Shipment and Storage.

RDT M 3-2T - Stainless and Alloy Steel Seamless Tubes (ASME SA-213 with Additional Requirements).

2.2 GOVERNMENT STANDARDS AND SPECIFICATIONS

14 CFR: Code of Federal Regulations, Title 14, "Aeronautics and Space." (Superintendent of Documents, Government Printing Office, Washington, D.C. 20402).

49 CFR: Code of Federal Regulations, Title 49, "Transportation," (Superintendent of Documents, Government Printing Office, Washington, D.C. 20402).

R. M. Graziano's Tariff No. 25, "Hazardous Materials Regulations of the Department of Transportation Including Specifications for Shipping Containers". (Issued by R. M. Graziano, Agent, 1920 L Street, N.W., Washington, D.C. 20036).

MIL-S-27626C (USAF) - Sampler, Liquid Oxygen TTU-131/E.

Official Air Transport Restricted Articles Tariff No. 6-D, Governing the Transportation of Restricted Articles by Air. (Issued by C. C. Squire, President and General Manager, Airline Tariff Publishers, Inc., 1825 K Street N.W., Washington, D.C. 20006).

2.3 AMERICAN SOCIETY FOR TESTING AND MATERIALS

ASTM A 510, General Requirements for Carbon Steel Hot-Rolled Wire Rods and Round Wire.

ASTM D 1428, Sodium and Potassium in Water and Water-Formed Deposits by Flame Photometry.

ASTM E 146, Chemical Analysis of Zirconium and Zirconium-Base Alloys.

ASTM E 178, Dealing with Outlying Observations.

2.4 OTHER DOCUMENTS

J. E. Cline, "Studies of Detection Efficiencies and Operating Characteristics of Ge(Li) Detectors", *IEEE Trans. on Nuclear Science*, Vol NS15, No. 3, pp 198-213 (1968).

R. L. Heath, "Scintillation Spectrometry Gamma-Ray Catalogue", 2nd Edition, USAEC Report IDO-16880 (1964).

Laboratory Equipment Company, "Instruction Manual for the R0-16 Oxygen Determinator Model 760-400". Form Number 200-065 (5-23-72).

Matheson Gas Products, "Matheson Gas Data Book", 5th Edition, Matheson Gas Products, East Rutherford, New Jersey (1971).

J. Van R. Smit *et.al.*, "Cation Exchange Properties of the Ammonium Heteropoly Acid Salts", *J. Inorganic and Nuclear Chem.* 12, 95 (1959).

Takaishi & Sensui, "Thermal Transpiration Effect of Hydrogen, Rare Gases and Methane," *Trans. Faraday Soc.* 59, 2503-2514 (1963).

3. SODIUM SAMPLING

It is recognized that sampling is an important and integral part of any analytical method and that, in principle, a complete analytical method should incorporate the sampling details along with other procedural details. However, in situations where a sampling procedure is required in a number of methods, practicality and convenience dictate that a separate section, appropriately cross-referenced, is more useful and more apropos. Such a situation exists in the case of both the bypass and the overflow sampling procedures. Therefore, separate treatment of these procedures is given below.

3.1 BYPASS SAMPLING

This procedure is required for the determination of hydrogen by the amalgam-reflux method, carbon by the oxyacidic flux method, oxygen by amalgamation, and nitrogen by the Kjeldahl method, (Sections 5, 7, 11, and 13). In addition, it may be used for the determination of cyanide, potassium, rubidium and cesium, tritium, and the purity of purchased sodium (Sections 10, 17, 18, 27, and Appendix I.)

3.1.1 Principle

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

3.1.2 Apparatus

Sampling Vessel. This vessel may be (a) a section of seamless metal tubing, for example, stainless steel tubing purchased per RDT M 3-2, having an ID $>3/8$ in. and an internal finish of 32 microinches RMS, or better; or (b) a vessel of the type shown in Fig. 3-1. The vessel in Fig. 3-1 consists of two matching sections clamped together; its main body, which has an ID of 0.855 in., tapers at each end to an ID of 9.279 in. Both types of vessel may be made of either nickel or stainless steel. Attachment of the vessel to a system is done by a mode of coupling consistent with locally-approved safety practices (see 3.1.4 Safety). The vessel must have provisions for heating it and maintaining it at the temperature of interest.

3.1.3 Procedure

1. Rinse the sampling vessel successively with dilute nitric acid, water, and acetone. Dry, cap, and store until used.
2. Attach the sampling vessel to the system in a manner consistent with local safety practices (see 3.1.4 Safety).
3. Check the sampling system for leaks according to locally-approved operating and safety practices. Helium leak testing should be⁻⁷ employed whenever possible. In that case, a helium leak rate of $<1 \times 10^{-7}$

Fig. 3-1

Typical Sample Vessel

cc-atm/sec through the connectors or welds should be attained. For systems which can tolerate introduction of small amounts of gas, this step may be replaced by 3a.

3a. Purge the vessel with purchased cover 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 (see 3.1.5 Discussion). Check the sampling system for leaks, according to locally-approved operating and safety practices. Helium leak testing should be employed whenever possible. In that case, a leak rate of $<1 \times 10^{-7}$ cc-atm/sec through the connector or welds should be attained.

4. Heat the entire sampling vessel system to a temperature greater than 212 F (100 C), 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 300 F (150 C).

5. Establish sodium flow by opening the outlet and inlet valves in the proper sequence. If step 3a has been used, the sequence of opening first the outlet and then the inlet valve is desirable because by this sequence the gas pressure in the vessel is relieved to the outlet line.

6. Adjust the sodium flow rate, if necessary. A *minimum* flow rate of 0.1 gpm should be maintained.

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

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 3-1 gives the minimum equilibration time required at several selected temperatures.

TABLE 3-1

Temperature of Sampling Vessel		Minimum Equilibration Time, hr
F	C	
1000	540	1
600	320	4
450	230	5 ^a

^a After equilibrating first at 600 F (320 C) for 1 hr (see 3.1.5 Discussion).

At temperatures between those given, the equilibration time should be established by interpolation. If the sample is to be used for the determined of hydrogen, prolonged flow (>24 hr) at any temperature is advantageous for reducing tubing blanks.

Note: The following three steps, 9 through 11, illustrate a typical sampling shut-down procedure. The actual steps used should conform to locally approved operating and safety procedures.

9. Close the outlet valve.

10. Cool the sample to the freezing point of sodium, 212 F (100 C), as quickly as operational limitations will allow.

11. Close the inlet valve, de-energize all sample heaters, and remove the sampling vessel, after further cooling to insure that inlet and outlet lines are frozen.

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

13. Deliver the vessel to the laboratory.

3.1.4 Safety

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 750 F; however, at low pressures, Swagelok and Conoseal fittings can be used successfully at temperatures moderately above 750 F. The fittings must be installed, maintained, and monitored according to locally-approved safety practices.

3.1.5 Discussion

This procedure, exclusive of equilibration time, requires approximately 4 hr.

The optional step, 3a in Section 3.1.3, to be used with sodium systems which can tolerate the introduction of gas and small amounts of contamination, eliminates the evacuation of the vessel as a necessary step in the sampling procedure. The rationale for this option is as follows: 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 which may be introduced as a result of the optional step. Hence, the evacuation of the sampling vessel is a time-consuming step which unnecessarily complicates the procedure.

The requirement given in Table 3-1 that for sampling at 230 C (450 F) the sample vessel be equilibrated for 1 hr at 320 C (600 F) and then for 5 hr at 230 C (450 F) arises from the fact that sodium does not appreciably wet stainless steel at 230 C.

3.2 OVERFLOW SAMPLING

This procedure is required by the determination of methanides and acetylides, carbon dioxide released by aqueous dissolution, fluoride, metals in a distillation residue, cadmium and zinc, silicon, boron, uranium, plutonium, general gamma assays, iodine, and chloride. It also is required for the determination in purchased sodium of (a) carbon, (b) purity and potassium, and (c) lithium, calcium, chloride, boron, and uranium. (Sections 8, 9, 14, 15, 16, 19, 20, 21, 22, 23, 24, 25, and Appendixes E, H, J and K.) In addition, this procedure may be used for the determination of cyanide, potassium, tritium, and of the purity of purchased sodium (Sections 10, 17, 27, and Appendix I).

3.2.1 Principle

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

3.2.2 Apparatus

Overflow Sampler. A typical device is pictured in Fig. 3-2. The body of the sampler is a flanged stainless steel pot. The captions in the figure show the other essential features of the sampler.

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

Sample Cup. This vessel may be a distillation cup or a beaker. It may be constructed of any material which will not contaminate either the sampled system or the sample itself at sampling temperature and which 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 which is acceptable is specified in each of the methods which use overflow sampling.

Transfer Chamber. A typical transfer chamber is shown in Fig. 3-2 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 makes a sliding seal through the O-ring and 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. 3-2. 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 (i.e. unvalved) transfer chambers ordinarily will accept a holder for four sample cups.

Sampling System. A typical and functionally adequate piping system for taking sodium samples is shown in the schematic drawing, Fig. 3-3. In the system as pictured, sodium enters through a normally-closed pneumatic bellows valve with the bellows downstream. Flow then is through an electromagnetic pump and electromagnetic flowmeter, next through a manually-operated bellows valve into the multiple spouts of the overflow sampler. Sodium leaves the sampler at the bottom, passes through another manually-operated bellows valve, through an optional filter and optional surge tank (see Discussion Section) and exits through a normally-closed pneumatic bellows valve with the bellows upstream.

Fig. 3-2

Typical Overflow Sampler with Transfer Chamber Attached

Fig. 3-3

Typical Sampling System

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

Additional requirements on the system are included under Safety.

3.2.3 Procedure

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

3.2.3.1 Procedure for Protected Samples

1. Wash tantalum sampling cups successively with hydrofluoric acid, aqua regia, demineralized water, and acetone. Wash titanium, quartz, and borosilicate glass cups successively with aqua regia, demineralized water, and acetone.
2. Dry the cup in an oven at 110 C.
3. Cool the cup to room temperature, grasp it with tongs, weigh it, and transfer it to the cup holder of the valved transfer chamber.
4. Retract the cup holder into the transfer chamber and close the gate valve.
5. Bring the transfer chamber to the overflow sampler and bolt or clamp the chamber to the sampler with a vacuum-tight seal.
6. Open the transfer chamber gate valve but keep the sampler gate valve closed.
7. Evacuate the chamber and back fill it with inert gas for three cycles.
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.
9. If there are unacceptable leaks, correct them and repeat the chamber flushing and leak test.
10. Pressurize the overflow sampler to the sodium system pressure.
11. Adjust the pressure in the transfer chamber to the pressure in the overflow sampler.
12. Open the gate valve at the top of the overflow sampler.
13. Lower the cup holder to the collection position and seat it in the socket provided in the overflow sampler.
14. Unscrew and raise the insertion rod.
15. Close the overflow sampler gate valve.

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. Readjust the pressure in the overflow sampler to match the system pressure.
18. Start sodium flow in the sampler by opening the outlet and inlet valves in the appropriate order.
19. Adjust the sodium level in the sampler by changing the inert gas pressure to bring the sodium-gas interface below the sample cups.
20. Maintain sodium flow for the collection time. Normally, a flow rate of 0.1 gpm or more should be maintained for at least 15 min.
21. Stop the sodium flow by closing inlet and outlet valves.
22. Shut off the heaters on the sampler inlet and outlet lines and allow the sodium in them to freeze. In those systems in which the sodium will be kept molten, this step is unnecessary.
23. Adjust the pressure in the transfer chamber to the pressure in the overflow sampler.
24. Open the sampler gate valve.
25. Lower the insertion rod and screw it into the cup holder.
26. Retract the cup holder into the transfer chamber.
27. Close the transfer chamber gate valve and sampler gate valve.
28. Shut off the heaters on the sampler and allow the sodium in it to freeze. In those systems in which the sodium will be kept molten, this step is unnecessary.
29. Allow the sodium samples to freeze if they are not already solid.
30. Remove the transfer chamber and install another chamber with clean cups.
31. Dispatch the transfer chamber with filled cups to the laboratory.

3.2.3.2 Procedure for Unprotected Samples

1. Wash tantalum sampling cups successively with hydrofluoric acid, aqua regia, demineralized water, and acetone. Wash titanium, quartz, and borosilicate glass cups successively and aqua regia, demineralized water and acetone.

-
2. Dry the cup in an oven at 110 C.
  3. Cool the cup to room temperature, grasp it with tongs, weigh it, and transfer it to the cup holder of the transfer chamber.
  4. Retract the cup holder into the transfer chamber and close the chamber opening temporarily with aluminum foil or a clamp-on flange.
  5. Bring the transfer chamber to the sampler and bolt or clamp the chamber to the sampler with a vacuum-tight seal.
  6. Evacuate the chamber and back fill it with inert gas for three cycles.
  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.
  8. If there are unacceptable leaks, correct them and repeat the chamber flushing and leak test.
  9. Pressurize the overflow sampler to the sodium system pressure.
  10. Adjust the pressure in the transfer chamber to the pressure in the overflow sampler.
  11. Open the gate valve at the top of the overflow sampler.
  12. Lower the cup holder to the collection position and seat it in the socket provided in the overflow sampler.
  13. Unscrew and raise the insertion rod.
  14. Close the overflow sampler gate valve.
  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 are kept molten, this step will be unnecessary.
  16. Readjust the pressure in the overflow sampler to match the system pressure.
  17. Start sodium flow to the sampler by opening the outlet and inlet valves.
  18. Adjust the sodium level in the sampler by changing the inert gas pressure to bring the sodium-gas interface below the sample cups.
  19. Maintain sodium flow for the collection time. Normally, a flow rate of 0.1 gpm or more should be maintained for at least 15 min.

20. Stop the sodium flow by closing the inlet and outlet valves.
21. Shut off the heaters on the sampler inlet and outlet lines and allow the sodium in them to freeze. In those systems in which the sodium in the sampler and piping will be kept molten, this step is unnecessary.
22. Adjust the pressure in the transfer chamber to the pressure in the overflow sampler.
23. Open the sampler gate valve.
24. Lower the insertion rod and screw it into the cup holder.
25. Retract the cup holder into the transfer chamber.
26. Close the sampler gate valve.
27. Shut off the heaters on the sampler and allow the sodium in it to freeze. In those systems in which the sodium will be kept molten, this step is unnecessary.
28. Allow the sodium samples to cool to room temperature.
29. Unbolt and remove the transfer chamber.
30. Transfer the samples to the laboratory according to one of the following plans:
  - a. 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.
  - b. Transfer the cup holder to an evacuable transfer vessel. (This may be a shatterproof vacuum desiccator). Close and evacuate the transfer vessel. Transfer the samples to the laboratory and into an inert-atmosphere box.

3.2.4. Safety

In contrast to the analytical procedures, which are expected to be performed in an environment under control of the analyst, the sampling procedures must be integrated with the operational and safety procedures which apply to the system being sampled.

To meet the operational restraints of some systems, this functionally adequate procedure must be expanded to include the following: (1) a leak detection system deemed adequate by local safety officials, (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, and (3) the necessary biological shielding and provision for remote operation of radioactive systems and of other systems considered hazardous because of high sodium pressures or temperatures.

3.2.5 Discussion

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

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true. If oxide and hydroxide formed in the sampler and washed back into the system will not cause unacceptable excursions in system sodium 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.

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 3.2.1 through 3.2.4.

The discussion of the sampling system and of Figure 3-3 mentioned an optional surge tank. In the 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; and the accumulated gas should be vented as necessary.

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

4. LABORATORY DISTILLATION OF SODIUM

This procedure is required for the determination of fluoride, selected metals, silicon, boron, uranium, plutonium, nonvolatile alpha assay, general gamma assay, and chloride (Sections 14, 15, 19, 20, 21, 22, 23, 24, and Appendix E).

4.1 PRINCIPLE

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

4.2 APPARATUS

Distillation Assembly (as shown in Fig. 4-1). This typical assembly is made up of the following units:

Distillation Unit. The distillation unit, shown in Fig. 4-2, is made of borosilicate glass. Details of the outer shell and the stopcock assembly appear in Fig. 4-3. The condenser system is detailed in Fig. 4-4.

Sample Cup with Thermocouple Well. A typical sample cup design is shown in Fig. 4-5. The cup may be constructed of either tantalum or titanium. Tantalum is commercially available with purity >99.95%, exclusive of interstitial elements. The thermocouple well extends into the cup's pedestal.

Thermocouple. A chromel-alumel thermocouple is installed in the bottom part of the outer shell, as shown in Fig. 4-3. The thermocouple must make good physical contact with the bottom of the distillation cup.

Vacuum Gauge and Associated Control. The gauge should be suitable for measuring 1×10^{-3} torr.

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

Induction Generator. A satisfactory generator is one rated at 2.5 kW at 450 kHz, and its output must be continuously variable from 25 to 100% of rated power.

Balance. An accuracy of ± 1 g is adequate.

Inert-Atmosphere Box. The box should have a purification train capable of controlling the moisture and oxygen contents of the atmosphere to <5 ppm. (See Appendix A.)

Mechanical Pump. A two-stage mechanical pump with capacity ≥ 25 liters/min at 1×10^{-3} torr is required for this purpose.

4.3 MATERIALS

Vacuum Grease.

Helium. Welding grade tank helium.

Fig. 4-1

Typical Vacuum Distillation Assembly

Fig. 4-2 Typical Sodium Distillation Unit

Fig. 4-3

Dimensions of a Typical Distillation Unit Shell

Fig. 4-4 Dimensions of a Typical Condenser System

Fig. 4-5

Typical Sample Cup with Thermocouple Well

4.4 PROCEDURE

Note: See the Discussion, Section 4.6, for comments about the desirability of exposing certain samples to laboratory air before they are distilled.

1. Transfer the distillation unit and the overflow sampling device containing the sample, obtained as described in Section 3.2, into the glovebox.
2. Open the sampling device and remove the filled sample cup.
3. Weigh the sample cup and record the weight.
4. Assemble the distillation unit with the sample cup in place (see Fig. 4-2). Close stopcock A.
5. Transfer the distillation unit from the glovebox and install it in the distillation assembly (Fig. 4-1).
6. Connect the thermocouple to the recorder.
7. Position the work coil of the induction heater, if necessary.
8. With stopcock B closed, open stopcocks A and C and evacuate the assembly to approximately 1×10^{-3} torr. Close stopcock C and check the system for leaks with the vacuum gauge.
9. Cool the trap with liquid nitrogen or liquid argon.
10. Open stopcock B and backfill the assembly with helium.
11. Close stopcock B.
12. Turn on the induction heater at a power setting (previously determined) which heats the sodium slightly above melting.
13. Open stopcock C gradually to evacuate the system and degas the sodium. Degas for 5 minutes.
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.
15. Distill at constant temperature until a sharp rise in temperature indicates that the distillation is complete.
16. Heat the sample cup to 400 ± 15 C.
17. Turn off the induction heater.
18. Close stopcock C. Open stopcock B momentarily to raise pressure in the system to about 1 torr. (Thermal convection in the helium will melt the sodium drops adhering to the condenser.)

19. Allow the system to cool to room temperature.
20. Open stopcock B to backfill the assembly with helium.
21. Close stopcocks A and B.
22. Disconnect the thermocouple and remove the distillation unit from the vacuum train.
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 in which 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.
24. Dispose of the sodium distillate according to a locally-approved procedure.

4.5 SAFETY

In addition to normal safety practice, the following specific hazards should be considered:

Sodium Metal. Be prepared to control a small sodium fire with Met-L-X or a similar material.

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

High Voltage. Insulate the output leads of the induction generator.

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

4.6 DISCUSSION

The entire procedure requires approximately 3 to 4 hr. The actual distillation requires 1 1/2 to 2 hr.

Some metals are not quantitatively recovered in the residue under the conditions of this distillation. Zinc, cadmium, and the alkali metals 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 temperature than specified. Intentional exposure to air for 1 to 5 min to produce a slight film of oxide on the surface of the sample should provide sufficient oxygen to retain up to 100 ppm of calcium or magnesium in sodium.

5. DETERMINATION OF HYDROGEN IN SODIUM BY THE AMALGAM-REFLUX METHOD

5.1 PRINCIPLE

An amalgam of sodium is prepared at low temperature and then heated to decompose hydrogen compounds. The chemical activity of the sodium is reduced sufficiently in the amalgam to inhibit recombination of the sodium and hydrogen. Gas chromatography is then used to measure the quantity of hydrogen released during heating.

5.2 SENSITIVITY AND PRECISION

This method is applicable to the determination of 0.15 to 45 μ g of hydrogen (0.05 to 15 ppm of hydrogen in a 3-g sample of sodium). The spread between duplicates is typically 15% for hydrogen in the range 1.0 to 5.0 ppm.

5.3 APPARATUS

Hydrogen Evolution System. This system is made up of the following units:

Hydrogen Evolution Vessel. Fig. 5-1.

Flexible Vacuum Tubing. Stainless Steel, 1/2 to 5/8 in. ID. The length of this tubing will depend on the geometry achievable in the inert-atmosphere box but it should not exceed 3 ft.

Gas Sampling System. The sampling system is located outside the box but as close as possible to the evolution vessel.

Vacuum System. The vacuum system consists of (1) a mechanical pump with a capacity ≥ 25 liters/min at 1×10^{-3} torr (2) an oil-vapor trap connected to the pump, (3) a Bourdon-tube vacuum/pressure gauge, (4) a vacuum gauge suitable for measuring pressures of 1×10^{-3} torr, and (5) appropriate stainless steel vacuum valves. All connections are to be made with 1/2-in.-dia stainless steel tubing.

Argon Inlet. This is connected to the vacuum system.

Heater. Induction heating is preferred; however, resistance heating is also acceptable practice. If induction heating is used, a suitable system consists of a ≥ 1 kW, 450 kHz induction generator connected to a 1/4-in.-dia copper work coil with leads through the wall of the inert-atmosphere box.

Inert-Atmosphere Box. The box must have a purification train capable of controlling the impurity levels in the atmosphere. For this analysis the moisture content of the atmosphere must be ≤ 1 ppm. Argon is the preferred atmosphere for this analysis, since any helium that leaked into the analytical train would be measured as hydrogen by most chromatographs. (See Appendix A.)

The above units are assembled as shown in Fig. 5-2. (NOTE: The hydrogen evolution vessel, the flexible tubing, and the work coil are located inside the box.)

Fig. 5-1

Typical Hydrogen Evolution Vessel

Fig. 5-2

Schematic of a Typical Hydrogen Evolution System

Gas Handling System. An apparatus suitable for preparing known dilutions of gas mixtures. A typical set-up is shown in Fig. 5-3. This system consists of a rough vacuum pump, a mercury diffusion pump, vacuum and pressure measuring equipment, and a tubular manifold consisting of gas storage vessels and ports.

Gas Chromatograph with Strip-Chart Recorder (1.0 mV Span). The instrument must be capable of separating hydrogen from the major components of air and be capable of detecting 5×10^{-3} μg of hydrogen in argon. For example, the Varian Model 90-P3 Gas Chromatograph equipped with a 6-ft Linde Molecular Sieve 5A column and a thermal conductivity detector and operated with an argon carrier, has been found suitable by the originator of this procedure.

Syringe, 5-ml Valved, Gas-Type. This is for sampling from the hydrogen evolution apparatus. A gas sampling loop, bulb or valve may also be used. Precision Sampling Corp. Pressure-Lok syringes have been found suitable for this purpose.

Analytical Balance.

5.4 MATERIALS AND REAGENTS

Argon. Dried by a molecular sieve column.

Mercury. See Appendix C for test and cleaning procedures.

Standard Gas Mixture. 1000 ppm H_2 in Ar.

Amalgam. 2 g Na and 0.4 g Ca dissolved in 200 ml mercury. This is prepared in the inert-atmosphere box.

Wash Bottle. 125 ml, polyethylene, containing mercury.

5.5 PROCEDURE

5.5.1 Preconditioning

1. Oven-dry the glassware under oil-vapor-free vacuum at 150 C for no less than 8 hr to minimize moisture on the surface of the glassware. (The hydrogen evolution vessel must be clean, dry, and as scratch-free as possible before insertion into the inert atmosphere box.) Transfer the vessel immediately to the inert atmosphere box after removal from the oven.

2. Add 50 ml of sodium-calcium amalgam to the reflux vessel. Assemble the vessel and install it on the vacuum manifold. Evacuate the system to approximately 1×10^{-3} torr and then pressurize with argon to 500 torr, as indicated on the pressure/vacuum gauge.

3. Isolate the reflux vessel from the system and heat the amalgam to reflux temperature (approximately 370 C) with the induction heater. Reflux for 3 hr. (This initial refluxing assures the complete removal of any water adsorbed on the surface of the amalgamation vessel.)

4. Allow the amalgam to cool.

Fig. 5-3

TYPICAL GAS HANDLING SYSTEM

5. Evacuate the system to approximately 1×10^{-3} torr and then pressurize with argon to 500 torr.
6. Isolate the reflux vessel from the system and reflux the amalgam for 20 min.
7. Allow the amalgam to cool.
8. Sample the argon above the amalgam with the 5-ml gas-tight syringe or with a gas sampling loop or bulb. To take gas samples after reflux, first evacuate the line and valve it off at the pump side of the septum. Then open the stopcock on the reflux vessel to allow vessel gas to expand up to the septum for sampling.
9. Inject a 5-ml sample into the gas chromatograph. If hydrogen is detected, repeat the evacuation and a 20 min reflux cycle until a suitable vessel blank is obtained. (A suitable vessel blank is 0.05 μg in the entire vessel.

5.5.2 Sampling and Tube Blank Preparation

1. Obtain a sample in a bypass tube by the procedure described in Section 3.1.
2. Rinse the exterior of the tube with water, acetone, and ethanol, and allow it to dry.
3. Immediately after cleaning the tube, introduce the sample into the air lock of the glove box and evacuate the air lock.
4. Pressurize the air lock with box atmosphere and introduce the sample into the box. Remove about 1 mil from the outside surface of the sample tube by filing or grinding. Cut off and discard at least 1 in. from one end.
5. Cut a section containing 2 to 3 g of sample from the freshly cut end of the tube. Handle this with tongs and mark it for later identification.
6. Immediately weigh this sample and introduce it into the side arm of a preconditioned reflux vessel. Begin evacuation (step 5.5.3.1) immediately.
7. While the reflux vessel is evacuating, cut another section containing 2 to 3 g of sample. Handle it with tongs and mark it for later identification as the tubing-blank. Melt the sodium from this section of tubing and carefully rinse the remaining sodium from the inside of the tubing with mercury from a wash bottle.

5.5.3 Amalgamation and Hydrogen Determination

1. Evacuate the entire system to a pressure $<1 \times 10^{-3}$ torr, as indicated on the thermocouple gauge, backfill to 500 torr with argon, and isolate the hydrogen vessel from the vacuum system.

2. Introduce the sample into the amalgam and agitate the reflux vessel until amalgamation is complete (approximately 3 to 5 min).

3. Heat to reflux (approximately 370 C) for a period of 10 to 30 min. Allow the amalgam to cool for about 30 min.

4. Remove separately at least three 5-ml aliquots of gas using the 5-ml gas-tight syringe or sample loop. Inject the aliquots into the injection port of the gas chromatograph, and record the peak heights. To take gas samples after reflux, first evacuate the line and valve it off at the pump side of the septum. Then open the stopcock on the reflux vessel to allow vessel gas to expand up to the septum for sampling.

5. Repeat 5-ml injections until reproducibility of the hydrogen peak height is $\pm 5\%$.

6. Repeat steps 1, 3, 4, and 5 with 15-min refluxes until hydrogen is no longer detected, i.e., until $<0.05 \mu\text{g}$ is released from the entire vessel.

7. Introduce the tubing-blank section into the apparatus and repeat steps 1 through 6.

8. Disconnect the hydrogen vessel from the vacuum system and remove the tubing sections. Measure the length of both sections. Weigh the section that contained the sample and subtract this weight from the total weight to get the sample weight.

5.5.4 Calibration of Chromatograph

1. Using the gas handling system, successively prepare secondary standard mixtures containing 500, 250, 100, 50, and 25 ppm H_2 in Ar at 500 torr.

2. Remove separately at least three 5-ml aliquots of each secondary standard mixture using either the 5-ml gas-tight syringe, or a sample loop. Inject the aliquots into the injection port of the gas chromatograph, or flush the sample loop into the analytical stream. Record the peak heights.

3. Prepare a calibration curve of micrograms H_2 vs peak height.

5.6 CALCULATIONS

1. Determine the total hydrogen released by the sample according to the following formula:

$$\text{H}_2, \mu\text{g} = fP$$

where

$$f = \frac{\text{gas volume of the reflux system}}{\text{volume of an aliquot}}$$

P = quantity of hydrogen (read from the calibration curve) corresponding to an individual peak height, μg .

2. Determine the total hydrogen released by the blank by the formula given in step 1.

3. Calculate the concentration of hydrogen in the sample according to the following formula

$$\text{Hydrogen concentration, ppm} = \frac{A - \frac{B}{L_B} \times L_S}{W}$$

where

A = hydrogen in the sample, μg (step 1 above)

B = hydrogen in the blank, μg (step 2 above)

L_B = length of blank tubing, cm

L_S = length of sample tubing, cm

W = weight of sample, g

5.7 SAFETY

Normal precautions for handling sodium should be observed. The additional precautions required by the use of mercury are the following:

1. *Mercury Vapor.* A mercury-vapor detector should be used to monitor the room atmosphere frequently. In case of spills, mercury should be cleaned up promptly and thoroughly.

2. *Mercury-sodium reaction.* The reaction of sodium with mercury is highly exothermic. A cooling period, therefore, should precede all vessel-handling operations with gloves.

3. *Vacuum pump exhaust.* All vacuum pumps on boxes which contain mercury should be vented to an exhaust and not into the laboratory.

5.8 DISCUSSION

This procedure, exclusive of sampling and glassware cleaning, requires 4 to 5 hr.

There is some uncertainty about the species yielding hydrogen during low-temperature and high-temperature refluxing. For the present, only total hydrogen will be used for inter-laboratory comparisons, regardless of the number and type of refluxes performed. At some later date, more complete information on all species responsible for the two types of hydrogen release may make reporting of the separate analyses desirable.

6. DETERMINATION OF HYDROGEN IN SODIUM BY THE HYDROGEN DIFFUSION METER

6.1 PRINCIPLE

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.

6.2 SENSITIVITY AND PRECISION

The hydrogen meter operating in the equilibrium mode is applicable to the measurement of hydrogen in sodium down to the level of 0.04 ppm. In the range from 0.05 to 5 ppm, the precision and accuracy expected are $\pm 20\%$ (2σ).

6.3 APPARATUS

A schematic representation of a typical hydrogen meter is shown in Fig. 6-1. The meter, components, controls, and instrumentation shall conform to the requirements for Type I meters as set forth in RDT C 8-6. In addition, temperature control of the membrane shall be ± 1 at 500 C.

6.4 PROCEDURE FOR EQUILIBRIUM MODE OPERATION

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

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

3. Take a pressure reading after 20 minutes 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} torr the spread of four consecutive measurements must fall within 10% of the last reading.) This pressure plateau should be attained within 1-1/2 hours. If it is attained, record the last reading and proceed to step 4. Otherwise, the performance of the meter is to be considered unsatisfactory, corrective action according to the meter manual should be taken, and the measurement should be restarted.

4. Correct the pressure recorded in step 3 for the thermal transpiration effect using the following equation developed by Takaishi & Sensui [see "Thermal Transpiration Effect of Hydrogen, Rare Gases and Methane," Trans. Faraday Soc. 59, 2503-2514 (1963)].

$$P_1 = \text{Corrected Pressure} = P_2 \left(\frac{1.25 \times 10^5 B^2 + 8.0 \times 10^2 B + 10.4 B^{1/2} + 1}{\sqrt{T_2/T_1} + 1.25 \times 10^5 B^2 + 8.0 \times 10^2 B + 10.4 B^{1/2}} \right)$$

$$\text{where } B = 2 \left(\frac{P_2 d}{T_1 + T_2} \right)$$

and P_2 = observed pressure, torr (from step 3)
 T_1 = temperature of membrane, K
 T_2 = temperature of pressure gauge, K
 d = internal diameter of hydrogen meter vacuum system, mm

Fig. 6-1

Schematic Representation of a Typical Hydrogen Meter

5. Calculate the hydrogen concentration according to the equation

$$S = \text{ppm hydrogen in sodium} = K P_1^{\frac{1}{2}}$$

where $K = 4.9 \pm 0.2 \text{ ppm/torr}^{\frac{1}{2}}$

6.5 PROCEDURE FOR CALIBRATION OF DYNAMIC MODE OPERATION

1. Fix the cold trap temperature or add hydrogen to the system so that the concentration of hydrogen is $\geq 0.05 \text{ ppm}$.
2. Establish that the ion pump is open to the membrane.
3. Evacuate the system until a steady ion pump current ($\pm 5\%$) is obtained.
4. Record this current.
5. Measure the hydrogen concentration in the system by operating the meter in the equilibrium mode. (Section 6.4, steps 2 to 5.)
6. Record the hydrogen concentration measured in step 5.
7. Change the hydrogen level and repeat steps 1 through 6.
8. Repeat step 7 until the range of interest of hydrogen in sodium is covered.
9. Construct a calibration curve of ion current vs hydrogen concentration in sodium.

6.6 PROCEDURE FOR DYNAMIC MODE OPERATION

1. Establish that the ion pump is open to the membrane.
2. Evacuate the system until a steady ion pump current ($\pm 5\%$) is obtained.
3. Record this steady state current.
4. Determine the hydrogen concentration in the system from the calibration curve.

6.7 DISCUSSION

Operation of the meter in the dynamic mode should permit measurements of hydrogen concentrations that are an order of magnitude lower than those measurable in the equilibrium mode. However, it should be noted that this increased sensitivity can be obtained only in systems in which calibration of the dynamic mode is possible (i.e., only in systems which are at, or which can be adjusted to, a hydrogen level which permits equilibrium mode measurements).

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 2 to 4 of Section 6.4. (In this case, pressure measurements may begin immediately.)

7. DETERMINATION OF CARBON IN SODIUM BY THE OXYACIDIC FLUX METHOD

7.1 PRINCIPLE

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 flashed into a gas chromatograph for measurement.

7.2 SENSITIVITY AND PRECISION

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

For carbon concentrations in the range 0.5 to 10 ppm, replicate determinations from the same bypass sample are expected to agree within 0.5 ppm at the 95% confidence level. This estimate of precision is based on recent EBR-II experience.

7.3 APPARATUS

Analytical System. The analytical system consists of the following equipment, whose relationships are shown in the block diagram of Fig. 7-1:

Gas Supply and Purification Tube. The tube (Fig. 7-2) consists of a quartz tube containing CuO (which is heated to $750 \pm 10^\circ\text{C}$ by a tube furnace), Ascarite, and BaO , and through which helium and oxygen are passed. The gas supply pressure is 10 psig. The gases are supplied from gas cylinders equipped with valve-controlled flow meters.

Inert-Atmosphere Glovebox. The box must have a purification system capable of controlling the impurity level of the box atmosphere. For this analysis, the carbon monoxide, carbon dioxide, and hydrocarbon gases (calculated as methane) of the atmosphere must each be ≤ 1 ppm, and oxygen and moisture < 20 ppm. All sampling and transfer operations must be performed in this box. The box should also be equipped with (1) a sodium extruder (Figs. 7-3 and 7-4); (2) a balance (± 0.05 g); (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); (4) a powder horn; and (5) holders for reaction bottles, shield tubes, and tools.

Combustion Tube. The combustion tube, shown in Fig. 7-5, 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 gastight seal is made of a wide, soft lead gasket soldered into and completely filling a machined groove in the port cover. A 45° 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 overtightening or undertightening

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.

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

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.

Carbon Dioxide Trap. This trap is a 3/16-in.-OD stainless steel tube 12 in. long containing 40 to 60 mesh Molecular Sieve 5A. Provisions to heat the trap rapidly to approximately 300 C to desorb the CO_2 must be included. [The SKC, Inc. Model 215 Component Concentrator has been found suitable for this application. A 3/16-in.-OD thin wall (approximately 15 mil) 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.]

Carbon Dioxide Measurement System. This system consists of the carbon dioxide trap listed above, a standard-volume loop, and a gas chromatograph, as shown in Fig. 7-6. The gas chromatograph should be suitable for the detection of 0.1 μg of carbon as CO_2 . A Beckman Series E Analyzer equipped with a recorder having a 1-mV span was found suitable for this application by the originator of the method. This chromatograph contained a 6-ft Porapak Q column at 50 to 60 C and a standard two-filament thermal conductivity detector, and was operated with helium carrier gas at 100 cc/min. (A 12-ft x 1/4-in. OD column packed with 30 to 60 mesh silica gel at 145 C has also been found suitable.)

Train Gas Composition and Volume Measurement System. This system (Fig. 7-7) consists of an oxygen sensor enclosed in a glass adaptor. (A Beckman Model 778 polarographic oxygen analyzer was found suitable for this application by the originator of the method.)

7.4 MATERIALS AND REAGENTS

Helium Gas.

Oxygen Gas. High purity.

Barium Oxide. 10 to 20 mesh.

Ascarite. 8 to 20 mesh.

Quartz Wool. This is preignited in air at 900 to 1000 C for 16 hr.

Copper. Light turnings, reagent grade.

Fig. 7-1 Block Diagram of Analytical System

Fig. 7-2

Typical Gas Purification Tube

Fig. 7-3

Typical Plunger-Type Extrusion Device

Fig. 7-4

Typical Vise-Type Extrusion Device

Fig. 7-5

TYPICAL COMBUSTION TUBE

Fig. 7-6

CO₂ MEASUREMENT SYSTEM

Fig. 7-7

TRAIN-GAS COMPOSITION & VOLUME MEASUREMENT

Potassium Dichromate. Reagent grade. Reagent grade $K_2Cr_2O_7$ contains from 5 to 10 ppm of carbon. This is readily removed by ignition for one hour at 700 C.

7.5 PREPARATION OF APPARATUS

1. Clean the quartz purification tube (Fig. 7-2) with detergents, rinse, and then etch inside for 5 min at room temperature with reagent grade 48% HF. Care must be taken to prevent etching of the ground joints. Rinse the tube with distilled water to remove HF and then with reagent grade acetone. After evaporation of the acetone, heat the tube to red heat by means of an oxyhydrogen (*not oxygen-hydrocarbon*) flame.
2. Place a small piece of quartz wool, preignited at 900 to 1000 C for 16 hr, inside the purification tube at the outlet end. Then, pack the tube with barium oxide to a length of 15 cm, lightly tapping to pack; add Ascarite (8 to 20 mesh) to give an Ascarite bed length of 20 cm and finally a 2 to 3 cm barrier of preignited quartz wool. Next, pack a 32-cm 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 hr. Both the temperature and oxygen flow should be increased slowly in order to limit the rate of the initial oxidation of the copper. After the CuO bed appears entirely black, stop the helium flow and pass pure oxygen over the CuO for an additional 8 hr.
3. Connect the outlet of the purification train to a flexible 1/8-in.-OD 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 CuO powder in 85% H_3PO_4 for about 10 min to give a creamy black paste; setting time is 24 hr.)
4. Prepare the quartz combustion tube (Fig. 7-5) in a manner similar to the purification tube, by a 5-min etch with 48% HF (care must be taken to prevent HF contact with the graded seal), a distilled water rinse, an acetone rinse, and finally by heating to red heat.
5. After cleaning, pack the combustion tube with approximately 32 cm of copper turnings. Convert the copper to copper oxide as described for the purification train in step 7.5.2.
6. Etch the shield tubes and reaction bottles shown in Fig. 7-8 by immersion in 48% HF for 5 min at room temperature, rinse with distilled water and then with reagent grade acetone, and then dry for 15 min at 120 C.
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.

REACTION BOTTLE

SHIELD-TUBE

Fig. 7-8

Typical Reaction Bottle and Shield-Tube

7.6 CALIBRATION OF CHROMATOGRAPH

1. Fill a sample loop of known volume with standard gas (0.25% CO₂ in He) at known temperature and pressure and insert it into the train between the combustion tube exit and the trap, point S in Fig. 7-6. 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.
2. Trap the standards from a stream of helium flowing at 100 ml/min.
3. After trapping, heat the CO₂ trap and obtain the CO₂ chromatogram.
4. Repeat the procedure, with adjustments of the chromatograph attenuator, until the desired calibration is achieved. Prepare a graph of peak height or area vs µg of C.

7.7 PROCEDURE

7.7.1 Preparation of Reaction Bottle

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.
2. Adjust the controller for the copper oxide furnace of the gas supply and purification tube to 750 ± 10 C and of the combustion tube to 600 ± 10 C.
3. When the oxygen analyzer indicates $\leq 0.5\%$ O₂, 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% O₂.
4. Place a clean shield tube and reaction bottle (Fig. 7-8) 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 by use of point contacts only.)
5. Close the combustion-tube port, and set the reaction-zone furnace controller so that a temperature of 980 ± 10 C is attained.
6. Replace the helium with oxygen flowing at 100 ml/min.
7. After ignition for 1 hr at 980 ± 10 C replace the oxygen with helium flowing at 100 ml/min and then turn off the reaction-zone furnace. Open the furnace to cool it down. To save time, the furnace can be cooled with a fan.
8. When the furnace has cooled to ≤ 150 C and the oxygen analyzer indicates $\leq 0.5\%$ O₂, 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.)

9. Grip the base of the reaction bottle, using a pair of very 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, it is placed on double-wedge-shaped pan adaptor made from a wide-base piece of stainless steel constructed with two V-shaped notches in alignment two inches apart. The bottle is placed horizontally in the notches for weighing operations, preventing the reaction bottle from rolling and preventing gross contact with the balance pan.)
10. Pour 8 ± 0.1 g of potassium dichromate into the bottle mouth from the powder horn and reweigh the bottle.
11. Replace the bottle with the flux in the reaction zone and heat in oxygen for 1 hr at 750 ± 10 C.
12. After 1 hr, replace the O_2 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 train-gas composition will remain above 1% O_2 at a helium flow of 100 ml/min for an unacceptable period of time.)
13. Remove the reaction bottle containing the preignited flux, cool it to glovebox temperature, and weigh it.
14. Proceed with Section 7.7.2 when running a sample, or with Section 7.7.3 when running a blank.

7.7.2 Aliquoting

The sample is obtained via the bypass procedure described in Section 3.1. The sodium is then extruded from the bypass tube, by one of the two procedures described below, into a reaction bottle prepared as described in 7.7.1.

7.7.2.1 Plunger-Type Sample Extrusion

1. Transfer the capped extrusion vessel into the inert atmosphere glovebox.
2. Separate the two sections. Uncap one section and place it in the extrusion device shown in Fig. 7-3.
3. Force the piston into the large end to extrude sodium from the small end. Cut off and discard an initial portion of sodium.
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, the sample weight may be estimated from the number of turns of the extruder or by measuring 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, any part of the glovebox, any glove, or any other thing except the handling tools.)
5. Go to Section 7.7.4.

7.7.2.2 *Vice-Type Sample Extrusion*

1. Transfer capped sample tube into the glovebox.
2. Cut off one end of the sample tube with a tubing cutter. Discard the end section.
3. Hold the tube about 2 in. from the cut end.
4. Put the tubing between the jaws of the vise. A Manco Guillotine M.C. 215 cutter obtained from the Manco Mfg. Co., Bradley, Ill., has been found suitable if the jaws are replaced with hardened steel 3/4 in. flat and round edged jaws (see Fig. 7-4). 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.
5. Press the foot switch to actuate the vise and squeeze one length of sodium from the tube.
6. Cut off the extruded sodium with a knife and discard the piece of sodium. The knife used is an all-metal scalpel which 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.
7. Pull the sample tube back to bring a new section of the tube between the jaws.
8. Actuate the vise again. Extrude and cut off about one gram 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, any part of the glovebox, any glove, or any other thing except the handling tools.)
9. Go to Section 7.7.4.

7.7.3 *Operational Blank*

An operational blank is to be obtained with each batch of samples, and also when changes are made in the system or reagents or discrepant results are observed. If the operational blank is demonstrated to be stable to $\pm 0.2 \mu\text{g}$ for at least one month, then one operational blank per week is sufficient.

The operational blank consists of (a) performing the steps of Section 7.7.1 (Preparation of Reagent Bottle), (b) carrying out dummy manipulations comparable to those of Section 7.7.2 (Aliquoting), and (c) continuing the steps of Section 7.7.4 (Combustion). Thus, this blank contains all the steps and manipulations involved in running a sample, except for the actual addition of the sample.

7.7.4 Combustion

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.)
2. After the bottle is properly positioned, close the port and switch the train-gas to the CO₂ trap.
3. Replace helium by O₂ at 100 ml/min. After the O₂ flow is started, obtain the initial wet-test meter reading.
4. As soon as the train gas is 95% O₂, heat the reaction zone to 200 C. At some point during heat-up, the sodium will ignite and burn to Na₂O. If the train-gas is less than 95% O₂, combustion will be delayed or erratic, and be accompanied by ejection of sodium oxide smoke, molten flux, and bits of burning sodium. If this occurs, reject the sample and start over.
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.
6. Maintain the furnace at 980 ± 10 C until 8 to 10 liters of O₂ have passed through the train, then cool the reaction-zone furnace. Replace the O₂ by helium and take a wet-test meter reading.
7. When the O₂ concentration has dropped to ≤0.5%, switch the CO₂ trap to the chromatograph.
8. As soon as the chromatograph has stabilized with the trap in the flow path, heat the trap to introduce the CO₂ into the chromatograph and obtain a chromatogram. Then switch the CO₂ trap back to the combustion flow path. Remove the reaction bottle.

7.8 CALCULATIONS

From the calibration graph prepared in Section 7.6, calculate the concentration of carbon in sodium by the following formula:

$$\text{Carbon, ppm} = \frac{\mu\text{g C in sample} - \mu\text{g C in blank}}{\text{g sample}}$$

7.9 SAFETY

Sodium. Normal precautions for handling sodium should be observed.

7.10 DISCUSSION

This procedure, exclusive of sampling, requires approximately 4 hr.

8. DETERMINATION OF HYDROCARBON GASES RELEASED FROM SODIUM BY AQUEOUS DISSOLUTION

8.1 PRINCIPLE

Sodium is dissolved in water and the volatile hydrocarbons (mostly methane and acetylene) are collected on a trap cooled with liquid nitrogen. Subsequently, the trapped gases are determined by gas chromatography.

8.2 SENSITIVITY AND PRECISION

Methane and acetylene may be determined in the range 0.4 to 20 μg (0.1 to 5 ppm when a 4-g sample is analyzed).

8.3 APPARATUS

Gas Handling System. An apparatus suitable for preparing known dilutions of gas mixtures. A typical set up is shown in Fig. 8-1. This system consists of a rough vacuum pump, a mercury diffusion pump, vacuum and pressure measuring equipment, and a tubular manifold consisting of gas storage vessels and ports.

Carbon Species Apparatus. A typical apparatus is shown in Fig. 8-2. (See the discussion in Section 8.8.) The apparatus includes the following items:

Dissolver Cell, as shown in Fig. 8-3.

Titration Buret, as shown in Fig. 8-4.

Condensation Traps, as shown in Fig. 8-4.

Sample Collection Trap. This trap, labeled A in Fig. 8-2, is filled with -50 +80 mesh Porapak Q.

Gas Chromatograph. The instrument must be capable of detecting 0.3 μg of carbon as methane and 1 μg of carbon as acetylene. A Hewlett-Packard Model 700 instrument with a 1/8-in.-OD x 6-ft-long Porapak Q column operated at 50 C and a flame-ionization detector or helium-ionization detector has been found satisfactory.

Inert-atmosphere Glovebox. The box must have a purification system capable of controlling the impurity level of the box atmosphere. For this analysis, carbon dioxide in the atmosphere must be ≤ 1 ppm, and oxygen and moisture < 20 ppm. Helium is the preferred atmosphere because it cannot interfere with the chromatographic finish (see Appendix A).

Filter Apparatus. The Millipore Corporation All Glass Filter Apparatus, Cat. No. XX15 047 00 for 47-mm-diameter filters has been found satisfactory for this application.

Balance. A balance weighing to 0.01 g is satisfactory for this analysis.

Safety Shield. For use during dissolution of sodium.

Fig. 8-1

TYPICAL GAS HANDLING SYSTEM

Fig. 8-2 Typical Carbon Species Apparatus

Fig. 8-3

TYPICAL DISSOLVER CELL

Fig. 8-4 Typical Titration Buret and Condensation Trap

8.4 MATERIALS AND REAGENTS

Alumina Crucibles, (>99.7% Purity), 100-ml and 5-ml sizes. The smaller crucible is used as a sodium sample cup and the larger one as a dissolver cup. McDaniel Refractory Porcelain Company type ACN crucibles have been found satisfactory. To improve blanks, heat the crucibles overnight in a muffle furnace at 1000 C.

Red Vacuum Wax. Dennison Manufacturing Co. No. 4 Express Sealing Wax has been found satisfactory.

Glass Filters, 47 mm. Gelman Instrument Company Glass Filters, Type A (nonbinder) have been found suitable for this application.

Purified Water. Filter 800 ml of distilled water through a 47-mm glass filter held in the filter apparatus. Rinse the receiver flask with the first 25 to 50 ml of filtrate and discard the rinse. After filtering the water, close the flask with a standard-taper cap. Prior to use, bring the water to a full rolling boil, partially cool it, and pour it directly into the titration buret.

8.5 PROCEDURE

8.5.1 Calibration of the Chromatograph

1. Bring the chromatograph to stable operation.
2. Inject gas samples containing 5 to 30 μg of CH_4 and C_2H_2 into the septum upstream of the sample trap.
3. Plot calibration curves of peak height vs μg CH_4 or C_2H_2 .

8.5.2 Sample Preparation

1. Use a 5-ml alumina crucible to obtain an overflow sample weighing 3 to 4 g by the procedure described in Section 3.2.
2. Pre-rinse the dissolver cell glassware, buret, and 100-ml alumina crucible with purified water and let them air dry.
3. Transfer the glassware, crucible, and sampling device containing the sample to an inert-atmosphere glovebox.

8.5.3 Determination of Hydrocarbon Gases

1. Open the overflow sampling device in the inert-atmosphere box.
2. Remove the cup plus sample, weigh it, and record the weight.
3. Place the 100-ml alumina crucible in the bottom section of the dissolver cell.
4. Place the sample cup in the crucible.

5. Seal on the top of the dissolver cell using red vacuum wax warmed by a heat gun. Seal the buret in place. Let the cell cool.
6. Close the stopcocks on the dissolver cell and buret, and transfer the unit from the glovebox to the carbon species apparatus (see Fig. 8-2).
7. Seal the dissolver cell and buret to the system by waxing-in the ball-and-socket joints at inlet and outlet. (Be sure to position the sodium cup beneath the buret tip before sealing.) Immerse purification trap B in liquid nitrogen.
8. Evacuate the carbon species apparatus with the exception of the dissolver cell and buret, and backfill with helium.
9. Open the stopcocks to the dissolver, evacuate and backfill with helium 5 times. Flush the whole gas train for 20 to 30 min with helium at a flow rate of approximately 500 ml/min.
10. Chill the first condensation trap, C, at the exit of the dissolver with ice-water mixture, and chill the second condensation trap, D, with Dry Ice-Freon mixture.
11. Fill the titration buret to the 30-ml mark with purified water. Sparge the water with helium from the dissolver cell for at least 1 min.
12. Close the buret stopcock, pressurize the region above the water with helium sufficiently to allow addition of water to the dissolver cell, and close the valve.
13. Reduce the helium flow rate to 200 ml/min.
14. Immerse the sample collection trap, A, in liquid nitrogen.
15. Dissolve the sample by dropping water from the buret at a rate not exceeding 0.2 ml/min.
16. When dissolution is complete (after addition of about 5 ml of water), drain the buret to 1 ml, leaving just enough water in the buret to retain extraneous floating matter.
17. Flush the system with helium at approximately 500 ml/min. Continue for 20 to 30 min.
18. Isolate the sample collection trap from the dissolver. Immerse purification trap E in liquid nitrogen. Adjust the valves to flow helium through purification trap E and through sample collection trap A. Valve off the flow meter.
19. Immerse the sample trap in hot water to release the sample. Measure and record elution times and peak heights.
20. Determine $\mu\text{g CH}_4$ and $\mu\text{g C}_2\text{H}_2$ in the sample from the calibration curves.
21. If CO_2 is to be determined on this sample, proceed to Section 9.5.2, Step 16.

22. Disassemble the dissolver. Remove, wash, dry, and weigh the empty sample cup. Compute the sample weight.

8.6 CALCULATIONS

$$\text{Methane, ppm} = \frac{A}{W}$$

$$\text{Acetylene, ppm} = \frac{B}{W}$$

where

A = total CH_4 released from the sample, μg
B = total C_2H_2 released from the sample, μg
W = sample weight, g.

8.7 SAFETY

The usual precautions for working with evacuated glassware and with closed glass systems must be observed.

Dissolve the sodium by adding the water dropwise. Do not allow an excess of water to accumulate. After starting the dissolution, continue without prolonged interruption to avoid the formation of a protective hydroxide surface coating on the sample.

8.8 DISCUSSION

The solution formed in step 15 may also be used for the determination of carbon dioxide as described in the next method (Method 9). The cell shown in Fig. 8-3, therefore, contains a sparge tube that is not needed for the determination of hydrocarbon gases but is required for the determination of carbon dioxide released from the solution after acidification. The distance between the tip of the glass sparge tube and the inner base of the alumina crucible (given in Fig. 8-3) is a critical dimension. For the volumes of components (e.g., dissolver cell) and reagents (water and acid) specified in Methods 8 and 9, the sparge tube has been positioned so that it will contact the solution only after the neutralization of alkaline solution formed on aqueous dissolution of the sample has been started. While Fig. 8-3 depicts a typical apparatus, dimensional variations must be guided by the prerequisite that the sparge tube remain out of the solution while it is alkaline.

This procedure, exclusive of sampling, takes approximately 4 hr.

9. DETERMINATION OF CARBON DIOXIDE RELEASED FROM SODIUM BY AQUEOUS DISSOLUTION

9.1 PRINCIPLE

Sodium is dissolved in water, the solution is acidified, and the carbon dioxide released is collected on a trap cooled with liquid nitrogen. Subsequently, the trapped gas is determined by gas chromatography.

9.2 SENSITIVITY AND PRECISION

Carbon dioxide may be determined in the range 0.4 to 20 μg (0.1 to 5 ppm when a 4-g sample of sodium is analyzed).

9.3 APPARATUS

Gas Handling System. An apparatus suitable for preparing known dilutions of gas mixtures. A typical set up is shown in Fig. 9-1. This system consists of a rough vacuum pump, a mercury diffusion pump, vacuum and pressure measuring equipment, and a tubular manifold consisting of gas storage vessels and ports.

Carbon Species Apparatus. A typical apparatus is shown in Fig. 9-2. See the discussion Section 9.8. The apparatus includes the following items:

Dissolver Cell, as shown in Fig. 9-3.

Titration Buret, as shown in Fig. 9-4.

Condensation Traps, as shown in Fig. 9-4.

Sample Collection Trap. This trap, labeled A in Fig. 9-2, is filled with -50 +80 mesh Porapak Q.

Gas Chromatograph. This instrument must be capable of detecting 0.3 g carbon as carbon dioxide. A Hewlett Packard Model 700 instrument with 1/8-in. OD x 6-ft long Porapak Q column operated at 50 C and a thermal conductivity detector has been found satisfactory.

Inert-Atmosphere Glovebox. The box must have a purification system capable of controlling the impurity level of the box atmosphere. For this analysis, carbon dioxide in the atmosphere must be ≤ 1 ppm, and oxygen and moisture < 20 ppm. Helium is the preferred atmosphere because it cannot interfere with the chromatographic finish (see Appendix A).

Filter Apparatus. The Millipore Corporation All Glass Filter Apparatus, Cat. No. XX15 047 00 for 47-mm-diameter filters has been found satisfactory for this application.

Balance. A balance weighing to 0.01 g is satisfactory for this analysis.

Safety Shield. For use during dissolution of sodium.

Fig. 9-1

TYPICAL GAS HANDLING SYSTEM

Fig. 9-2 Typical Carbon Species Apparatus

Fig. 9-3

TYPICAL DISSOLVER CELL

Fig. 9-4 Typical Titration Buret and Condensation Trap

9.4 MATERIALS AND REAGENTS

Alumina Crucibles (>99.7% Purity), 100-ml and 5-ml sizes. The smaller crucible is used as a sodium sample cup and the larger one as a dissolver cup. McDaniel Refractory Porcelain Co. type ACN crucibles have been found satisfactory. To improve blanks, heat the crucibles overnight in a muffle furnace at 1000 C.

Red Vacuum Wax. Dennison Manufacturing Co. No. 4 Express Sealing Wax has been found satisfactory.

Glass Filters, 47 mm. Gelman Instrument Company Glass Filters, Type A (nonbinder) have been found suitable for this application.

Purified Water. Filter 800 ml of distilled water through a 47-mm glass filter held in the filter apparatus. Rinse the receiver flask with the first 25 to 50 ml of filtrate and discard the rinse. After filtering the water, close the flask with a standard-taper cap. Prior to use, bring the water to a full rolling boil, partially cool it, and pour it directly into the titration buret.

Sulfuric Acid, 6M. Cautiously add 330 ml of concentrated sulfuric acid to 670 ml of distilled water. Filter, store, boil, and dispense as specified above for purified water.

9.5 PROCEDURE

9.5.1 Calibration of the Chromatograph

1. Bring the chromatograph to stable operation.
2. Inject gas samples containing 5 to 30 μg of CO_2 into the septum upstream of the sample trap.
3. Plot a calibration curve of peak height vs μg CO_2 .
4. If this determination is to be performed on the solution remaining from determination of hydrocarbon gases, Section 8, proceed to Section 9.5.2, Step 16. (See Discussion Section 9.8 on apparatus before proceeding.)

9.5.2 Sample Preparation

1. Use a 5-ml alumina crucible to obtain an overflow sample weighing 3 to 4 g by the procedure described in Section 3.2.
2. Pre-rinse the dissolver-cell glassware, buret, and 100-ml alumina crucible with prepared water and let them air dry.
3. Transfer the glassware, crucible, and sampling device containing the sample to an inert-atmosphere glovebox.

9.5.3 Determination of Carbon Dioxide

1. Open the overflow sampling device in the inert-atmosphere box.
2. Remove the cup plus sample, weigh it, and record the weight.
3. Place the 100-ml alumina crucible in the bottom section of the dissolver cell.
4. Place the sample cup in the crucible.
5. Seal on the top of the dissolver cell using red vacuum wax warmed by a heat gun. Seal the buret in place. Let the cell cool.
6. Close the stopcocks on the dissolver cell and buret, and transfer the unit from the glovebox to the carbon species apparatus (see Fig. 9-2).
7. Seal the dissolver cell and buret to the system by waxing-in the ball-and-socket joints at inlet and outlet. (Be sure to position the sodium cup beneath the buret tip before sealing.) Immerse purification trap A in liquid nitrogen.
8. Evacuate the carbon species apparatus with the exception of the dissolver and buret, and backfill with helium.
9. Open the stopcocks to the dissolver, evacuate and backfill with helium 3 times. Flush the whole gas train for 20 to 30 min with helium at a flow rate of approximately 500 ml/min.
10. About 10 min before flushing is completed, immerse the purification trap, B, immediately preceding the dissolver cell in liquid nitrogen. Chill the first condensation trap, C, at the exit of the dissolver with ice-water mixture, and chill the second condensation trap, D, with Dry Ice-Freon mixture.
11. Fill the dissolver buret to the 30-ml mark with purified water. Sparge the water with helium from the dissolver cell for at least 1 min.
12. Close the buret stopcock, pressurize the region above the water with helium sufficiently to allow addition of water to the dissolver cell.
13. Reduce the helium flow rate to 200 ml/min.
14. Dissolve the sample by dropping water from the buret at a rate not exceeding 0.2 ml/min.
15. When dissolution is complete (after addition of about 5 ml of water), drain all but 1 ml into the dissolver cell and release the excess pressure in the buret.
16. Add 20 ml of freshly boiled 6M H_2SO_4 solution to the titration buret. Sparge the acid with helium from the dissolver cell for at least 1 min.

17. Close the buret stopcock, pressurize the region above the acid with helium sufficiently to allow addition of acid to the dissolver cell, and close the valve.
18. Reduce the helium flow rate to 200 ml/min.
19. Immerse the sample collection trap, A, in liquid nitrogen.
20. Neutralize the dissolver liquid by addition of acid at the rate of 0.5 ml/min. Add all of the acid except 1 ml to retain floating contamination in the buret. The tip of the sparge tube will be immersed in the solution at this point.
21. Agitate the liquid in the dissolver crucible by helium flow through the sparger. Also, flush with helium at approximately 500 ml/min. Continue for 20 to 30 min.
22. Isolate the sample collection trap from the dissolver. Immerse purification trap E in liquid nitrogen. Adjust the valves to flow helium through purification trap E and through sample trap A. Valve off the flow meter.
23. Immerse the sample trap in hot water to release the sample. Measure and record elution times and peak heights.
24. Determine $\mu\text{g CO}_2$ in the sample from the calibration curve.
25. Disassemble the dissolver. Remove, wash, dry, and weigh the empty sample cup. Compute the sample weight.

9.6 CALCULATIONS

$$\text{Carbon dioxide, ppm} = \frac{A}{W}$$

where

A = total CO_2 released from the sample, μg
W = sample weight, g

9.7 SAFETY

The usual precautions for handling acids and for working with evacuated glassware and with closed glass systems must be observed.

Dissolve the sodium by adding the water dropwise. Do not allow an excess of water to accumulate. After starting the dissolution, continue without prolonged interruption to avoid the formation of a protective hydroxide surface coating on the sample.

9.8 DISCUSSION

The distance between the tip of the glass sparge tube and the inner base of the alumina crucible given in Fig. 9-3 is a critical dimension. For the volumes of the components (e.g., dissolver cell) and reagents (water and acid) specified, the sparge tube has been positioned so that it will contact the solution only after the acid has been partially added, i.e., only after the alkaline solution formed on aqueous dissolution of the sample has been neutralized. While Fig. 9-3 depicts a typical apparatus, dimensional variations must be guided by the prerequisite that the sparge tube remain out of the solution while it is alkaline.

This procedure, exclusive of sampling, takes approximately 4 hr.

10. DETERMINATION OF CYANIDE IN SODIUM BY SPECTROPHOTOMETRY

10.1 PRINCIPLE

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.

10.2 SENSITIVITY AND PRECISION

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.)

For cyanide concentrations in the range 0.1 to 1.0 ppm, replicate determinations from the same sample are expected to agree with 25%.

10.3 APPARATUS

Spectrophotometer. A Beckman Model B instrument has been found suitable.

Absorption Cells. Matched cells with 1-cm optical path lengths.

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 ppm. (See Appendix A.)

Balance. A balance that is capable of weighting to ± 0.01 g is adequate.

Safety Shield. For use during dissolution of sodium.

pH Meter.

Magnetic Stirrer.

Mixing Cylinders. Stoppered 100-ml graduated cylinders of alkali-resistant plastic.

10.4 MATERIALS AND REAGENTS

Sulfuric Acid, 4M. Cautiously pour 220 ml of concentrated sulfuric acid into about 700 ml of water. Add sufficient water to make 1 liter.

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

Chloramine T Solution. Dissolve 0.20 g of Chloramine T in 100 ml of water. Make fresh on the day of use.

Epstein's Reagent. Stir 500 ml of water with 1 g of 3-methyl-1-phenyl-2-pyrazolin-5-one (Eastman 1397) for one hour. 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.

Tartaric Acid Solution. Dissolve 10 g of tartaric acid in sufficient water to make 100 ml of solution.

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 ml.

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.

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

n-Butanol. Reagent grade.

Methanol. Reagent grade.

10.5 PROCEDURE

10.5.1 Sample Preparation

Separate treatments are outlined below for the preparation of three different types of samples; the solution from a Kjeldahl nitrogen determination, a bypass sample, and an overflow sample.

10.5.1.1 Kjeldahl residue (From Section 13)

1. Add 50 ml of water to the methanol-water-sodium hydroxide residue in the distillation flask after distillation of ammonia in the Kjeldahl nitrogen analysis.
2. Boil until the odor of methanol no longer can be detected.
3. Dilute the aqueous sodium hydroxide solution to 100 ml in a graduated mixing cylinder.
4. Go to Section 10.5.2.

10.5.1.2 Bypass sample (From Section 3.1)

1. Obtain a sodium sample in a bypass tube by the procedure described in Section 3.1.
2. Rinse the exterior of the tube with deionized water and methanol.
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.)
4. Cut off at least a one-inch section from the end of the sample tube with a tubing cutter. Discard the end section.

5. Cut off and weigh a section containing approximately 2 g of sodium.
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.
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.
8. Dry the tube section, weigh it, and record the weight.
9. Dilute the aqueous sodium hydroxide solution to 100 ml in a graduated mixing cylinder.
10. Go to Section 10.5.2.

10.5.1.3 Overflow cup sample (From Section 3.2)

1. Obtain a sodium sample weighing about 50 g in an overflow cup by the procedure described in Section 3.2. (If the sample size is appreciably larger or smaller than 50 g, adjust all volumes in steps 3 to 5 below accordingly.) Tantalum is a suitable cup material.
2. Weigh the cup plus sample and record the weight.
3. Place the cup in a stainless steel beaker and dissolve the sodium in approximately 450 ml of methanol.
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.
5. Dry the cup, weigh it, and record the weight.
6. Transfer the aqueous sodium hydroxide solution to a 250-ml volumetric flask and dilute to the mark with water.
7. Transfer an aliquot of the solution, containing approximately 2 g Na, to a graduated mixing cylinder and dilute to 100 ml. Go to Section 10.5.2.

10.5.2 Cyanide Determination

1. From the mixing cylinder, pour an aliquant containing exactly 1.00 g Na into a 100-ml beaker. Add a magnetic stirring bar.
2. Dilute the sample to 60 to 70 ml; and, while stirring, add 2 ml of tartaric acid solution.
3. Insert the electrodes from a pH meter, continue to stir, and add 4M sulfuric acid from a buret until the pH is 5.5 ± 1 . (Approximately 5 ml of acid will be required.)

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.

5. Add 10 ml of Epstein's Reagent, mix and dilute to volume. After 1-1/2 hr 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 1 cm spectrophotometer 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.

6. 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 2 through 5 above.

7. Prepare a calibration curve of absorbance *vs* total micrograms cyanide added.

8. From the calibration curve, determine μg cyanide in the 1-g portion of sample.

10.6 CALCULATIONS

Cyanide, ppm = $\mu\text{g CN}^-$ in a 1-g portion.

10.7 SAFETY

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 respect. Dispose of cyanide residues in compliance with locally-administered safety procedures.

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.

10.8 DISCUSSION

The recovery of cyanide standards carried through the procedure with sodium averages 95% and is consistently above 85%. The detection limit is 0.03 μg of cyanide and the sensitivity is 0.7 absorption unit per microgram of cyanide. 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 ppm level have no effect on color development. Complex cyanide anions such as ferricyanide are decomposed by hot sodium into determinable form.

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.

The original article by J. Epstein is in *Analytical Chemistry* 19, 272 (1947).

This procedure, exclusive of sampling, takes approximately 4 hr.

11. DETERMINATION OF OXYGEN IN SODIUM BY AMALGAMATION

11.1 PRINCIPLE

Sodium is reacted with mercury to form a high-density amalgam. Oxygen-containing impurities float to the surface and are washed several times with fresh mercury. The residue is dissolved in water and the sodium content of the solution is determined by flame photometry. Oxygen content of the sodium is calculated on the assumption that the residue is Na_2O .

11.2 SENSITIVITY AND PRECISION

This method is applicable for the determination of 3 to 300 μg of oxygen (1 to 100 ppm of oxygen in a 3-g sample of sodium). The estimate of precision of this method is $\pm 30\%$ for concentrations above 3 ppm.

11.3 APPARATUS

Inert-Atmosphere Box. The box should be equipped with a purification system for controlling impurity levels in the atmosphere. For this analysis, the oxygen and moisture content of the atmosphere must each be ≤ 1 ppm. (See Appendix A.) The suitability of the inert atmosphere must be tested with two samples which have approximately equal exposed surface areas and which have been taken from a homogeneous batch of sodium. Analyze the first sample as described below (Section 11.5 et seq). Analyze the second sample after exposing it to the inert atmosphere for a period ten times longer than the first sample. The atmosphere is suitable if these two analytical results agree within the established precision of the analytical method.

Vacuum Drying Oven. The oven should be capable of continuous operation at 150 C.

Amalgamation Funnels. These are glass-stoppered, 125- or 250-ml separatory funnels of special design (see Fig. 11-1), made from heavy-walled borosilicate glass with a formed ring to support them in a holder.

Flame Photometer. Suitable for the determination of sodium. Typical specifications may be found in ASTM Method D 1428.

Balance. The balance should be located in the inert-atmosphere box and should be capable of weighing to ± 0.1 g.

11.4 MATERIALS AND REAGENTS

Mercury. To pass test. (See Appendix C for test.)

Standard Sodium Solutions for Flame Photometry. Commercially available or prepared solutions may be used.

11.5 PROCEDURE

11.5.1 Glassware Preparation

1. Wash the separatory funnels with dilute hydrochloric acid.

Fig. 11-1

Typical 125 ml Amalgamation Funnel

2. Rinse the funnels repeatedly with demineralized water.
3. Dry the funnels for 8 hr at 150 C in the vacuum oven.
4. Transfer the funnels immediately after removal from the oven to the entry lock of the inert-atmosphere box.
5. Quickly evacuate the lock to 2×10^{-2} torr or less.
6. Pressurize the lock with box atmosphere and transfer the equipment into the box.
7. Add mercury to the funnels. The initial volume of mercury should be: 50 ml for 1 to 3 g Na, 75 ml for 3 to 5 g Na, 100 ml for 5 to 15 g Na. The 125-ml funnel is suitable for samples ≤ 5 g; the 250-ml funnel is suitable for samples > 5 g.

11.5.2 Amalgamation

1. Obtain a sample in a bypass tube by the procedure described in Section 3.1.
2. Obtain a section of blank tubing from the same lot of tubing that was used to contain the sample in step 1.
3. Free loose material from the outside of the sample tube and from both the inside and the outside of the blank tube; rinse both with water, acetone, and ethanol, and allow them to dry. Immediately transfer the tubes into an inert-atmosphere box.
4. Cut off and discard at least 1 in. of the sample tube.
  - 4a. (Optional see Section 11.8, Discussion.) Remove approximately 1 mil from the outside surface of the sample tube by filling or grinding. Cut off and discard at least 1 in. of the sample tube. (If this optional step is used, all references made below to a tubing blank should be ignored.)
5. Cut off, weigh, and measure an appropriate length of sample tube; cut off and measure an appropriate length of blank tube. For oxygen concentrations > 10 ppm, Na samples should weigh 1 to 5 g. For oxygen concentrations < 10 ppm, samples should weigh 10 to 15 g. To reduce heating and spattering effects, samples > 3 g should be subdivided and added a section at a time.
6. Add the sample section to the funnel.
7. Loosely stopper the funnel until the initial vigorous reaction subsides.
8. Agitate the funnel for a minimum of 3 min to facilitate complete dissolution of the sample.
9. Wait 5 min for the residue to separate from the amalgam.

10. Drain all but about 0.3 ml of the amalgam into a second funnel labeled "vessel blank." At least one vessel blank should be run with each batch of samples.

11. Using this second funnel, carry out steps 8 and 9; drain all but about 0.3 ml of amalgam into a third funnel labeled "tubing blank."

12. Add the blank tube (from step 5) to the third funnel, carry out steps 8 and 9, drain all but about 0.3 ml of the amalgam into a waste flask, and carry both blanks through the rest of the procedure along with the samples. See Section 9.8, Discussion.

13. Add 20 ml of mercury to each funnel.

14. Cap the funnels and agitate for 3 min.

15. Wait 5 min for insolubles to separate from the amalgam; drain all but 0.3 ml of amalgam into the waste flask.

16. Repeat steps 13 through 15 three more times, and drain the mercury into a common waste container.

17. Remove the funnels and waste flask from the inert-atmosphere box.

11.5.3 Sodium Measurement

1. Rinse the inside surfaces of the funnels with 3 portions of deionized water, quantitatively transferring the solution from each funnel into a separate 100-ml volumetric flask.

2. Dilute each flask to 100 ml and mix well.

3. Remove the tube sections from the funnels, weigh them, and record each weight.

4. Analyze the solutions for sodium by flame photometry in accordance with standard practice as described in ASTM Method D 1428.

11.6 CALCULATIONS

Set the tubing blank, T, equal to zero if no blank tube was run. Otherwise, calculate the tubing blank, T, for each sample according to the following formula:

$$T, \mu\text{g} = \frac{M - N}{2\ell}$$

T = Tubing blank, μg

ℓ = Length of tubing used in tubing blank, cm

L = Length of tubing containing sample, cm

M = Weight of sodium in tubing blank residue, μg

N = Weight of sodium in vessel blank residue, μg

Calculate the oxygen content of the sodium according to the following formula:

$$\text{Oxygen, ppm} = \frac{A - N - T}{C(D - E)}$$

where

A = Weight of sodium in the sample residue, μg

B = Weight of sodium in the blank residue, μg

C = Oxygen equivalent of sodium = 2.87

D = Weight of sample plus tube, g

E = Weight of empty sample tube, g

11.7 SAFETY

Normal precautions for handling sodium should be observed. The additional precautions required by the use of mercury are the following:

Mercury Vapor. A mercury-vapor detector should be used to monitor the room atmosphere frequently. In case of spills, mercury should be cleaned up promptly and thoroughly.

Mercury-Sodium Reaction. The reaction of sodium with mercury is highly exothermic. A cooling period, therefore, should precede all vessel-handling operations with gloves.

Vacuum Pump Exhaust. All vacuum pumps on boxes which contain mercury should be vented to an exhaust system and not into the laboratory.

11.8 DISCUSSION

For a single sample and blank, the time required for this procedure is 2 to 3 hr. Multiple samples will increase this time by about 30 to 45 min per added sample. This time estimate does not include cleaning of glassware, nor sample and glassware transfers.

Experience has shown that the use of optional step 4a in Section 11.5.2 rarely leads to results which differ significantly from results obtained with its omission. This more elaborate and vigorous cleaning procedure has been included, however, so that it is available to verify the magnitude of the tubing blank correction. The use of this optional step is especially recommended when oxygen levels <5 ppm are to be determined, and for rechecks whenever unexpectedly high results are obtained.

12. DETERMINATION OF OXYGEN ACTIVITY IN SODIUM BY THE EQUILIBRATION METHOD USING VANADIUM WIRES

12.1 PRINCIPLE

A vanadium wire is immersed in sodium for a time sufficient to establish equilibrium with respect to oxygen. Subsequent measurement of the oxygen concentration in the wire is related to an oxygen activity in sodium by means of the distribution coefficient.

12.2 SENSITIVITY AND PRECISION

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

12.3 APPARATUS

Specimen Equilibration Device Options. Fig. 12-1 is a schematic drawing of the Specimen Equilibration Module for use on reactors and large sodium systems. Fig. 12-2 is a schematic drawing of a typical Specimen Equilibration Device for use on small experimental systems. These modules shall conform to the requirements of RDT C 8-8. Fig. 12-3 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. 12-4. A holder of similar design may also be used with modular- or device-type apparatus.

Electropolishing Apparatus. This apparatus consists of a 3- to 4-cm-diameter by 7-cm-long hollow platinum or tantalum cathode and a 6.0- to 7.5-V low-impedance dc power supply.

Oxygen Determination Apparatus. This apparatus must be capable of determining 0.1 to 1.5% oxygen in vanadium metal by an inert-gas or vacuum-fusion technique. A LECO RO-16 Oxygen Determinator, manufactured by the Laboratory Equipment Company, has been used successfully by the originator of this method.

Magnetic Stirrer, with Teflon-coated stirring bars.

Forceps, self-locking type.

12.4 MATERIALS AND REAGENTS

Oxygen Standards. Approximately 100 and approximately 300 ppm oxygen in steel. LECO Oxygen Standards, Stock Numbers 501-645 and 501-646 have been found satisfactory.

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

Acetone. Technical grade.

Ethanol. Technical grade.

Fig. 12-1 Schematic of a Typical Specimen Equilibration Module

Fig. 12-2

SCHEMATIC of a TYPICAL SPECIMEN EQUILIBRATION DEVICE

Fig. 12-3

Typical Basket Type Sample Holder and Equilibration Device

Fig. 12-4

Typical Sample Holder for use on Static Sodium Pots with Access
Ports and Inert Gas Locks Above the Sodium Level

Electropolishing Solution. This solution is composed of 80 vol % absolute methanol-20 vol % concentrated sulfuric acid.

High-Purity Vanadium Wire. 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 ppm total metallic impurities (Ti + Zr + Hf shall be <20 ppm), <300 ppm total of oxygen, nitrogen, hydrogen, and carbon (none of which shall be >150 ppm). 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 under the conditions described in paragraph A2.8 of ASTM A 510, which states in part:

"One end of the specimen is clamped in a vise or bending machine, the jaws of which are rounded to a specific radius; and the wire is bent back and forth at a uniform rate through a total of 180°. Each 90° movement in either direction is counted as one bend."

12.5 PROCEDURE

12.5.1 Wire Preparation and Equilibration

1. Cut the high-purity vanadium wire into 9- to 10-cm lengths and straighten the pieces. Measure and record the length of wire to be equilibrated.
2. Holding the wire with clean dissecting forceps, carefully degrease the lengths of wire with lintless tissue moistened with acetone. (After degreasing, the wire must be handled only with the forceps.)
3. Insert the wires into the appropriate wire holder. If a basket-type holder is used, bend each wire into an equal-armed U and drop it into the basket with the bend toward the wire-mesh bottom. If a holder like that in Fig. 12-4 is used, fix the wires in place by bending their ends around the holder.
4. Insert the sample holder into the sodium system.
5. Choose an equilibration time from Table 12-1 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 ppm.) The equilibration time for 0.25-mm-dia. wires must be in the range of 4 to 30 hr. The equilibration time for 0.50-mm-dia. wires must be in the range of 16 to 120 hr.
6. Find the minimum sodium flow rate by multiplying the length of the wire sample (in cm) by the minimum-flow-rate parameter.
7. Establish at least the minimum sodium flow rate through the equilibration device and equilibrate the wires at 750 ± 5 C for the chosen time.

Table 12-1. Flow-Rate Parameter for Vanadium Wire Equilibration

Oxygen Concentration in Sodium, ppm	Equilibration Time for 0.25-mm Wire, hr				
	4	5	10	20	30
	Equilibration Time for 0.50-mm Wire, hr				
	16	20	40	80	120
Minimum-Flow-Rate Parameter, gal/min per cm of wire					
10.	1.5×10^{-4}	1.2×10^{-4}	6.0×10^{-5}	3.0×10^{-5}	2.0×10^{-5}
1.	7.4×10^{-4}	5.9×10^{-4}	3.0×10^{-4}	1.5×10^{-4}	1.0×10^{-4}
0.1	2.2×10^{-3}	1.8×10^{-3}	9.2×10^{-4}	4.4×10^{-4}	2.9×10^{-4}
0.01	3.3×10^{-3}	2.6×10^{-3}	1.3×10^{-3}	6.6×10^{-4}	4.4×10^{-4}

12.5.2 Post-Equilibration Treatment

12.5.2.1 Procedure for Non-Radioactive Systems

1. Shut off sodium flow by closing inlet and outlet valves.
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 is prohibited by local safety practices, cool the sodium in the device at a rate of at least 50 C/min down to 500 C before draining the sodium. Cooling may be accomplished, for example, by turning off the heaters and flowing cool sodium over the wires.)
3. Shut the drain valve and inert gas inlet valve.
4. Cool the equilibration device to a convenient temperature no less than 110 C.
5. Pull the wire holder from the equilibration device. Insert a holder to close the device.

NOTE: If withdrawal of wires at temperatures ≥ 110 C is prohibited by local safety practices, omit steps 4 and 5 and substitute steps 4a and 5a.

4a. Cool the equilibration device to ambient temperature.

5a. 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 and repeat steps 2 through 5a. Finally, insert a spare holder to close the device.

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.)

7. Rinse holder and wires with distilled water and allow the wires to dry.

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

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.

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

10. Store the archival wires in a capped vial that is properly marked for identification.

11. Set the electropolish solution container on the magnetic stirrer and adjust the stirring rate to keep the solution moving steadily. Electropolish the wires for analysis to remove approximately 0.01 mm (0.0004 in.) from the surface. (An electropolishing current, 0.2 to 0.5 amp, should flow for about 30 sec total, 15 sec for each end.) Rinse with distilled water, then with methanol.

12. Determine the oxygen content of the wire by a standard inert-gas fusion or vacuum-fusion technique (e.g., by ASTM Method E 146, or if a LECO RO-16 Oxygen Determinator is used, by the procedure described in Section 12.5.3 below).

12.5.2.2 Procedure for Radioactive Systems

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

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 is prohibited by local safety practices, cool the sodium in the device at a rate of at least 50 C/min down to 500 C before draining the sodium. Cooling may be accomplished, for example, by turning off the heaters and flowing cool sodium over the wires.)

3. Shut the drain valve and the inert gas inlet valve.

4. Cool the equilibration device to a convenient temperature no less than 110 C.

5. Wait until activity has decayed to a tolerable level.

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

NOTE: If withdrawal of wires at temperatures ≥ 110 C is prohibited by local safety practices, substitute steps 4a, 5a, and 6a for steps 4, 5, and 6.

4a. Cool the equilibration device to ambient temperature.

5a. Wait until activity has decayed to a tolerable level.

6a. 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 and repeat steps 2 through 6a. Finally, insert a spare holder to close the device. Follow local radiation safety practices during this operation.

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

8. Transport the protected wire holder to the laboratory.

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 and according to 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.

10. Rinse the holder and wires with distilled water and allow the wires to dry.

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

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.

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

13. Store the archival samples in a capped glass or metal vial that is properly marked for identification.

14. Set the electropolish solution container on the magnetic stirrer and adjust the stirring rate to keep the solution moving steadily. Electropolish the wires for analysis to remove approximately 0.01 mm (0.0004 in.) from the surface. (An electropolishing current, 0.2 to 0.5 amp, should flow for about 30 sec total, 15 sec for each end). Rinse with distilled water, then with methanol.

15. Determine the oxygen content of the wire by a standard inert-gas fusion or vacuum-fusion technique (e.g., by ASTM Method E 146, or if a LECO RO-16 Oxygen Determinator is used, by the procedure described in Section 12.5.3 below).

12.5.3 Procedure for the Determination of Oxygen in Vanadium Using the LECO RO-16 Oxygen Determinator

1. Check the instrument per the LECO instruction manual and per the precautions noted in Section 12.7, Discussion. Determine a crucible blank, and standardize the instrument with one high (approximately 300 $\mu\text{g O}$) and one low (approximately 100 $\mu\text{g O}$) standard.
2. Cut 1/4 in. off each end of the wire sample.
3. Cut the rest of the wire into lengths just under 3/8 in. and place them into clean glass vials. (About 10 pieces are obtained per wire.)
4. Select and weigh a sample, based upon the estimated oxygen concentration, that will contain 100 to 300 μg of oxygen.
5. Put approximately 0.5 g of iron chips into a new graphite crucible, and insert the crucible into the lower electrode. (The iron chips function as a flux, without which the wires do not always completely fuse.)
6. 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.)
7. 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.)
8. Close the furnace assembly and proceed according to the LECO instruction manual.
9. Record the readout.
10. 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.
11. Analyze a standard that will correspond to the level of the oxygen in the samples after approximately every six determinations.

12.6 CALCULATIONS

1. Calculate the oxygen concentration in the vanadium wire sample by the following formula:

$$\text{Oxygen in vanadium, wt \%} = \frac{(A - B) 100}{C}$$

where

A = oxygen content of sample, mg

B = oxygen content of fusion blank, mg

TABLE 12-2. Corresponding Equilibrium Oxygen Concentrations,
Vanadium vs. Sodium at 750°C

V, wt % O	Na, ppm O	V, wt % O	Na, ppm O	V, wt % O	Na, ppm O
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

C = weight of sample, mg

2. Determine the oxygen concentration in sodium (in ppm) corresponding to the weight percent oxygen in the equilibrated vanadium wire by reference to Table 12-2, interpolating linearly between tabulated values if necessary.

12.7 DISCUSSION

This entire procedure, excluding the equilibration time, requires approximately 3 to 4 hr.

Table 12-2 was calculated by using the following equation applicable to the equilibrium oxygen distribution between vanadium and sodium at 750 C.

$$\ln \frac{N_{O-V}}{N_{O-Na}} = -28.22 + 39.42 (1 - N_{O-V})^2$$

where

N_{O-V} = atom fraction of oxygen dissolved in vanadium

N_{O-Na} = atom fraction of oxygen dissolved in sodium

While the general procedure does not require a specific oxygen analyzer, the current or planned use of the LECO RO-16 Oxygen Determinator in a majority of the laboratories in the sodium technology community made it desirable to describe precautions and deviations from the recommended procedure that experience dictates are required for successful operation with this instrument. Because a step-by-step method was deemed to be the best way of highlighting potential operational problems and of presenting precautionary measures, a detailed procedure has been given in Section 12.5.3. Even this approach, however, has not proven satisfactory to identify all potential difficulties and their solution. Two additional problems are as follows:

1. Successful operation requires that both a "purge" and a "measure" pressure be approximately 12 psig and that they be equal within 0.1 psig.

2. Effective operation requires the maintenance of a fixed nitrogen purge rate of 0.8 to 2.0 liters/min. To prevent blockage of the purge gas exit orifice by particulates, the instrument is equipped with a paper filter in the line. This filter may become plugged and will require removal and replacement. The revised LECO instruction manual (1972) covers this maintenance step.

13. DETERMINATION OF NITROGEN IN SODIUM BY THE KJELDAHL METHOD

13.1 PRINCIPLE

Sodium is converted to aqueous sodium methoxide. Ammonia resulting from the hydrolysis of nitrogen compounds is distilled into dilute acid, converted to indophenol by reaction with phenol and sodium hypochlorite, and the blue color developed is measured photometrically. The nitrogen determined in this procedure originates only from compounds which produce ammonia when hydrolyzed. For example, the nitrogen in amides, azides, imides, and some nitrides is determined quantitatively, whereas the nitrogen in methylamine and cyanide is not.

13.2 SENSITIVITY AND PRECISION

This method is suitable for the determination of 0.2 to 200 μg of nitrogen (0.1 to 100 ppm of nitrogen in a 2-g sample of sodium). The range can be adjusted upward by decreasing the sample size.

For nitrogen concentrations in the range 0.5 to 10 ppm, replicate determinations from the same sample are expected to agree within 15%.

13.3 APPARATUS

Kjeldahl Apparatus. This apparatus is illustrated in Fig. 13-1. To prevent accidental introduction of the acid catch-solution into the distillation flask, use a condenser with an internal volume great enough to prevent back flow of trap solution into the flask should the flask become partially evacuated.

Spectrophotometer. A photoelectric spectrophotometer that has provisions for insertion of 4-cm cells and that covers the visible region of the spectrum may be used.

Absorption Cells. These must be matched cells with 4-cm optical path lengths.

Inert-Atmosphere Box. The box must have a purification system capable of controlling the impurity levels of the atmosphere. For this analysis the oxygen and moisture contents of the atmosphere should each be ≤ 5 ppm. (See Appendix A.)

Balance. A balance that is capable of weighing to ± 0.1 g is adequate.

Safety Shield. For the Kjeldahl apparatus.

Vacuum Pump (Trapped). A pump with a capacity of 25 liters/min at 10^{-2} torr is adequate. This pump is needed for drying glassware.

Weighing Bottle.

Flowmeters. To indicate argon delivery rates of 500 and 20 ml/min.

Fig. 13-1

Typical Kjeldahl Apparatus

13.4 MATERIALS AND REAGENTS

Absorbent Cartridges. Aquasorb or equivalent may be used. (Aquasorb is a P_2O_5 -based water absorbent which also will remove ammonia from gases passed through it. It is a proprietary product of the Mallinckrodt Chemical Works.)

Water. Pass distilled water through a high-quality commercial mixed-bed ion exchange column. Store under ammonia-free air protected by an ammonia-absorbing cartridge. (If Aquasorb is used, it will pick up water. This does not decrease the efficiency of ammonia absorption.) Use this quality of water throughout the procedure.

Phenol Solution. Dissolve 60 g of colorless phenol in sufficient water to make 1 liter of solution. Store in a dark bottle.

Sodium Carbonate Solution. Dissolve 106 g of anhydrous, reagent grade sodium carbonate in sufficient water to make 1 liter of solution.

Phenol-Sodium Carbonate Solution. Mix 20 ml of phenol solution with 100 ml of sodium carbonate solution. Use within 4 hr.

Manganese Chloride Solution. Dissolve 0.06 g of reagent grade $MnCl_2 \cdot 4H_2O$ in sufficient water to make 1 liter of solution.

Sodium Hydroxide Solution (Saturated). By additions in small portions, with cooling if necessary, dissolve approximately 50 g of reagent grade NaOH pellets in 50 ml water. Store in a polyethylene bottle.

Sodium Hypochlorite Solution. Dilute reagent grade sodium hypochlorite solution (available chlorine 5.0% min) with 6 volumes of water. Store in a dark bottle and use within 1 month.

Nitrogen Standard Solution. Dissolve 0.382 g reagent grade NH_4Cl in sufficient water to make 1 liter of stock solution containing 1000 μg nitrogen per ml. Prepare a working standard solution daily by diluting 10 ml of stock solution to 100 ml with water.

Dilute Hydrochloric Acid. Dilute 0.9 ml concentrated acid to 1 liter with water.

Methanol. Reagent grade absolute methanol, low in acetone (acetone and aldehydes, as acetone, 0.001% max.).

Argon. Welding-grade tank argon passed through an ammonia-absorbing cartridge to remove any residual ammonia.

13.5 PROCEDURE

13.5.1 Standard Curve

1. Mix 30 ml of methanol with 25 ml of dilute hydrochloric acid in each of four 100-ml graduated mixing cylinders.

2. Add, respectively, 0.0, 0.5, 1.0, and 2.0 ml of nitrogen working-standard solution to the graduates. Mix.
3. Add 1 ml of sodium hypochlorite solution to each graduate and mix immediately.
4. Let each solution stand 5 ± 1 minutes after mixing.
5. Add 1 ml of manganese chloride solution and mix.
6. Add 12 ml of phenol-carbonate solution. Quickly mix and dilute with water to 100 ml.
7. Allow at least 30 min for color development.
8. Determine absorbance at 650 nm in 4-cm cells using water as a reference.
9. Construct a calibration curve by plotting absorbance as a function of micrograms of nitrogen taken. Typically, 10 μg of nitrogen will give an absorbance of about 0.25.

13.5.2 Equipment Preparation

1. Set up the apparatus as shown in Fig. 13-1.
2. Add 75 to 90 ml of water to the reservoir.
3. Drain the reservoir into the flask.
4. Distill approximately 50 ml of water from the flask into the 100-ml cylinder without cooling water circulating through the condenser.
5. Discard the condensate.

13.5.3 Blank Determination

Note: Steps 2 through 5 should be performed within 5 min of elapsed time.

1. Start water flowing through the condenser jacket.
2. Disconnect and empty the flask.
3. Quickly rinse the flask with water and then with methanol.
4. Vacuum dry the flask briefly.
5. Reconnect the flask to the system.
6. Put 25 ml of dilute hydrochloric acid in the 100-ml cylinder.
7. Put 30 ml of methanol, 50 ml of water, and 1 drop of saturated sodium hydroxide solution in the reservoir.

8. Drain the reservoir into the flask.
9. Distill 50 ml of water into the 100-ml cylinder.
10. Perform color development and measurement as in steps 3 through 8 of Section 13.5.1.
11. Determine the nitrogen content of the blank by reference to the calibration curve.

13.5.4 Sample Preparation

1. Obtain a bypass sample as described in Section 3.1.
2. Rinse the capped bypass tube containing the sample successively with actone, water, and acetone. Hold the tube by the ends, which will later be cut off and discarded.
3. Allow the sample tube to air dry.
4. Wrap the sample tube in aluminum foil.
5. Transfer the sample tube into the glove box.
6. Cut off and discard approximately 2.5 cm of sample tube.
7. Cut a section which will contain approximately 2 g of sodium. With experience, the sample weight may be estimated with sufficient precision from the length of the section of tube.
8. Place this sample section in a weighing bottle. Cap and transfer the bottle out of the glove box.
9. Weigh the bottle plus sample and record the weight.

13.5.5 Analysis

Note: Steps 2 through 5 should be performed within 5 min of elapsed time.

1. Make certain water is flowing through the condenser jacket.
2. Disconnect and empty the flask.
3. Quickly rinse the flask with water and then with methanol.
4. Vacuum dry the flask briefly.
5. Reconnect the flask to the system.
6. Flush the flask with argon while adjusting the argon flow to about 500 ml/minute.
7. Remove the stopper, drop in the sample from the weighing bottle, and quickly replace the stopper.

8. Put 30 ml of methanol in the reservoir and 25 ml of dilute HCl in the 100-ml cylinder.
9. After a 5-min purge, reduce the argon flow to 20 ml/min.
10. Slowly drip methanol onto the sodium.
11. After the sodium has dissolved, add the rest of the methanol, if any remains.
12. Add 50 ml of water to the flask through the reservoir.
13. Heat the flask to boiling and distill 50 ml of liquid into the 100-ml cylinder.
14. Remove the cylinder from the system before allowing the flask to cool so that distillate will not be sucked back.
15. Empty the flask and retrieve the section of bypass tubing.
16. If more samples are to be run, immediately prepare the flask according to steps 3 to 5 of this section.
17. Weigh weighing bottle plus section of bypass tubing and determine the weight of the sodium sample by difference from the weighing in step 9 of Section 13.5.4.
18. Perform color development and measurement as in steps 3 through 8 of Section 13.5.1. At least one standard should be run with each group of samples.
19. Determine the micrograms of nitrogen in the sample by reference to the calibration curve.

13.6 CALCULATIONS

Calculate the concentration of nitrogen in sodium by the following formula:

$$\text{Nitrogen, ppm} = \frac{A - B}{C - D}$$

where

- A = weight of nitrogen in the sample, μg
- B = weight of nitrogen in the blank, μg
- C = weight of sample plus tube plus bottle, g
- D = weight of tube plus bottle, g

13.7 SAFETY

The dissolution of sodium produces heat and large amounts of hydrogen gas. Serious explosions can occur if air-hydrogen mixtures ignite in a confined space.

Observe these precautions:

1. Be sure that the dissolution apparatus is dry before starting an analysis.
2. Flush all air from the flask with argon.
3. Perform the dissolution behind a safety shield.
4. Maintain a positive pressure in the flask so that trap solution cannot suck back. The internal volume of the condenser should be great enough to prevent back flow of the 25 ml of trap solution into the flask even if a vacuum should occur during the dissolution.

13.8 DISCUSSION

This procedure, exclusive of sampling and preparation of standard curve and equipment, requires approximately 2 to 3 hr.

The concentration of the undiluted sodium hypochlorite solution varies from batch to batch and with age. It may be necessary to adjust the dilution ratio so that full color development is attained with standards, but a large excess of hypochlorite is to be avoided.

14. DETERMINATION OF FLUORIDE IN SODIUM BY SPECIFIC ION ELECTRODE

14.1 PRINCIPLE

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

14.2 SENSITIVITY AND PRECISION

This method is suitable for the determination of 1 to 10 μg of fluoride (0.02 to 0.2 ppm of fluoride in 50-g sample of sodium). The range can readily be adjusted upward. For fluoride concentrations in the range 0.05 to 0.2 ppm, replicate determinations from the same sample are expected to agree within 25%.

14.3 APPARATUS

pH Meter, suitable for use with specific ion electrodes. The Corning Model 101 instrument has been found suitable.

pH Electrode.

Fluoride Specific Ion Electrode, with calomel reference electrode.

Magnetic Stirrer, with stirring bars.

14.4 MATERIALS AND REAGENTS

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

Total Ionic Strength Adjustment Buffer ("TISAB"). To approximately 500 ml of H_2O , add 57 ml reagent grade glacial acetic acid, 58 g reagent grade sodium chloride, and 0.30 g reagent grade sodium citrate. Titrate the solution to pH 5.0-5.5 using reagent grade 5M NaOH. Cool and dilute to 1 liter.

Sodium Fluoride Standard (1 mg F^-/ml). Dissolve 2.210 g reagent grade NaF in water and dilute to 1 liter.

Fluoride Working Standard. Dilute 10 ml of the sodium fluoride standard to 1 liter. Prepare fresh on the day of use.

14.5 PROCEDURE

1. Obtain a distillation residue prepared by the method of Section 4. Use a tantalum cup.
2. Compute the sample weight from information recorded on the distillation residue container (Section 4.4, step 23).
3. Rinse the cup with 20 ml of buffer solution and two 10-ml portions of buffer solution.

4. Combine all washings and dilute to 50 ml with additional buffer.
5. Prepare standards by adding 1.0, 3.0, and 10.0 micrograms of fluoride (0.1, 0.3, and 1.0 ml of working standard) to 50-ml portions of buffer.
6. Immerse the fluoride specific ion electrode in the standard containing 10 μ g while stirring the solution with a magnetic stirrer. Set the instrument zero to 1000 and adjust the meter response to 1000 by turning the "Calibrate" control.
7. Rinse the electrode with buffer and immerse it in the standard containing 1 μ g. Adjust the meter response to 100 by turning the "Slope" control.
8. Rinse the electrode with buffer and check for linearity of response by measuring the standard containing 3 μ g.
9. Rinse the electrode with buffer and immerse in the unknown solution. Record the meter reading.

14.6 CALCULATIONS

$$\text{Fluoride, ppm} = \frac{0.01 \times A}{W}$$

where

A = meter reading

W = sample weight, g (step 2 above)

14.7 SAFETY

This procedure presents no unusual safety hazards.

14.8 DISCUSSION

This procedure takes approximately 1/2 hr.

15. DETERMINATION OF Ag, Al, Au, Ba, Bi, Ca, Co, Cr, Cu, Fe, In, Li, Mg, Mn, Mo, Ni, Pb, Sc, Sn, Sr, Ti, and V IN A SODIUM DISTILLATION RESIDUE

15.1 PRINCIPLE

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.

15.2 SENSITIVITY AND PRECISION

Typical working ranges for the various elements are shown in column 4 of Table 15-1. For the concentrations given in column 5 of Table 15-1, a relative standard deviation of $\pm 25\%$ may be expected. As the upper portion of the working range is approached, the precision is expected to approach 5 to 15%.

15.3 APPARATUS

Atomic Absorption Spectrophotometer. Any commercially-available grating instrument or laboratory-assembled equivalent instrument may be used. A Perkin-Elmer Model 303 instrument has been found suitable for this use.

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

Hollow Cathode Lamps. As needed for the elements determined.

15.4 MATERIALS AND REAGENTS

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

Nitric Acid. Distill concentrated reagent-grade 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 thereby.

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

Ethyl Alcohol. 95% ethyl alcohol. Distill alcohol in a fused silica or borosilicate glass still and store in a polyethylene bottle.

Aqua Regia. Prepare fresh by mixing 1 part concentrated HNO_3 and 3 parts concentrated HCl.

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

Hydrochloric Acid-NaCl Solution. 2N HCl containing 200 $\mu\text{g/ml}$ NaCl.

TABLE 15-1. Calibration Ranges and Lower Limits of Analysis

Element	Measurement Method ^a	Medium	Typical Working Range: Metal Concentration, ppm	Analytical Limit ^b , ppm
Aluminum	AA	Alcoholic	1 to 10	0.6
Barium	FE	Alcoholic	0.25 to 2.5	0.05
Bismuth	AA	Alcoholic	0.05 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	0.05
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	0.1
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	0.1
Vanadium	AA	Aqueous	0.2 to 4	0.1

^aAA = atomic absorption. FE = flame emission.^bFor a 50-g sample of sodium.

Standard Metal Solutions. (1 mg/ml) in 2N HCl containing 200 µg/ml NaCl. 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 NaCl as the sample. Solutions containing approximately 200 µg/ml NaCl normally result when a residue from the procedure in Section 15.5 is used. However, should experience show that the concentration of NaCl in the sample solutions differ from 200 ppm by ±25%, adjustments must be made.

Lanthanum Solution. Dissolve 1.17 g of La_2O_3 in 10 ml concentrated HCl and dilute to 1 liter with water. The analyst has considerable freedom in choosing the concentrations of the working standard solutions. If it becomes necessary or desirable, he may change the dilution volume of the sample solution and the concentration of lanthanum added.

Sodium Chloride. Check the specific batch used for Ca and other impurities of interest.

Ethanol-NaCl Solution. Redistilled ethanol containing 200 ppm dissolved NaCl. Check the solution to assure absence of trace metal impurities.

Acetylene Gas. Purified, 99.6% min.

Nitrous Oxide Gas. Purity 98.0% min.

Air, Dry. Compressed gas in a cylinder, or a suitably-filtered lab supply.

15.5 PROCEDURE

1. Obtain a distillation residue from approximately 50 g of sodium by the procedure described in Section 4. Use a tantalum cup.

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

3. Add 1.5 ml aqua regia to the cup containing the distillation residue. Tilt and rotate the cup to moisture its inner surface.

4. Add 1 ml of La solution to prevent depression of Ca and Mg and enhancement of Mo responses.

5. Dilute the solution in the cup to 5 ml with water. Carefully heat the cup in near-boiling water for 5 min.

NOTE: If aqueous solutions are not to be prepared for tin determinations or for determining other elements at higher concentrations, omit steps 6 through 8.

6. Transfer the sample solution by transfer pipet and syringe to a 25-ml volumetric flask. Rinse the cup with 2N HCl and add the washings to the volumetric flask.

7. Dilute to volume with 2N HCl.

8. Pipe 5 ml of solution to be used for the determination of tin (and, possibly, for high-concentration impurities) and reserve for step 12. If the increased sensitivity obtainable with organic solutions is not necessary (i.e. if the concentrations involved are high enough to be determined precisely in aqueous media), omit steps 8 and 9.

9. Evaporate the sample solution to dryness but do not bake it, add 1 ml of concentrated HCl to the residue, and dilute to 25 ml with ethanol.

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-NaCl 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 in 4 ml of concentrated HCl, and dilute to 100 ml with the ethanol-NaCl solution.

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-NaCl 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 HCl and dilute to 100 ml with the ethanol-NaCl solution.

12. With the spectrophotometer adjusted to the proper settings (see Tables 15-2 and 15-3 for typical settings) alternately aspirate the standard, sample, and blank solutions, for 5 to 15 sec each.

13. Readjust the spectrophotometer settings for the next metal to be determined, if necessary, and repeat step 12.

14. Prepare a calibration curve for each element to be determined by plotting $\mu\text{g}/25\text{-ml}$ of standard solution *vs* the instrumental reading obtained.

15. From the calibration curves, obtain the total amount of each element in each sample solution.

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

TABLE 15-2. Typical Parameters for Atomic Absorption

Hollow-Cathode Lamp Used	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	328.1	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	304.0	Triple-Slot	Air
Aluminum	309.3	Nitrous Oxide	N ₂ O
Molybdenum	313.3	Nitrous Oxide	N ₂ O
Scandium	391.2	Nitrous Oxide	N ₂ O
Strontium	460.7	Nitrous Oxide	N ₂ O
Tin	286.3 or 224.6	Nitrous Oxide	N ₂ O
Titanium	365.3	Nitrous Oxide	N ₂ O
Vanadium	318.4	Nitrous Oxide	N ₂ O

^aAcetylene is the fuel in all cases.

TABLE 15-3. Typical Parameters for
Flame Emission Spectrometry

Element	Wave Length nm	Burner Type	Flame Oxidant ^a
Barium	553.6	Nitrous Oxide	N ₂ O
Lithium	670.8	Triple-Slot	Air

^aAcetylene is the fuel in both cases.

15.6 CALCULATIONS

Calculate the concentration of each element in the sample by the following formula:

$$\text{Concentration of element, ppm} = \frac{A \times B}{C - D}$$

where

A = weight of element from calibration curve, μg

B = Dilution factor (1.25 for alcoholic solutions when step 8 is performed; in all other instances, 1.0)

C = weight of sample plus container, g

D = weight of empty container, g

15.7 SAFETY

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

Acetylene. 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. Do not distribute it through copper tubing. Consult the Matheson Gas Data Book for further safety recommendations.

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

15.8 DISCUSSION

This procedure, exclusive of sampling, distillation, and standard curve preparation requires approximately 6 to 8 hr.

16. DETERMINATION OF CADMIUM AND ZINC IN SODIUM BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

16.1 PRINCIPLE

Sodium metal is dissolved in an alcohol-water solution and zinc and cadmium are separated by extraction into dithizone-chloroform. After back extraction into an acid medium, zinc and cadmium are determined by atomic absorption spectrophotometry.

16.2 SENSITIVITY AND PRECISION

The detection limit is 0.6 μg zinc or cadmium (0.06 ppm zinc or cadmium in a 10-g sample of sodium). Determinations on replicate aliquots are expected to agree within 25% in the range 0.1 to 1.0 $\mu\text{g}/\text{ml}$.

16.3 APPARATUS

Atomic Absorption Spectrophotometer. Any commercially-available grating instrument or laboratory-assembled equivalent instrument may be used. A Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer has been found suitable.

Quartzware. This is used for the dissolving of sodium and for the storing of strongly acidic and alkaline solutions.

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

Safety Shield. For use during dissolution of sodium.

16.4 MATERIALS AND REAGENTS

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

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 (NH_4OH) (concentrated NH_4OH diluted 1:99). Combine the NH_4OH extracts and acidify with HCl . Extract with liberated dithizone with 25-ml portions of chloroform and dilute to 100 ml with chloroform.

Chloroform. Reagent grade.

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

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

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

Methyl Alcohol. Absolute, reagent grade.

Ammonium Acetate Buffer, 1M. 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 20 ml portions of chloroform. Dilute to 100 ml with water.

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 2N HCl.

Cadmium Standard Solutions. Dissolve a known weight of $\text{CdCl}_2 \cdot 2\frac{1}{2} \text{H}_2\text{O}$ in 2N HCl, and by suitable dilution prepare a series of working standard solutions in the range 0.1 to 1.0 μg of cadmium/ml 2N HCl.

Acetylene Gas. Purified (minimum purity of 99.6%).

Air, Dry. Compressed air in a cylinder, or a suitably filtered lab supply.

16.5 PROCEDURE

1. Obtain a 10 to 12 g sodium sample by the overflow sampling procedure described in Section 3.2. Borosilicate glass or quartz beakers have been found suitable.
2. Weigh the sample plus beaker and place it in a 500-ml quartz beaker.
3. Dissolve the sample by dripping methyl alcohol-water mixture (90 ml CH_3OH + 30 ml H_2O) from a separatory funnel onto the sodium at the rate of one drop per second.
4. Cool the beaker in ice and acidify the solution with 35 to 40 ml of 12N hydrochloric acid.
5. Remove the sample beaker. Dry and weigh it.
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.
7. Cool, and transfer the solution to a 500-ml separatory funnel. Dilute to about 250 ml with water.
8. Add 5 ml of 1M ammonium acetate and adjust the pH to 8 with ammonium hydroxide.
9. Add 15 ml of chloroform and 5 drops of the 0.1% dithizone in chloroform.
10. Extract for 2 min and drain the extract into a 125-ml separatory funnel.
11. Perform three more extractions and combine all of the extracts.
12. Wash the solution with 10 ml of chloroform and combine the wash with the extracts.

13. Discard the aqueous phase.
14. Add 8 ml of 2N HCl to the extracts and back extract by shaking for 3 min.
15. Reject the chloroform phase and collect the acid phase in a 10-ml volumetric flask. Dilute to volume with 2N HCl.
16. Prepare a reagent blank solution as follows: Evaporate the acid and alcohol from a mixture of 90 ml alcohol + 30 ml H₂O + the volume of 12M HCl used to acidify the dissolved sample. Add 5 ml of 1M ammonium acetate buffer and dilute to 200 ml with H₂O. Adjust to pH 8 with NH₄OH and follow steps 9 to 15 above.
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.
18. Plot calibration curves in terms of micrograms of zinc or cadmium versus absorption.
19. Read micrograms of zinc and cadmium from calibration curves.

16.6 CALCULATIONS

The concentration of zinc or cadmium in the sodium sample is calculated by the following equation:

$$\text{Zinc or cadmium, ppm} = \frac{A}{(B - C)} \times \frac{1}{E}$$

where

A = weight of Zn or Cd, μg

B = weight of sample plus beaker, g

C = weight of empty beaker, g

E = extraction efficiency (approximately 0.9). This may be checked by measuring the fraction recovered of known quantities of Zn and Cd, added to a NaCl solution previously purified by dithizone extraction and processed through the procedure.

16.7 SAFETY

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 which could permit an explosive atmosphere to build up never should 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.

16.8 DISCUSSION

This procedure, exclusive of sampling, requires approximately 3 hr.

17. DETERMINATION OF POTASSIUM IN SODIUM BY FLAME SPECTROPHOTOMETRY

17.1 PRINCIPLE

A sample of sodium is dissolved in methanol, acidified, and diluted to volume. Potassium is determined by flame spectrophotometry without separation from sodium.

17.2 SENSITIVITY AND PRECISION

This method is suitable for the determination of 100 to 1000 μg of potassium (100 to 1000 ppm of potassium in a 1-g sample of sodium). The range can be extended downward by optimizing instrument parameters, using additional standards, and increasing the sample size. A detection limit of 4 to 10 μg of potassium can readily be attained.

At the 100 ppm level, replicate samples are expected to agree within $\pm 5\%$.

17.3 APPARATUS

Flame Spectrophotometer. This instrument should be a scanning spectrophotometer suitable for the determination of potassium at the 766.5 nm emission line. Typical specifications, except for the scanning feature, may be found in ASTM Method D 1428. A scanning instrument is preferred because automatic peak scanning offers the advantage of obtaining background correction with greater ease and precision than manual scanning procedures. The Perkin-Elmer Model 403 has been found suitable.

Polypropylene Graduated Cylinders. 100-ml graduated cylinders are used as dissolution vessels and as volumetric ware for samples and working standards.

17.4 MATERIALS AND REAGENTS

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

Methanol. Redistill methanol from a quartz or borosilicate glass still and store it in polyethylene bottles. Ethanol may be substituted for methanol.

Nitric Acid. Redistill nitric acid from a quartz still and store it in Teflon bottles after dilution to approximately 5M.

Bromocresol Green Indicator. Dissolve 0.04 g of bromocresol green in 100 ml of ethanol.

Potassium Standard Solution. Dissolve 0.24 g of KNO_3 , dried at 110°C , in 100 ml of water to make a 1 mg/ml standard.

Sodium Carbonate. Select reagent grade anhydrous sodium carbonate for low potassium content.

17.5 PROCEDURE

17.5.1 Sample Preparation

Separate treatments are described below for two different types of samples; a bypass sample, and an overflow sample.

17.5.1.1 Bypass sample (From Section 3.1)

1. Obtain a sodium sample in a bypass tube by the procedure described in Section 3.1.
2. Rinse the exterior of the bypass sample tube with dilute hydrochloric acid, deionized water, and methanol or ethanol. Dry the tube.
3. Cut off at least one inch section from the end of the sample tube with a tubing cutter. Discard the end section.
4. Cut off and weigh a section containing approximately 2 g of sodium.
5. Dissolve the sample in a minimum of methanol (approximately 20 ml) in a 100-ml polypropylene graduated cylinder.
6. Retrieve the empty tubing section and weigh it.
7. Proceed to Section 17.5.2.

17.5.1.2 Overflow Cup Sample (From Section 3.2)

1. Obtain a sodium sample weighing approximately 50 g in an overflow cup by the procedure described in Section 3.2. If appreciably larger or smaller samples are obtained, adjust the volumes in steps 3 and 4 below accordingly. Quartz and tantalum cups have been found suitable.
2. Weigh the cup plus sample.
3. Place the cup in a 1200-ml stainless steel beaker and dissolve the sodium in approximately 450 ml of methanol.
4. Transfer the solution to a 500-ml polyethylene volumetric flask and dilute to the mark with methanol.
5. Pipet an aliquot of solution containing approximately 1 g of sodium into a 100-ml polypropylene graduated cylinder.
6. Weigh the empty cup.
7. Proceed to Section 17.5.2.

17.5.2 Determination of Potassium

1. Prepare a series of working standards by adding 0, 100, 250, 500, 750, and 1000 microliters of the potassium standard solution to individual polypropylene mixing graduates containing 2.25 g of sodium carbonate. Add an amount of methanol equal to that in the sample aliquot and carry these standards through the remaining steps of the procedure.

2. Add several drops of bromcresol green indicator to each sample aliquot and standard.

3. Add sufficient dilute nitric acid to weakly acidify the solution, i.e., to turn the indicator from blue to yellow.

4. Dilute each acidic solution to 100 ml with water and mix.

5. Scan the flame spectrum over the range of 762 to 768 nm. This is to be done for both samples and standards. Also, samples and standards must be flamed consecutively.

6. Using the readings obtained on the standards, plot a calibration curve of emission intensity versus micrograms of potassium. Determine the weight of potassium in the samples by referring to this curve.

17.6 CALCULATIONS

The concentration of potassium in sodium is calculated by the following formula:

$$\text{Potassium, ppm} = \frac{A}{B - C} \cdot F$$

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

F = aliquot factor

17.7 SAFETY

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 which 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 alcohol. To eliminate the chance of igniting a large amount of methanol, the methanol added during the dissolution process should be poured from a beaker rather than directly from a bottle.

17.8 DISCUSSION

This procedure, exclusive of sampling, requires approximately 1 hr.

If the potassium level is <5 ppm, either an ultra-pure grade of sodium carbonate or a standard addition technique is required. Selected batches of reagent grade sodium carbonate are suitably low in potassium to be used in preparing standards for most sodium samples.

If a scanning flame spectrophotometer is not available, atomic absorption spectrophotometry is an acceptable alternate, but at reduced sensitivity.

18. DETERMINATION OF RUBIDIUM AND CESIUM IN SODIUM BY FLAME SPECTROPHOTOMETRY

18.1 PRINCIPLE

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.

18.2 SENSITIVITY AND PRECISION

The detection limits are 0.2 μg for each element (0.05 ppm for each element in a 4-g sample of sodium). Duplicate determinations are expected to agree within 10 percent at the 5 ppm level.

18.3 APPARATUS

Scanning Double-Beam Flame Spectrophotometer. Equipped with a 3-slot air-acetylene burner and a strip-chart recorder. A Perkin-Elmer Model 403 instrument has been found satisfactory. Alternatively, an atomic absorption spectrophotometer may be used if wavelength scanning is not available.

Ion Exchange Columns. Borosilicate glass columns 1-cm ID by 15 cm long, with the top enlarged to a 100-ml reservoir.

Safety Shield. For use during dissolution of sodium.

18.4 MATERIALS AND REAGENTS

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

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

Nitric Acid. Redistill concentrated acid from a quartz still; store in a Teflon bottle.

Bromocresol Green Indicator. Dissolve 40 mg of bromocresol green in 100 ml of ethanol.

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

Wash Solution (0.3M HCl). Dilute 50 ml of concentrated hydrochloric acid to 1 liter and store in a polyethylene bottle.

Rubidium-Cesium Stock Standard (200 µg/ml). Dissolve 71 mg of rubidium chloride and 63 mg of cesium chloride (both dried at 150°C) in 250 ml of wash solution.

Rubidium-Cesium Dilute Standard (20 µg/ml). Dilute 10 ml of the stock standard to 100 ml with wash solution (0.3M HCl).

Ammonium-12-Molybdophosphate (AMP). Prepare by the direct method of J. Van R. Smit *et al.* [see "Cation Exchange Properties of the Ammonium Heteropoly Acid Salts," *J. Inorganic and Nuclear Chem.* 12, 95 (1959)]. A similar material is available from Bio-Rad Laboratories.

Potassium Chloride Solution. Dissolve 6.4 g of potassium chloride containing less than 5 ppm each of rubidium and cesium in sufficient water to make 100 ml of solution.

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

AMP/Cotton. Dissolve 5 g of AMP in 15 ml of 2M ammonium hydroxide. Add this solution to ten 1x4 cm cotton dental rolls (or equivalent--about 4 g of absorbent cotton). Squeeze to uniformly distribute the solution, then add 100 ml of 8M nitric acid (distilled in quartz) 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.

18.5 PROCEDURE

1. Obtain a bypass sample by the procedure described in Section 3.1.
2. Cut off and discard about 1 in. from the end of the sample.
3. Cut off a section containing 3 to 4 g of sodium and weigh it.
4. Dissolve the sample in 50 ml of methanol in a polypropylene beaker.
5. Add two drops of bromcresol green indicator, then cautiously add 2 ml of 6M hydrochloric acid in excess of that required to turn the indicator from blue to yellow.
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.
7. Evaporate the methanol by heating until almost dry. Evaporation to dryness by heating overnight is convenient and not harmful. Dissolve the crystals and dilute to about 75 ml with wash solution (0.3M HCl).
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.
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.

10. Recover rubidium and cesium by adding 2M ammonium hydroxide to the column in increments of 1 to 2 ml 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.

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 critical instrument settings for the Perkin-Elmer 403 spectrophotometer are:

Grating: visible

Filter: in

Wavelength drive speed: 3

Flame: oxidizing

Burner: 3-slot

Slit: 4 for cesium, 3 for rubidium

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

13. Prepare a calibration curve of relative emission intensity vs micrograms of Rb or Cs from the standards. Read the micrograms of rubidium and cesium in the sample from this calibration curve.

18.6 CALCULATIONS

$$\text{Rubidium or cesium, ppm} = \frac{A}{W}$$

where

A = Rb or Cs found in the sample, μg

W = sample weight, g

18.7 SAFETY PRECAUTIONS

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 which 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.

18.8 DISCUSSION

As an ion exchanger, AMP has two undersirable 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.

This procedure, exclusive of sampling, takes approximately 6 hr in addition to the time required to evaporate the methanol (overnight).

19. DETERMINATION OF SILICON IN A SODIUM DISTILLATION RESIDUE BY SPECTROPHOTOMETRY

19.1 PRINCIPLE

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

19.2 SENSITIVITY AND PRECISION

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

For silicon concentrations in the range 1 to 4 ppm, replicate determinations are expected to agree within 25%.

19.3 APPARATUS

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

Spectrophotometer, with matched 1-cm cells. A Beckman Model B instrument has been found satisfactory.

pH Meter

Centrifuge

Magnetic Stirrer, with Teflon-covered stirring bars.

Teflon Beakers

Polyethylene Test Tube

19.4 REAGENTS AND MATERIALS

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

Nitric Acid, Concentrated, silica-free.

Hydrochloric Acid, Concentrated, silica-free.

Hydrofluoric Acid, silica-free.

Molybdic Acid Solution, 10%. Dissolve 7 g of ammonium molybdate in 35 ml of water in a Teflon beaker, using a magnetic stirrer and Teflon-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.

Boric Acid Solution. Dissolve 40 g of boric acid in 800 ml of luke-warm silica-free water. Cool, dilute to 1 liter, and store in a plastic bottle.

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.

Ammonium Hydroxide Solution. Saturate silica-free water, kept in an ice bath, with tank ammonia. Store the solution in a polyethylene bottle.

Silicon Standard Solution. Prepare a standard silicon solution containing 1.0 mg SiO_2 /ml (0.47 mg Si/ml) by diluting a sodium silicate standard volumetric concentrate with silica-free water. Store in a polyethylene bottle. The resulting solution is stable indefinitely. Acculate ampoules supplied by Anachemia Chemicals, Inc. have been found suitable.

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.

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.

Potassium Permanganate Solution. 0.004 M.

19.5 PROCEDURE

1. Obtain a distillation residue from approximately 10g of sodium in a tantalum cup according to the procedure of Section 4.
2. Record the weights of the sodium-filled and empty cup, as marked on the transfer vessel.
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 Teflon stirring rod.
4. Transfer the solution to a polyethylene test tube. Wash the cup with 5 ml H_2O . Add 3 drops of hydrofluoric acid and let the solution stand overnight.
5. Centrifuge to remove any insoluble residue.
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 H_2O .
7. Transfer the sample and blank to 100-ml Teflon beakers.
8. Add 4 drops of 0.004 M potassium permanganate solution and then 20 ml of boric acid solution.
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.

10. Add 5 ml of sulfuric-tartaric acid solution and mix by swirling.

11. Immediately add 1 ml of reducing solution and mix by swirling.

12. Transfer the solutions from the Teflon beakers to 50-ml volumetric flasks and dilute to the mark with water.

13. Let the solutions stand for 20 to 30 minutes for color development.

14. Measure the absorbance of the solutions in 1-cm cells at 800 nm against water as a blank.

15. Prepare standard solutions containing 5 to 40 μg Si by pipeting working standard solution into 100-ml Teflon beakers and carrying out steps 8 through 13.

16. Measure absorbance of the standards and prepare a calibration curve of μg Si vs absorbance.

17. Read μg Si in sample and blank from the calibration curve.

19.6 CALCULATIONS

$$\text{Silicon, ppm} = \frac{A - B}{W} \times \frac{100}{R}$$

where,

A = silicon in sample, μg

B = silicon in blank, μg

W = weight of sample, g

R = % recovery. Assume R to be 100 or determine it by carrying spiked sample through the analysis

19.7 SAFETY

Standard safety practices should be followed in handling strong acids.

19.8 DISCUSSION

Recovery of silicon (added as sodium silicate) from sodium by the vacuum distillation technique is close to 100%. Phosphate, arsenate, and titanium interfere in the spectrophotometric procedure.

This procedure, exclusive of sampling and distillation, takes approximately 4 hr in addition to the overnight dissolution.

20. DETERMINATION OF BORON IN A SODIUM DISTILLATION RESIDUE BY SPECTROPHOTOMETRY

20.1 PRINCIPLE

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

20.2 SENSITIVITY AND PRECISION

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

For boron concentrations in the range 0.1 to 0.35 ppm, replicate determinations are expected to agree within 25%.

20.3 APPARATUS

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

Spectrophotometer with matched 1-cm cells. The Beckman Model B instrument has been found suitable.

Platinum Dishes.

Polyethylene Stirring Rods.

Centrifuge.

Polycarbonate Centrifuge Tubes.

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

20.4 MATERIALS AND REAGENTS

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

Curcumin-Acetic Acid. Dissolve 0.125 g of curcumin in 100 ml of reagent grade glacial acetic acid. (This reagent, stored in polyethylene bottles, is stable for several months if kept in the dark.)

Sulfuric-Acetic Acid Reagent. Cautiously add 50 ml of reagent grade

sulfuric acid (sp. gr. 1.84) to 50 ml of reagent grade glacial acetic acid with constant stirring.

Aqua Regia. Prepare fresh by mixing 3 parts concentrated hydrochloric acid and 1 part concentrated nitric acid.

Sodium Hydroxide Solution (10% w/v). Dissolve 10 g of reagent grade sodium hydroxide pellets in 100 ml of distilled water in a polyethylene beaker. Store in a polyethylene bottle.

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

Boron Standard Solution, 1 mg B/ml. Dissolve 5.715 g reagent grade boric acid (H_3BO_3) in 500 ml of water and dilute to 1 liter. Store in a polyethylene bottle.

Boron Working Standard Solution, 10 μg B/ml. Dilute 10 ml of the Boron Standard Solution to 1 liter with water. Keep in a polyethylene bottle and prepare fresh on the day of use.

20.5 PROCEDURE

1. Obtain a distillation residue from approximately 10g of sodium in a tantalum cup according to the procedure of Section 4.
2. Compute the sample weight from the information recorded on the transfer vessel holding the cup and residue. (Section 4.4, step 23.)
3. Add 0.5 ml of 10% sodium hydroxide to the distillation residue in the sample cup and stir with a polyethylene rod.
4. Evaporate the solution in the sample cup gently to dryness on a boiling water bath.
5. Add 1.5 ml of curcumin-acetic acid reagent and warm the sample cup gently to dissolve the residue.
6. Cool the sample cup to room temperature and add 1.5 ml of sulfuric acid--acetic acid reagent.
7. Stir well with a polyethylene rod and allow to stand for 15 min.
8. Dilute the mixture by stirring in about 15 ml of ethyl alcohol and transfer the resulting slurry to a 50-ml volumetric flask.
9. Rinse the sample cup with ethyl alcohol and add the rinses to the volumetric flask.
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.)

11. Mix the solution and centrifuge a portion in a polycarbonate tube. Measure the absorbance in a 1-cm cell at 555 nm on a spectrophotometer. A reagent blank is prepared similarly, using a platinum dish rather than a sample cup.

12. Pipet 0, 1, 2, and 3.5 μg of boron into platinum dishes and follow the procedure as given for sample steps 4 to 12.

13. Measure the absorbance at 555 nm on a spectrophotometer.

14. Plot the absorbance vs μg of boron to obtain the calibration curve.

15. Determination micrograms of boron in the sample and in the blank by reference to the calibration curve.

20.6 CALCULATIONS

$$\text{Boron, ppm} = \frac{A - B}{W} \cdot \frac{100}{R}$$

where,

A = boron in sample, μg

B = boron in the blank, μg

W = weight of the sample, g

R = percent recovery of boron in the procedure. Assume R to be 95, or determine it by carrying spiked samples through the distillation and analysis.

20.7 SAFETY

Standard safety practices should be followed in the preparation and use of strong acid reagents and in handling flammable organic materials.

20.8 DISCUSSION

This procedure, exclusive of sampling and distillation, requires approximately 2 hr.

Recovery of boron, added as boric acid or sodium borate to sodium metal, by vacuum distillation and colorimetric analysis is 90 to 95%. The method has excellent reproducibility and is free of several interferences. Fluoride, nitrate, and titanium ions interfere in complex formation, and hence they should be avoided in the procedure.

21. DETERMINATION OF URANIUM IN A SODIUM DISTILLATION RESIDUE BY FLUORIMETRY

21.1 PRINCIPLE

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 NaF-2% LiF. The uranium content of the fused fluoride bead is measured fluorometrically.

21.2 SENSITIVITY AND PRECISION

The detection limit is 0.1 μ g of uranium (0.002 ppm uranium in a 50-g sample of sodium). The precision of this analysis is approximately $\pm 10\%$.

21.3 APPARATUS

Fluorophotometer. The fluorophotometer must be equipped with a light source for inducing fluorescence of uranium and must be capable of measuring the fluorescence of 0.01 μ g of uranium. The Model 26000 G-M Fluorometer, produced by the Jarrell-Ash Division of Fisher Scientific Co., has been found suitable.

Platinum Dishes. The platinum dishes are 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.

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

Meker-Type Burner.

Laboratory Centrifuge.

Centrifuge Cones, 15-ml capped type.

Pellet Press. This is a device to prepare 0.4-g pellets of flux.

21.4 MATERIALS AND REAGENTS

All reagents and glassware must be uranium free.

Concentrated Nitric Acid.

Nitric Acid, 2N. Add 130 ml of concentrated nitric acid to 500 ml of distilled water and dilute to 1 liter.

Salting Solution. 1.9M aluminum nitrate, acid deficient, and 0.019M tetrapropyl ammonium nitrate. Dissolve 725 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in a minimum amount of water with the aid of heat. Slowly add 95 ml concentrated NH_4OH 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 one liter with deionized water.

Hexone (Methyl isobutyl ketone).

Flux 98% NaF-2% LiF (powder).

Uranium Standard Solution. 0.5 μg U/ml in 2N HNO_3 .

21.5 PROCEDURE

1. Obtain a distillation residue from approximately 50 g of sodium by the procedure described in Section 4. Use a tantalum cup. Remove the distillation cup from its container. Record the weights marked on the container.
2. Add 1.5 ml of concentrated nitric acid to the distillation residue. Tilt and rotate the cup to moisten the inner surface.
3. Add about 3.5 ml of distilled water to the cup.
4. Carefully heat the cup in near-boiling water for 5 min.
5. Transfer the sample solution to a 30-ml beaker. Rinse the cup into the beaker with 5 ml of 2N HNO_3 .
6. Evaporate the solution to approximately 0.5 ml, cool, and add 5 ml of the aluminum nitrate salting solution.
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.
8. Accurately pipet 2 ml of hexone into the centrifuge cone and extract the uranium by thorough mixing for 3 min.
9. Centrifuge for 2 min to separate the phases.
10. Pipet a 200- μl aliquot of a standard uranium solution into one of the platinum dishes and evaporate to dryness under a heat lamp.
11. Pipet a 200- μl aliquot of a standard uranium solution into one of the sample dishes to serve as a check for possible fluorescence quenching. See Discussion in Section 21.7.
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.

13. Add a pellet (approximately 0.4 g) of NaF-2% LiF flux to each of the platinum dishes including a dish for the blank.

14. Fuse the flux in each dish over a Meker-type burner by holding the platinum dish with the wire loop just above the reducing portion of the flame. After the flux is entirely liquefied, remove the dish from the flame and allow to 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: Fuse and cool all fluxes in the same set under the same conditions, since the fluorescence is affected by fusion temperature, cooling rate, etc.

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

16. Prepare a calibration curve of (fluorescence of standard - fluorescence of blank) vs (micrograms of uranium).

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.

21.6 CALCULATIONS

Calculate the uranium concentration in sodium according to the following formula:

$$\text{Uranium, ppm} = \frac{10 A}{W}$$

where

A = weight of uranium in sample aliquot, μg

W = weight of sodium sample, g

21.7 SAFETY

This procedure presents no unusual safety hazards.

21.8 DISCUSSION

This procedure, exclusive of sampling and distillation, requires approximately 1 hr.

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.

22. DETERMINATION OF PLUTONIUM IN SODIUM BY ALPHA ASSAY

22.1 PRINCIPLE

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.

22.2 SENSITIVITY AND PRECISION

Approximately 0.015 μg of ^{239}Pu (0.3 ppb ^{239}Pu in a 50-g sample of sodium) can be determined to $\pm 10\%$ in a distillation residue from a 50-g sample, assuming 50% counter geometry. The detection limit is approximately 0.03 ppb ^{239}Pu under these conditions.

22.3 APPARATUS

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.

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.

Planchets. Stainless steel planchets adaptable to the alpha counter and alpha spectrometer should be used.

Electrodeposition Cell. (See Fig. 22-1 for a typical cell.)

Separatory Funnels. 60 ml.

22.4 MATERIALS AND REAGENTS

Concentrated Nitric Acid. Reagent grade acid.

Nitric Acid, 2N. Add 130 ml of concentrated nitric acid to 500 ml of distilled water and dilute to 1 liter.

Ascorbic Acid Solution. 5% aqueous solution.

Ammonium Citrate Solution. 20% aqueous solution.

Fig. 22-1

Typical Electrodeposition Cell for Plutonium

Thioglycolic Acid (TGA) Solution. 16% aqueous solution.

NaHCO₃ Solution. Saturated aqueous solution.

KCN Solution. 5% aqueous solution.

N-benzoyl-N-phenylhydroxylamine (BPHA) Solution. Dissolve 4 g BPHA in 100 ml of ethanol.

Benzene.

NaOCl Solution, 5% aqueous solution.

NaOH, 2N aqueous solution.

Perchloric Acid. 70-72% reagent grade acid.

22.5 PROCEDURE

22.5.1. Gross Alpha Assay

1. Obtain a distillation residue from approximately 50 g of sodium as described in Section 4. Use a tantalum cup. Record the weights given on the transfer container.
2. Remove the distillation cup from the container and weight 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 7 through 10 of this section and step 1 of Section 22.5.2.
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.
4. Carefully heat the cup in a simmering water bath for 20 min to dissolve any PuO₂ in the residue.
5. Transfer the solution to a 30-ml beaker. Rinse the cup with concentrated nitric acid and combine the rinsings with the solution.
6. Evaporate the solution to 1 ml and cool. Proceed to step 2 of Section 22.5.2. if steps 7 through 10 are to be omitted.
7. Transfer the solution quantitatively to a 10-ml volumetric flask and dilute to volume with 2N HNO₃.
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 step 1 of Section 22.5.2.
9. Carefully flame the planchet to dull red heat over a gas burner.

10. Alpha assay the planchet in a calibrated alpha counter and calculate the alpha activity. If the alpha count obtained is significant, proceed to Section 22.5.2.

22.5.2 Plutonium Extraction and Alpha Assay

1. Transfer the solution remaining from step 22.5.1.8 into a 30-ml beaker, evaporate to approximately 1 ml, and cool.

2. To the solution from step 22.5.1.6. or step 1 above, 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 NaHCO_3 solution. Next, add 1 ml of 5% KCN solution and 1 ml of 4% BPHA in ethanol. Mix and allow the solution to stand for 5 minutes.

NOTE: The *order* of addition of the reagents is important. Follow the above directions exactly.

3. Transfer the solution into a 60-ml separatory funnel, add 10 ml of benzene, and extract the Pu-BPHA complex into the benzene phase by shaking for 2 min.

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 Section 22.5.3.

22.5.3 Plutonium Separation by Electrodeposition and Assay by Alpha Spectrometry

1. Back-extract the plutonium from the benzene phase into 5 ml of 0.5 N HNO_3 . Drain the aqueous phase into a 30-ml beaker. Wash the benzene with approximately 5 ml of 0.5 N HNO_3 and add the washings to the 30-ml beaker.

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 HClO_4 will remove any organic material and oxidize all plutonium to Pu(VI).]

3. During evaporation of the solution, prepare the electrodeposition cell. Clean the Type 304 stainless steel plate in warm chromic acid cleaning solution, rinse it with water, and assemble the cell as indicated in Fig. 22-1. (Handle the plate with tweezers during this operation--do not touch it with fingers.) Immediately fill the cell with 2 N NaOH and set it aside until ready to continue with the electrodeposition.

4. Add approximately 2 ml of water, 8 ml of 2 N NaOH, and 1 ml of 5% NaOCl solution to the 0.5 ml of perchloric acid from step 2 above.

5. Discard the 2 N NaOH in the cell and transfer the solution from Step 4 into the cell. Wash the beaker with 2 ml of water and add the

washings to the cell.

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 1 to 1.5 cm 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 Pu at approximately 70 C for 3 hr at 150 mA while stirring at about 100 rpm.

7. Disconnect the power source at the end of the 3-hr 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.

8. Identify the isotopes present in the electrodeposited plutonium by alpha spectrometry. The yield under the above conditions is 95 to 100%.

22.6 CALCULATIONS

Calculate the gross alpha activity or the plutonium alpha activity by the following formula:

$$\text{Activity, pCi/g} = \frac{R \times F}{G \times (A - B) \times 2.22}$$

where

R = net count rate, cpm

F = total volume of sample solution divided by volume of aliquot

G = geometry factor of counter, counts/dis

A = weight of sodium sample plus cup, g

B = weight of empty cup, g

22.7 SAFETY

Local safety practices for handling alpha-active samples must be observed.

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 which will be present if good phase separations are achieved.

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 cyanide solutions. Handle solid potassium cyanide with respect. Dispose of cyanide residues in compliance with locally-administered safety practices.

22.8 DISCUSSION

this entire procedure, exclusive of sampling and distillation, requires 5 to 8 hr. The gross alpha count (Section 22.5.1.) requires about 1 hr.

An additional hour is required for the plutonium extraction and counting (Section 22.5.2).

The gross alpha assay (step 22.5.1.10) is not specific for plutonium. Neptunium is the only known interference in the plutonium assay (step 22.5.2.4).

The results obtained on the alpha counting (steps 22.5.1.10 and 22.5.2.4) 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.

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 22.5.1.2 is based on the assumption that the planchet is approximately 1 in. in diameter and that the bulk composition of the solids is sodium nitrate.

23. DETERMINATION OF NONVOLATILE ALPHA ACTIVITY IN SODIUM

23.1 PRINCIPLE

The residue from vacuum distillation of a sodium sample is dissolved in concentrated nitric acid and a gross alpha assay of an aliquot of the solution is performed.

23.2 SENSITIVITY AND PRECISION

An alpha disintegration rate of approximately 12 dis/sec (0.25 dis/sec in one gram of sodium, using a residue from the laboratory distillation of a 50-g sodium sample and a 50% counter geometry) can be determined to $\pm 10\%$. The detection limit is about 1 dis/sec under these conditions.

23.3 APPARATUS

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.

Planchets. Stainless steel planchets adaptable to the alpha counter should be used.

23.4 MATERIALS AND REAGENTS

Concentrated Nitric Acid. Reagent grade concentrated acid.

23.5 PROCEDURE

1. Obtain a distillation residue in a tantalum or titanium cup from approximately 50 g of sodium as described in Section 4. Record the two weights given on the transfer container.

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. A residue weight >10 mg indicates that the initial sample was excessively contaminated. Since contamination at this level will complicate the analysis, discard the sample and obtain another residue.

3. Add 5 ml of concentrated HNO_3 to the distillation residue in the distillation cup. Tilt and rotate the cup to moisten the inner surface.

4. Carefully heat the cup in a simmering water bath for 20 min.

5. Transfer the solution to a 30-ml beaker. Rinse the cup with concentrated HNO_3 , and add the rinsings to the solution.

6. Evaporate the solution to 1 ml and cool.

7. Transfer the solution quantitatively to a 10-ml volumetric flask and dilute to volume with water.

8. Pipet a 1-ml aliquot of the above solution onto a stainless steel planchet and carefully evaporate under a heat lamp.

9. Carefully flame the planchet to dull red heat over a gas burner.

10. Alpha assay the planchet in a calibrated alpha counter and calculate the alpha activity.

23.6 CALCULATIONS

Calculate the alpha content in the sodium sample by the following formula

$$\text{Alpha content, dis/(sec) (g Na)} = \frac{\left[\frac{C}{T} - B\right]}{W \times G}$$

where

B = counter background, cps

C = total counts from sample

T = time, sec

G = geometry factor for counter, counts/dis

W = weight of sodium sample, g

23.7 SAFETY

Local safety practices for handling alpha active samples must be observed.

23.8 DISCUSSION

This entire procedure, exclusive of sampling and distillation, requires approximately 1 hr.

24. GENERAL GAMMA ASSAY OF A DISTILLATION RESIDUE OF RADIOACTIVE SODIUM

24.1 PRINCIPLE

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.

24.2 SENSITIVITY AND PRECISION

The sensitivity will vary with the branching ratio of the particular isotope being determined and on the activity levels of other isotopes present. Detection limits on the order of 1×10^{-5} $\mu\text{Ci/g}$ of sodium for isotopes with favorable branching ratios, e.g. (^{54}Mn , ^{125}Sb) have been obtained in EBR-II primary sodium. For activities 10 times the detection limit, a precision of $\pm 10\%$ should be obtained.

24.3 APPARATUS

Multichannel Analyzer System. This 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. The system must be calibrated for both efficiency and geometry by standard gamma spectrometric techniques. These techniques are given in J. E. Cline, "Studies of Detection Efficiencies and Operating Characteristics of Ge(Li) Detectors," IEEE Trans. on Nuclear Science, Vol. NS-15, No. 3 pp. 198-213 (1968) and in R. L. Heath, "Scintillation Spectrometry Gamma-Ray Catalogue," 2nd Edition, USAEC Report IDO-16880 (1964).

Counting Vials. The vials must be calibrated to contain a standard volume.

24.4 MATERIALS AND REAGENTS

Aqua Regia. Prepare fresh by mixing 1 part concentrated HNO_3 with 3 parts concentrated HCl .

24.5 PROCEDURE

1. Obtain a distillation residue from approximately 50 g of sodium in either a tantalum or titanium cup according to the procedure described in Section 4. Record the weights given on the sample container.
2. Add 5 ml of aqua regia to the distillation cup. Swirl to dissolve the residue.
3. Transfer the solution quantitatively to a counting vial and dilute to volume.
4. Check the cup for residual activity. If activity is detected, repeat steps 2 and 3.

5. Obtain a gamma spectrum under previously-established standard conditions.

24.6 CALCULATIONS

Calculate the gamma activity of each isotope identified according to the following formula:

$$\text{Activity, } \mu\text{Ci/gNa} = \frac{R}{B \times E \times G (C-D) \times 2.2 \times 10^6}$$

where

R = net count rate, cpm

B = fraction of total disintegrations emitting measured energy

E = efficiency of counting system for the energy of the gamma radiation used

G = geometry factor, counts/dis

C = weight of sample plus cup, g

D = weight of empty cup, g

24.7 SAFETY

Standard safety practices for handling radioactivity should be used.

24.8 DISCUSSION

This procedure, exclusive of sampling and distillation, requires approximately 1/2 hr.

25. GENERAL GAMMA ASSAY OF RADIOACTIVE SODIUM IN BASIC SOLUTION

25.1 PRINCIPLE

A sodium sample is dissolved in a methanol-water mixture and the isotopes present are determined by standard techniques of gamma spectrometry.

25.2 SENSITIVITY AND PRECISION

The sensitivity will vary with the branching ratio of the particular isotope being determined. Typically, 0.01 μCi of isotope per gram of sodium can be determined with a precision of $\pm 10\%$.

25.3 APPARATUS

Multichannel Analyzer System. This 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. The system must be calibrated for both counting efficiency and geometry according to conventional gamma spectrometric techniques. These techniques are described in J. E. Cline, "Studies of Detection Efficiencies and Operating Characteristics of Ge(Li) Detectors," IEEE Trans. on Nuclear Science, Vol. NS-15, No. 3, pp. 198-213 (1968) and in R. L. Heath, "Scintillation Spectrometry Gamma-Ray Catalogue," 2nd Edition, USAEC IDO-16880 (1964).

Separatory Funnel, 125-ml

Safety Shield. For use during dissolution of sodium.

25.4 MATERIALS AND REAGENTS

Demineralized Water. Pass tap distilled water through a high-quality commercial mixed-bed ion exchange column. Store in polyethylene bottles.

Methanol. Anhydrous, reagent grade.

Aqua Regia. Prepare fresh by mixing 1 part concentrated HNO_3 with 3 parts concentrated HCl .

25.5 PROCEDURE

1. Obtain a sample of sodium (approximately 10g) either as a section of tubing from a bypass sample obtained by the procedure of Section 3.1, or in a quartz, tantalum, or titanium cup obtained by the overflow sampling procedure of Section 3.2. For most samples, it will be necessary to allow the ^{24}Na activity to decay to a safe level before the sample is handled.

2. Weigh the sample plus the container.

3. Place the sample and its container in a 250-ml beaker.

4. Dissolve the sodium by dropping 120 ml of a water-methanol mixture (1 volume of water to 3 volumes of methanol) from a separatory funnel onto

the sodium surface at a rate of 30 to 60 drops/min.

5. Quantitatively transfer the sodium solution to a 100-ml volumetric flask, dilute to volume with water and mix thoroughly.

6. Transfer an appropriate aliquot of the solution to a counting vessel and obtain the gamma spectrum under standardized counting conditions.

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.

8. Transfer the solution quantitatively to a counting vial and dilute to volume.

9. Check the crucible for residual activity. Repeat steps 6 and 7 until no activity is detected.

10. Obtain a gamma spectrum under previously-established standard conditions.

11. Dry and weigh the empty sample container.

25.6 CALCULATIONS

Calculate the gamma activity of each basic and acidic aliquot by the following formula:

$$\text{Activity, } \mu\text{Ci/g Na} = \frac{R \times F}{B \times E \times G \times (C-D) \times 2.2 \times 10^6}$$

where

R = net count rate, cpm

F = total volume of sample solution divided by volume of aliquot

B = fraction of total disintegrations emitting measured energy

E = efficiency of counting system

G = geometry factor of counter, counts/dis

C = weight of sample plus container, g

D = weight of empty container, g

Sum the activities of each aliquot to determine the total gamma activity of the sodium.

25.7 SAFETY

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 which 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.

Locally-approved safety procedures for handling radioactive materials should be practiced at all times.

25.8 DISCUSSION

This procedure, exclusive of sampling, requires 1 hr.

This assay is useful in determining only the more abundant gammas emitted by radioisotopes in a sodium sample. Thus, the radiation level of the more abundant activities will dictate the sensitivities achievable by this procedure.

26. RADIOCHEMICAL DETERMINATION OF IODINE IN SODIUM

26.1 PRINCIPLE

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 oxidation-reduction and solvent extraction steps. The iodine activity is then determined by standard radiochemical techniques.

26.2 PRECISION AND SENSITIVITY

The sensitivity will depend on the type of detector used. A detection limit of approximately 1×10^{-5} $\mu\text{Ci/g}$ should be obtainable using a NaI detector in conjunction with a multichannel analyzer. At activity levels 10 times this limit, a precision of $\pm 10\%$ should be obtained.

26.3 APPARATUS

Multichannel Analyzer System. This system consists of a gamma detector and associated electronics. The preferred system is one using either a NaI 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. The system must be calibrated for both efficiency and geometry by standard gamma spectrometric techniques. The techniques are described in: J. E. Cline, "Studies of Detection Efficiencies and Operating Characteristics of Ge(Li) Detectors," IEEE Trans. on Nuclear Science, Vol. NS-15, No. 3, pp 198-213 (1968) and in R. L. Heath, "Scintillation Spectrometry Gamma Ray Catalogue" 2nd Edition USAEC Report IDO-16 880 (1964).

Counting Vials. The vials must be calibrated to contain a standard volume.

Separatory Funnel, 125-ml.

Safety Shield. For use during dissolution of sodium.

26.4 MATERIALS AND REAGENTS

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

Methanol. Anhydrous, reagent grade.

NaI. Reagent grade.

H₂SO₄. 9N and 3N

CCl₄. Reagent grade.

NaNO₂, 1M. Aqueous solution prepared from reagent grade NaNO₂.

Na₂SO₃, 1M. Aqueous solution prepared from reagent grade Na₂SO₃.

NaOH, 10M. Aqueous solution prepared from reagent grade NaOH.

26.5 PROCEDURE

1. Obtain 10 to 15 g sample of sodium by the overflow sampling procedure described in Section 3.2. Borosilicate glass or quartz beakers have been found suitable.
2. Weigh the sample plus the container.
3. Place the sample and container in a 250-ml Pyrex beaker.
4. Dissolve the sodium by dripping 120 ml of a water-methanol mixture (1 volume of water to 3 volumes of methanol) containing 10 mg of iodine carrier (NaI) from a separatory funnel onto the sodium surface at 30 to 60 drops/min. The volume at the completion of this step is expected to be <100 ml because some of the alcohol evaporates in the process.
5. Quantitatively transfer the sodium solution to a 100-ml volumetric flask, dilute to volume, and mix thoroughly.
6. Weigh the empty sample container. If the iodine level is known to be high enough, omit extraction steps 7 through 18 and go directly to step 19.
7. Transfer a 50-ml aliquot of the sodium solution to a 200-ml beaker.
8. Add $9N$ H_2SO_4 (25 to 30 ml), to make the solution slightly acid. Cool in an ice bath.
9. Add a 5-ml excess $9N$ H_2SO_4 and transfer the solution quantitatively to a 125-ml separatory funnel.
10. Add 15 ml of CCl_4 to the separatory funnel.
11. Add five to ten drops of $1M$ Na_2SO_3 to reduce all iodine to iodide.
12. Add enough $1M$ $NaNO_2$ to oxidize all iodide to free iodine.
13. Extract the iodine into the CCl_4 .
14. Transfer the CCl_4 to a second separatory funnel and repeat steps 10 to 13 until no iodine color remains in the aqueous solution.
15. Combine all CCl_4 extracts.
16. Wash the CCl_4 extracts with 15 ml of $3N$ H_2SO_4 containing a few drops of $NaNO_2$.
17. Discard the wash solution.
18. Extract the iodine from the CCl_4 into 15 ml of water containing 1 ml of $1M$ Na_2SO_3 and 4 to 5 drops of $10M$ $NaOH$.
19. Transfer the aqueous solution from the previous step, or an aliquot from step 5 to a counting vial, dilute to volume with water, and gamma count under standard counting conditions.

26.6 CALCULATIONS

Calculate the activity of each iodine isotope in sodium by the following formula:

$$\text{Activity, } \mu\text{Ci/g of Na} = \frac{R \times F}{G \times B \times E (C-D) \times 2.2 \times 10^6}$$

where

R = count rate, cpm

F = aliquot factor

G = geometry factor, counts/dis

B = fraction of total disintegrations emitting measured energy

E = efficiency of analyzer system for gamma energy used

C = weight of sample plus container, g

D = weight of empty container, g

26.7 SAFETY

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 which 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.

Observe locally-approved safety procedures for handling radioactive materials.

26.8 DISCUSSION

This procedure, exclusive of sampling, requires 2 to 3 hr.

No yield correction is required; the recovery is >95%.

27. DETERMINATION OF TRITIUM IN SODIUM BY LIQUID SCINTILLATION COUNTING

27.1 PRINCIPLE

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.

27.2 SENSITIVITY AND PRECISION

The detection limit is $<1 \times 10^3$ pCi/g of sodium. The precision of this method is approximately 15% at adequate count rates (100 cpm).

27.3 APPARATUS

Sodium Dissolution Flask and CuO Train. (See Fig. 27-1). The dissolution flask must be round-bottomed to provide immediate and intimate contact of the added water with the sodium sample. Prepare the CuO train by (a) packing the quartz tube with copper turnings, (b) heating the tube to 600 C, (c) flowing oxygen over the heated copper at a flow rate of 25 to 50 cc/min until the packing is completely black, and (d) continuing heating and the flow of oxygen for 3 to 4 hr longer.

Liquid Scintillation Counter. Any commercially-available low-noise liquid-scintillation counter is adequate for counting tritium.

Water-cooled Condenser. The condenser must be equipped with a 45/50 standard taper joint to fit the dissolution flask.

Heat Gun.

27.4 MATERIALS AND REAGENTS

Tritiated Water Standards

Concentrated Hydrochloric Acid, reagent grade.

Phenolphthalein Indicator. Dissolve 0.1 g of phenolphthalein in 50 ml of ethanol and add 50 ml of distilled water.

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 naphthalene, and 980 ml p-dioxane.

27.5 PROCEDURE

1. Bring the CuO train to operating temperature, 600 C.
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

Fig. 27-1

Typical Sodium Dissolution Flask and CuO Train

every 10 to 12 sec by adjusting the lower stopcock. Close the upper stopcock.

3. Obtain a 2 to 4 g sample of sodium by the overflow sampling procedure described in Section 3.2. Borosilicate glass or quartz beakers have been found suitable.

4. Transfer the protected sample into an inert-atmosphere glove box, 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 glove box.

5. Remove the plug from the dissolution flask and quickly connect the flask to the train at the inner 45/50 standard taper joint.

6. Start helium flowing through the flask and train at the rate of 80 to 100 cc/min and maintain this flow rate throughout the dissolution.

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.

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.

9. Allow the flask to cool.

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.

11. With the helium still flowing, gently warm with a heat gun first the inlet tube and then the outlet tube of the CuO train to drive any water which may have condensed at these points into the water trap.

12. Shut off the helium flow and remove the dissolution flask at the 45/50 standard taper joint.

13. Carefully withdraw the sample cup into the mouth of the dissolution flask with a pair of tweezers.

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.

15. Dry and weigh the empty sample cup.

16. Cool the flask in an ice bath and carefully neutralize the NaOH solution to the phenolphthalein end-point by addition of concentrated hydrochloric acid. Do not add any excess acid.

17. Connect a water-cooled condenser to the dissolution flask and distill all water from the flask. Combine this distillate with the water from the trap on the CuO train. Dilute the solution to a known volume.

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.

27.6 CALCULATIONS

Calculate the activity of tritium in sodium by the following formula:

$$\text{Activity, pCi/g Na} = D_s \times \frac{R_u}{R_s} \times \frac{V \times A_s}{(B-C) \times A_u \times 2.22}$$

where

D_s = disintegration rate of standard, dpm/ml

R_u = count rate of sample aliquot, 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

B = weight of sample plus container, g

C = weight of empty container, g

27.7 SAFETY

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 should never be attempted without a safety shield between the operator and the apparatus.

27.8 *DISCUSSION*

This procedure, exclusive of sampling, requires approximately 4 hr.

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.

28. DETERMINATION OF PARTICULATES IN SODIUM BY FILTRATION

28.1 PRINCIPLE

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 it, and residual sodium removed by vacuum distillation. Particulates are separated from the stainless steel filter by ultrasonic cleaning in xylene, and then in water, and are collected on membrane filters.

28.2 APPARATUS

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.

Sintered metal powder elements manufactured by the Mott Metallurgical Corporation, sintered metal felt elements manufactured by Fluid Dynamics, Incorporated, and woven elements manufactured by the Wintec Corporation have been found suitable for this application.

Before it is installed, the filter element should be ultrasonically precleaned as specified in Section 28.4.1.

Filter Cartridge. This is a stainless steel holder for the replaceable filter element. The cartridge, which is reusable, is an all-welded design for high temperature systems ($>400^\circ\text{C}$), or it may be a flanged type for low temperature use. See Figs. 28-1 and 28-2 for typical designs.

Distillation Assembly. This is an evacuable glass assembly in which the residual sodium is removed from the filter element by distillation at 400°C .

Membrane Filter Holder. Holders for 25-mm filters, as manufactured by the Millipore Corporation, have been found satisfactory for this use.

Membrane Filters. Filters of 25-mm diameter and with a pore size of 1.2 μm are required. Filters produced by the Millipore Corporation have been found suitable for this purpose.

Ultrasonic Cleaner. A small 80-W bath-type ultrasonic cleaner is used for removing particulates from the stainless steel filter.

Balance. A standard analytical balance with a ± 0.2 mg precision.

Microscopes. (Optional) A low-power stereo microscope for preliminary examination of collected particles and a petrographic microscope for particle counting and identification.

28.3 MATERIALS AND REAGENTS

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

Fig. 28-1

Typical Welded Filter Cartridge

Fig. 28-2

TYPICAL FLANGED FILTER CARTRIDGE

Xylene. Store reagent grade xylene over sodium, used as a drying agent, in a glass-stoppered bottle.

28.4 PROCEDURE

28.4.1. Precleaning and Testing

1. Ultrasonically clean the filter element in a bath of prefiltered xylene for 30 min.
2. Filter the bath xylene through a 1.2- μ m-porosity membrane filter.
3. Dry the membrane filter and weigh it.
4. Repeat steps 1, 2, and 3 with a new membrane filter until the weight gain is negligible (<1 mg).
5. Assemble the filter element in the cartridge either by bolting or welding.
6. Helium leak test the filter cartridge. If it is not leak-tight, repair or reject the cartridge.

28.4.2. Sampling

1. Attach a tested and leak-tight cartridge to the system in a bypass arrangement upstream from the cold trap. Care should be taken to avoid introduction of particulates during attachment.
2. Evacuate the filter cartridge. (This is done to avoid gas bubble blockage of sodium flow.)
3. Heat the filter cartridge and connecting lines, and establish sodium flow.
4. Monitor the rate of flow through the filter to determine the volume of sodium sampled.

For systems <100 gal, a volume equal to the entire sodium inventory must be passed through the filter. For systems >100 gal, filter 100 gal or at least 1% of the total inventory, whichever is greater.

5. Cool the cartridge and freeze the sodium.
6. Remove the filter cartridge from the system.

28.4.3 Particulate Determination

1. In an inert-atmosphere box, scoop out some sodium at the inlet end to remove particles which may result during disconnection from the system, wrap the cartridge with heating tape, and heat to approximately 125 C.
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.

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.
4. Remove the filter element from the disassembled cartridge. This may require reheating.
5. Place the filter element in a glass distillation assembly and remove it from the inert-atmosphere box.
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.
7. Remove the filter element from the distillation assembly.
8. Ultrasonically agitate the filter element for 30 min in dry xylene which has been freshly filtered through a membrane filter of 1.2 μ m porosity.
9. Pass the bath xylene through a 1.2- μ m-porosity membrane filter.
10. Dry the filter quickly and weigh it.
11. Repeat steps 8, 9, and 10 with new membrane filters until the weight gain is <1 mg.
12. Ultrasonically agitate the filter element in prefiltered water.
13. Filter the water through a 1.2- μ m-porosity membrane filter.
14. Dry the filter and weigh it.
15. If the weight of particulates on a filter exceeds 1 mg, repeat steps 12, 13, and 14 until the weight gain of a membrane is <1 mg.
16. Calculate the concentration of particulates in the sodium.
17. (Optional) Perform microscopic examinations of the material collected on the membrane filters to determine particle size distributions, to identify particles, etc.

28.5 CALCULATIONS

The concentration of particulates is calculated by:

$$\text{Particulates, ppm} = \frac{(W_1 + W_2 + \dots W_n)}{S}$$

where

W_1 (etc.) = net weight of particulate material collected on a membrane filter, mg.

S = weight of sodium passed through stainless steel filter, kg. This weight may not exceed the system inventory, i.e., if the total system sodium is passed through the filter more than one time, this weight is that of a single sodium inventory.

28.6 SAFETY

Observe the usual precautions for handling sodium and flammable organic liquids.

28.7 DISCUSSION

This procedure, exclusive of the sampling steps in Section 28.4.2, requires approximately 3 days.

29. DETERMINATION OF NOBLE GAS RADIOISOTOPES IN COVER GAS

29.1 PRINCIPLE

A cover-gas sample which has passed through vapor and aerosol traps is collected and counted under standard temperature, pressure, and geometry, using gamma spectrometry. The radioisotopes of noble gases contained in the sample are determined from the resulting gamma spectrum.

29.2 SENSITIVITY AND PRECISION

The sensitivity will vary with the branching ratio of the particular isotope being determined. Typically, 1×10^{-4} μCi of isotope per ml of cover gas can be determined with a precision of $\pm 10\%$.

29.3 APPARATUS

Multichannel Analyzer System. This 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. The system must be calibrated for both efficiency and geometry by standard gamma spectrometric techniques. These techniques are given in J.E. Cline, "Studies of Detection efficiencies and Operating Characteristics of Ge(Li) Detectors," IEEE Trans. on Nuclear Science, Vol. NS-15, No. 3 pp. 198-213 (1968), and in R.L. Heath, "Scintillation Spectrometry Gamma-Ray Catalogue," 2nd Edition, USAEC Report IDO-16880 (1964).

Gas Sampling Bulb. The bulb, which is made of borosilicate glass or stainless steel, must be 10 ml or larger in capacity. It must have entrance and exit stopcocks and an adapter to fit the cover-gas sampling system. Calibration of this vessel is accomplished by filling it with an aqueous solution containing a known amount of a gamma-emitting radioisotope of known disintegration rate, and gamma-counting under the same geometry that will be used for cover-gas samples.

29.4 PROCEDURE

1. Collect a sample in the sampling bulb by passing cover gas through the bulb for 5 to 10 min.
2. Close the downstream stopcock of the bulb against system pressure.
3. Close the upstream stopcock, thus assuring that the bulb is filled with cover gas at slightly above atmospheric pressure while at ambient temperature.
4. Vent the excess pressure to bring the sample to atmospheric pressure while at ambient temperature.
5. Record the pressure and temperature.
6. Count the sample under standard, calibrated geometry and calculate the activity from the photopeak area and calibration constants.

29.5 CALCULATIONS

Calculate a calibration constant from the gas sampling bulb data by the following formula:

$$K = \frac{C_s \times B_s \times E_s}{R_s}$$

where

K = calibration constant

C_s = microcuries of standard isotope used

B_s = fraction of total disintegrations emitting measured energy

E_s = counting efficiency for standard isotope

R_s = count rate of standard

Calculate the activity of each isotope in the cover gas by the following formula:

$$\text{Activity, } \mu\text{Ci/ml} = \frac{K \times R_u \times T \times 760}{B_u \times E_u \times 273 \times P \times V}$$

where

R_u = count rate of sample, cpm

P = pressure at which sample was vented, torr

B_u = fraction of total disintegrations emitting measured energy

E_u = counting efficiency for sample isotope

T = temperature at which sample was vented, K

V = volume of sampling bulb, ml

29.6 SAFETY

Standard radiochemical techniques are adequate in carrying out this analysis.

29.7 DISCUSSION

This procedure requires approximately 1/2 hr.

30. DETERMINATION OF TRITIUM IN COVER GAS BY LIQUID SCINTILLATION COUNTING

30.1 PRINCIPLE

A cover gas sample which has passed through vapor and aerosol traps is collected, and the tritiated hydrogen gas is converted to tritiated water over hot copper oxide. The tritiated water is collected in an ice bath, diluted to volume, mixed with liquid scintillator solution, and assayed by liquid scintillation counting.

30.2 SENSITIVITY AND PRECISION

The sensitivity is on the order of 1 pCi/ml of cover gas. A precision of $\pm 15\%$ should be obtained on a sample containing approximately 5 pCi/ml of cover gas.

30.3 APPARATUS

Liquid Scintillation Counter. Any commercially available low-noise liquid scintillation counter is adequate for counting tritium.

CuO Train. (See Fig. 30-1). Prepare the CuO train by (a) packing the quartz tube with copper turnings, (b) heating the tube to 600 C, (c) flowing oxygen over the heated copper at a flow rate of 25 to 50 cc/min until the packing is completely black, and (d) continuing the heating and oxygen flow for 3 to 4 hr longer.

Gas Sampling Bulb. This bulb is made of borosilicate glass and has a capacity of two liters. It is equipped with entrance and exit stopcocks and two adapters, one to fit the gas sampling system, the other to fit the CuO train.

30.4 REAGENTS

Tritiated Water Standards.

Liquid Scintillation Solution. Any scintillator solution in which water will dissolve 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 naphthalene, and 980 ml p-dioxane.

Helium Gas.

30.5 PROCEDURE

1. Collect a sample of cover gas by evacuating the gas sampling bulb, connecting it to the cover gas system, and opening the entrance stopcock. (An acceptable alternative step involves flowing the cover gas through the bulb for 10 min at a flow rate of 1 liter/min.)

Fig. 30-1
Typical CuO Train

2. Close the stopcock and transport the bulb to the laboratory.
3. Bring the CuO train to operating temperature, 600 C.
4. Connect one outlet of the sampling bulb to the CuO train and the other to the helium supply.
5. Open the stopcocks and flush the sample through the copper oxide train at 100 ml/min. Continue helium flow for 1 hr.
6. Discontinue the helium flow and remove the bulb from the system.
7. Remove the collection beaker from the ice bath, transfer the condensate to a volumetric flask with water rinses, and dilute to a known volume.
8. Pipet a suitable aliquot of this solution and of scintillation liquid into a counting vial. (The amount of scintillator solution added will depend on the volume of the counting vials used with the liquid scintillation counter).
9. Count the sample and an aliquot of the tritiated water standard under the same conditions.

30.6 CALCULATIONS

Calculate the tritium activity of the cover gas by the following formula:

$$\text{Activity, pCi/ml} = \frac{D}{2.22} \times \frac{R_u}{R_s} \times \frac{A_s}{V} \times f \times \frac{T}{273} \times \frac{760}{P}$$

where

D = disintegration rate of standard, dpm/ml

R_u = count rate of sample aliquot, cpm

R_s = count rate of standard, cpm

A_s = volume of standard aliquot, ml

V = volume of gas sample, ml

f = aliquot factor for the sample

T = temperature of gas, K

P = pressure of gas, torr

30.7 SAFETY

Local practices for handling radioactive materials should be observed. Also, observe the usual precautions in handling evacuated glassware.

30.8 DISCUSSION

This procedure requires approximately 2 to 3 hr.

31. DETERMINATION OF GASEOUS IMPURITIES IN COVER GAS

31.1 PRINCIPLE

After appropriate concentration and pretreatment steps where necessary, most of the gaseous impurities in cover gas are determined by standard techniques of gas chromatography. In certain cases, however, more sensitive instruments are specified, e.g. the flame ionization detector for CH_4 , CO, and CO_2 , and the electrolytic oxygen analyzer for oxygen in argon.

31.2 SENSITIVITY AND PRECISION

Detection limits for the various impurities in each cover gas are shown in Tables 31-1 and 31-2. The reproducibility of replicate determinations is $\pm 10\%$ when the concentration of an impurity is greater than 10 times the detection limit. The detection limit for oxygen is <1 ppm if an electrolytic oxygen analyzer is used, and the detection limits for CH_4 , CO, and CO_2 are <1 ppm if flame ionization detector procedures are used.

31.3 APPARATUS

Gas Chromatograph. The procedures of this section make stringent demands on the versatility of the chromatographic system. For the procedures using thermal conductivity detectors, the Beckman Model GC-2A and the Varian Aerograph Model 90 are suitable. For flame ionization detection, the Varian Aerograph Model 1200 is suitable. Use of more than one such instrument may be desirable to avoid frequent, time-consuming alterations of analytical set-ups.

When a helium ionization detector is required, the Varian Aerograph Model 1731 Trace Gas Analyzer, equipped as described below, has been found suitable. The chromatograph should be equipped with a 0 to 500 V variable power supply. The column oven should operate from 25 to 300 C. The preferred recorder is a strip-chart potentiometer with a 1-mV span.

Electrolytic Oxygen Analyzer. This type of instrument ordinarily uses a silver cathode and a lead or cadmium anode in an alkaline electrolyte. Instruments manufactured by Beckman Instruments, Inc., by the Manufacturers Engineering and Equipment Company, and by Lockwood and McLorie, Inc. have been found satisfactory.

Helium Purifier, to further purify the carrier gas for the helium ionization detector. An Electron Technology, Inc. Model SLM-1 apparatus has been found satisfactory.

Gas Sampling Loop. The loop should have a known volume, approximately 10 ml, and should be detachable. See Fig. 31-1.

Gas Handling System. An apparatus suitable for preparing known dilutions of gas mixtures. A typical set up is shown in Fig. 31-2. This system consists of a rough vacuum pump, a mercury diffusion pump, vacuum and pressure measuring equipment, and a tubular manifold consisting of gas storage vessels and ports.

Fig. 31-1 Typical Gas Sampling Loop

Fig. 31-2

TYPICAL GAS HANDLING SYSTEM

Regulators. Diffusion-resistant metal-diaphragm regulators which are evacuable without damage and which are purchased with a vendor's helium leak rate certification should be used to avoid contaminating standard gases and gas samples. The Matheson Gas Products Two-Stage Metal-Diaphragm Regulator-Model 3104 has been found satisfactory.

31.4 MATERIALS AND REAGENTS

Helium Gas, $\geq 99.995\%$ purity, for carrier gas with thermal conductivity detectors and, after further purification, as carrier gas for the helium ionization detector.

Argon Gas, $\geq 99.999\%$ purity, for carrier gas.

Helium Gas, $\geq 99.9999\%$ purity, matrix gas for preparing standard mixtures.

Nitrogen Gas, $\geq 99.9995\%$ purity, matrix gas and impurity gas for preparing standard mixtures.

Argon Gas, $\geq 99.9999\%$ purity, matrix gas for preparing standard mixtures.

Neon Gas, $\geq 99.99\%$ purity. A lecture bottle is a suitable quantity.

Hydrogen Gas, $\geq 99.95\%$ purity.

Oxygen Gas, $\geq 99.99\%$ purity. This is not needed if oxygen determinations are performed by the electrolytic oxygen analyzer.

Standard Gas Mixture, a cylinder of helium containing 4 to 6 ppm of oxygen and purchased with a certified analysis from the vendor. This is needed only to calibrate the electrolytic oxygen analyzer.

Methane Gas, $\geq 99.97\%$ purity.

Carbon Monoxide Gas, $\geq 99.5\%$ purity.

Carbon Dioxide Gas, $\geq 99.5\%$ purity.

Krypton Gas, $\geq 99.9\%$ purity. A lecture bottle is a suitable quantity.

Xenon Gas, $\geq 99.9\%$ purity. A lecture bottle is a suitable quantity.

Methanation Gas Mixture, He containing 6% H_2 for procedures using a flame ionization detector.

Methanation Catalyst. A mixed metal oxide catalyst sieved to -60+80 mesh. Katalco 11-2, a product of Katalco Corporation, 180 N. Michigan Avenue, Chicago, Illinois, has been found suitable for this purpose.

31.5 PROCEDURE

This section provides that certain determinations will be done by specialized procedures in order to achieve the desired detection limits. These

specialized cases are:

a) Perform the analysis according to Section 31.5.2 if O₂ is to be determined in Ar at <200 ppm or in He or N₂ at <5 ppm.

b) Perform the analysis according to Section 31.5.3 if CO is to be determined at <100 ppm.

Perform all other analyses according to Section 31.5.1.

31.5.1 Generic Gas Chromatographic Procedure

1. Specify the cover gas to be analyzed, the specific impurity to be determined, and assume the presence of interfering impurities unless accumulated experience has demonstrated their absence.

2. Bring the gas chromatograph to stable operation. Table 31-1 gives typical operating parameters which are suitable if interfering impurities may be present, and Table 31-2 gives typical operating parameters which are suitable if interfering impurities may be assumed to be absent.

3. Prepare at least 3 known gas mixtures to be used as calibration standards. Typically this step is accomplished by attaching a cylinder of the gaseous impurity and a cylinder of the purest available specimen of cover gas (e.g., 99.9999% pure He) to the gas handling system and then by appropriate manipulations and dilutions producing approximately 1 liter of standard mixture.

4. Using the gas handling system, successively fill a 10-ml sample loop with 3 replicates of each standard at NTP* and elute the standard samples through the chromatograph. Record the chromatograms.

5. Prepare a calibration curve of peak height vs ppm of the impurity.

6. Obtain successively in a 10-ml sample loop at NTP, 3 samples of the gas to be analyzed. The samples may be supplied to the analyst in sample loops, or he may wish to use the gas handling apparatus to extract the sample from some other sampling vessel that is supplied to him.

7. Elute each 10-ml sample through the chromatograph and record the peak height.

8. By reference to the calibration curve, determine ppm of impurity in the cover gas.

9. If further impurities remain to be determined, return to step 1 of this procedure.

31.5.2 Procedure for the Determination of Oxygen by the Electrolytic Oxygen Analyzer

*NTP is an abbreviation for "normal temperature and pressure" and means some convenient temperature and pressure (e.g., 25 C and 745 mm Hg absolute) to which all gas samples will be adjusted.

Table 31-1

Typical Chromatographic System Parameters for the Determination
of One Constituent when Interfering Impurities may be Present

Constituent to be Determined	Principal Interference ^a	Sample Gas	Analytical Parameters					Detection Limit, vol/ ppm	Detector ^d
			Column			Carrier Gas			
			Packing ^b	Dimensions	Temp. C	Identity	Flow Rate ml/min		
Ne	H ₂	He	5A	20' x 1/8"	0	He	40	~10	TCD
	H ₂	Ar,N ₂	5A	3' x 1/8"	25	He	40	~5	TCD
H ₂	Ne ^e	He	5A	20' x 1/8"	0	He	40	<1	HID
	Ne	Ar,N ₂	5A	20' x 1/8"	0	Ar	40	~5	TCD
O ₂	Ar	He,N ₂	5A	8' x 1/4"	-78	He	60	~100	TCD
		Ar	Use the procedure of Table 31-2						
N ₂	Kr	Ar,He	5A	20' x 1/8"	25	He	40	~100	TCD
CH ₄	CO	He, Ar, N ₂	Use the procedure of Section 31.5.3						
CO	CH ₄	He, Ar, N ₂	Use the procedure of Section 31.5.3						
CO ₂	--	He, Ar, N ₂	Use the procedure of Section 31.5.3						
Kr	N ₂	He,Ar	5A	3' x 1/4"	25	N ₂	20	~100	TCD
Xe	CO	He,Ar N ₂	5A	20' x 1/8"	25	He	40	~400	TCD

For footnotes, see next page

Footnotes for Table 31-1

^aH₂, Ne, Ar, Kr, CO₂, CH₄, and CO above 200 ppm. N₂ above 600 ppm.

^b_{5A} is Linde Molecular Sieve 5A.

^cDetection limits are typical for a TCD with a sample of 10 ml at NTP. Actual limits may deviate from these by a factor of 2 to 3 for various detector configurations and filaments. Operate TCD filaments at 250 mA in He, or at 100 to 125 mA in Ar or N₂.

^dTCD = thermal conductivity detector.
HID - helium ionization detector.

^eThis is the only case in which the HID must be used.

Table 31-2

Typical Chromatographic System Parameters for the Determination of One
Constituent with No Interfering Impurities Present

Constituent to be Determined ^a	Cover Gas or Sample Gas	Packing ^b	Analytical Parameters					Detection Limit, ^c vol ppm	Detector ^d
			Column		Carrier Gas				
			Dimensions	Temp °C	Identity	Flow Rate ml/min			
Ne	He, Ar, N ₂	5A	3' x 1/4"	25	He	40	~10	TCD	
H ₂	He ^e	5A	3' x 1/4"	25	He	40	<1	HID	
	Ar, N ₂	5A	3' x 1/4"	25	Ar	40	~5	TCD	
O ₂	Ar	5A	3' x 1/4"	25	Ar	60	~200	TCD	
	He, H ₂	5A	3' x 1/4"	25	He	60	~5	TCD	
N ₂	Ar	5A	20' x 1/8"	25	He	60	~50	TCD	
CH ₄	He, Ar, N ₂	Use the procedure of Section 31.5.3							
CO	He, Ar, N ₂	Use the procedure of Section 31.5.3							
CO ₂	He, Ar, N ₂	Use the procedure of Section 31.5.3							
Kr	He, Ar	5A	20' x 1/8"	25	He	40	~50	TCD	
	N ₂	5A	3' x 1/4"	25	N ₂	20	~100	TCD	
Xe	He, Ar, N ₂	5A	3' x 1/4"	100	He	100	~25	TCD	

For footnotes, see the next page

Footnotes for Table 31-2

^aDetermination is optimized for this constituent only. It is assumed that there are no interferences.

^b5A is Linde Molecular Sieve 5A.

^cDetection limits are typical for a TCD with a sample of 10 ml at NTP. Actual limits may deviate from these by a factor of 2 to 3 for various detector configurations and filaments. Operate TCD filaments at 250 mA in He, or at 100 to 125 mA in Ar or N₂.

^dTCD = thermal conductivity detector,
HID = helium ionization detector.

^eThis is the only case in which the HID must be used.

1. Pass a standard mixture of oxygen in helium through the oxygen analyzer while operating the analyzer according to the manufacturer's specifications. Typically, these call for a gas flow of 100 ml/min until the meter readout is stable for at least 1 hour.

2. Record the indicated analysis of the standard gas and verify that the oxygen meter is in calibration.

3. Obtain a sample of the gas to be analyzed. Preferably this will be at moderate pressure in a cylinder, since quantities up to 3 cubic feet will be used for the analysis.

4. Pass the gas sample through the oxygen analyzer operating as in step 1, above.

5. Record the indicated oxygen content of the sample.

31.5.3 Procedure for the Determination of Methane, Carbon Monoxide, and Carbon Dioxide Using a Flame Ionization Detector

1. Bring the gas chromatograph to stable operation. Typical operating parameters are a He-6% H₂ carrier gas flow of 20 ml/min through a 8-ft x 3/16-in.-OD Porapak Q column maintained at 0C, then through a 4-in. x 1/4-in.-OD column packed with -60+80 mesh mixed metal oxide catalyst (Katalco 11-2 at 400 C, or equivalent) and finally through the flame ionization detector.

2. Activate the catalyst according to the manufacturer's specified procedure. Typically, this consists of slowly heating the material to 350 to 400 C in a reducing atmosphere.

3. Prepare at least 3 known gas mixtures to be used as calibration standards. Typically this step is accomplished by attaching a cylinder of each impurity to be determined and a cylinder of the purest available specimen of cover gas (e.g., 99.9999% pure He) to the gas handling system and then by appropriate manipulation and dilutions producing approximately 1 liter of standard mixture.

4. Using the gas handling system successively fill a 10-ml sample loop with 3 replicates of each standard at NTP and elute the standard samples through the chromatograph. Record the chromatograms.

5. Establish the retention time of the system for each impurity by analyzing standards containing only one impurity at a time. Elution of a mixture proceeds in the order: CO, CH₄, and CO₂.

6. Prepare calibration curves of peak height vs ppm of each impurity.

7. Obtain successively in a 10-ml sample loop at NTP, 3 samples of the gas to be analyzed. The samples may be supplied to the analyst in sample loops, or he may have to use the gas handling apparatus to extract the sample from some other sampling vessel that is supplied to him.

8. Elute each 10-ml sample through the chromatograph and record the peak heights.

9. By reference to the calibration curve, determine ppm of CH₄, CO, and CO₂ in the cover gas.

31.6 CALCULATIONS

Ordinarily, ppm of impurity is read from a calibration curve or from a calibrated instrument and no calculations are required.

31.7 SAFETY

These procedures require the usual safety precautions for handling evacuated and pressurized glassware, compressed gases in cylinders, liquefied cryogenic gases, catalysts in the reduced (pyrophoric) state, and catalyst dust containing chromia.

31.8 DISCUSSION

Exclusive of sampling time, the determination of all specified impurities in one sample of cover gas takes 2 to 3 days.

The procedures of this section are designed as guides, in that the conditions specified have been found quite satisfactory to achieve the detection limits listed. It should not, however, be construed that they are the only conditions that might result in satisfactory avoidance of interferences or that they optimize detection limits. Thermal conductivity detectors are widely available, they are relatively inexpensive, and they are convenient to use. On this basis, the above procedures specify this type of detector wherever possible.

The restricted application herein of the helium ionization detector is not intended to rule out its use when improved sensitivity would be attained thereby. One has to consider, however, the added operational difficulties that will be encountered when it is used. For example, an unexpectedly high concentration of an impurity will saturate the detector and will require the analysis of smaller aliquots to achieve all of the required determinations. Also, a significant change in the column operating parameters may result in a delay of a day to a week before stable operation is reattained. However, if one is able to permanently combine a chromatograph column with a HID, stable operation without excessive delays can be expected.

The Materials and Reagents section of this procedure calls for a full set of gases in cylinders so that any necessary standard can be prepared in the laboratory. This seems to be the most reasonable approach if a wide variety of standards is required. On the other hand, if a restricted spectrum of analyses is required, then purchase of a few multiple-component certified standard mixtures is considered to be an acceptable alternative.

The following generalities are supplied to aid the inexperienced chromatographer in selecting operating procedures and in interpreting chromatograms.

a) The elution order on molecular sieve columns at 25 C is: H₂ + He, Ar + O₂, N₂, Kr, CH₄, Xe, and CO.

b) 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.

c) The elution order on silica gel columns at 25 C is: H_2 + Ne, Ar + O_2 + N_2 , CO, CH_4 , Kr, and Xe.

d) Longer columns and lower temperatures improve separations but decrease sensitivity.

e) Although peak height measurements are mentioned as the only indication of detector response, in certain cases (particularly for large retention times) the measurement of peak area may be a more suitable choice.

Appendix A

INERT-ATMOSPHERE GLOVEBOXES--MAINTENANCE PRACTICES AND
ANALYSIS OF GLOVEBOX ATMOSPHERES

Many of the methods in this manual call for operations to be done in inert-atmosphere boxes and for control of selected impurity levels in the atmospheres of the boxes. Impurity levels must be low enough to meet the specifications called for in a given method, and the stipulated specifications must be established by analysis. This section describes procedures that should be followed to maintain the required atmospheric purity and methods of analysis to demonstrate that specifications have been met.

A.1 MAINTENANCE PRACTICES

The following maintenance practices are recommended:

1. Materials which may contribute to the impurity level of the inert atmosphere should neither be introduced into the glovebox nor be used in its construction. Examples of undesirable material include many sealants, finishes, and cellulosic fibrous substances.
2. Several cycles of evacuation and inert-backfilling of the entry lock constitute the most efficient procedure for keeping air contamination to a minimum when transferring items into the glovebox.
3. Gloves should have low permeability to water vapor and gases. Neoprene and butyl rubber are suitable base materials. Either formulation may be obtained with various elastomeric coatings.
4. All glove ports should be covered and sealed when the glovebox is not in use. Preferably, the air on the operator side of the gloves should be replaced with glovebox atmosphere or vacuum after the ports have been covered and sealed.
5. As a general practice to reduce moisture transmission, the operator should wear a pair of surgical rubber gloves within the gloves attached to the box. For added comfort, thin cotton gloves may be worn under the surgical gloves; but each additional layer of glove material reduces the operator's dexterity.

*A.2 ANALYSIS OF INERT ATMOSPHERES**A.2.1 Moisture*

Commercially available moisture monitors provide a convenient, sensitive, and continuous method for measuring the moisture levels in glovebox atmospheres. Monitors that are recommended for use operate on the following principles:

1. Measurement of the electrolysis current due to moisture absorbed on a film of phosphoric oxide which is deposited between a pair of electrodes.

Beckman Instrument Corp., E. I. du Pont de Nemours and Co., Inc., Instrument Products Division (formerly Consolidated Electrodynamics Corp.), and Manufacturers Engineering and Equipment Co., among others, supply moisture monitors of this type.

2. Measurement of the capacitance of an aluminum-aluminum oxide-gold condenser as the capacitance varies with the moisture absorbed by the aluminum oxide film. Panametrics, Inc. manufactures this type of instrument.

Each of the two types of recommended monitors suffers from a drawback which should be recognized. The phosphoric acid type (Type 1 above) is adversely affected by sodium vapor, whereas the capacitance type (Type 2 above) shows irreversible changes in response with time when mercury vapor exists in the glovebox atmosphere. A monthly check on the response of either type of monitor by comparison with a newly-calibrated second monitor is recommended whenever a harmful vapor may be present.

A.2.2 Oxygen

Determination of the oxygen levels in glovebox atmospheres by commercially-available monitors is recommended. Analysis by gas chromatography is an equally acceptable practice; however, its utilization should be limited to boxes in which helium is used.

Two types of oxygen monitors are available and both operate on electrolytic cell principles. One type ("wet cell") is a chemical cell and consists of a silver cathode, a lead or cadmium anode, and aqueous hydroxide electrolyte. The second type ("hot cell") is a concentration cell that utilizes calcia- or yttria-stabilized zirconia as the electrolyte and operates at approximately 800 C. The hot-cell type has two advantages over the wet-cell type: (1) it requires very much less maintenance and (2) probe-type arrangements that can be placed directly in the box are available. Hence, use of the "hot-cell" type is recommended for routine monitoring of oxygen. It should be recognized, however, that any combustible gas present in the glovebox atmosphere (such as H_2 , CO, CH_4) will oxidize in the "hot cell" and will result in low oxygen readings. Therefore, readings from a hot-cell monitor should be compared with those from a wet-cell monitor at least on a monthly basis to establish the absence of this effect. Also, this comparison should be made whenever low oxygen readings are observed.

A.2.3 Carbon-Containing Gases--CO, CO_2 , CH_4 , and Hydrocarbon Vapors

To determine the levels of carbon-containing gas present in glovebox atmospheres, use of the carbon-combustion-and-trapping train of Section 7 is recommended. The analysis is done by passing a known volume (1 to 10 liters) of box atmosphere through this train to convert the carbonaceous gases to CO_2 and by measuring, with the associated gas chromatograph, the levels of the CO_2 formed. This arrangement is also recommended for determining the nature of the carbon-bearing species. This can be done simply by bypassing the combustion section of the train and operating the silica gel column at a temperature required to effect the desired chromatographic separations.

Programmed-temperature operation of a silica gel column (if such capability is available) is especially suitable. Use of a Porapak R column instead of silica gel is also acceptable. Alternatively, a gas chromatograph set up as in Section 31 may be used.

A.2.4 Hydrogen

The gas chromatographic approach described in either Section 5 or Section 31 may be used to determine the hydrogen level of a glovebox atmosphere when argon is used. When helium is used instead of argon, a chromatograph equipped with a helium ionization detector should be used.

Appendix B

TREATMENT OF DATA

Classical statistical methods for establishing confidence levels and rejection criteria may be used when data are available from analyses of a large number of similar samples by a given method. This situation, however, will not exist for all the methods currently described in the manual. In a few cases, the exact procedures have been in force only for a short period; and, in other instances, the methods are not yet in use in all laboratories. Hence, a period may be expected when only a small number of observations* with a given method may be available. To cover both conditions, this section has been divided into two parts. The first part recommends a classical procedure for the treatment of accumulated data to obtain an estimate of precision, the application of precision estimates to subsequent samples, and the rejection of data. The second part recommends a procedure for the treatment of small numbers (10 or less) of replicate observations through the use of range statistics.

*B.1 RECOMMENDED CLASSICAL TREATMENT**B.1.1 Treatment of Accumulated Data to Establish a Confidence Factor*

The procedure for the statistical treatment of previous data to establish confidence levels and rejection criteria is given below. This procedure may be followed as soon as sufficient data are available to give at least 25 degrees of freedom, df (see definition below).

1. For each replicate set of analyses to be used in the statistical treatment, calculate S_i^2 by the following formula:

$$S_i^2 = \sum_j Y_j^2 - \frac{(\sum_j X_j Y_j)^2}{\sum_j X_j^2}; j = 1 \text{ to } n_i.$$

where

- i = the ith sample,
- j = the jth observation on the ith sample,
- Y = measurement of an analytical variable,
- X = weight of volume measurement of the sample,
- n_i = number of replicate analyses in the ith set.

2. Calculate the degrees of freedom using the following formula:

$$df = A - K$$

---

* Classical statistical methods for large numbers of observations are inaccurate for small numbers of observations unless corrections are made. Although tables providing correction factors are available, this step introduces a complication that can be avoided by using small-number statistics.

where

A = total number of observations used in the statistical treatment

K = total number of sets of samples used in the treatment

A set shall consist of either (1) all individual analyses performed for a specific element on aliquots from a single bypass sample, (2) all individual analyses performed for a specific element on aliquots from the dissolution of a single distillation residue or the dissolution of a single total overflow sample, or (3) all individual analyses performed on vanadium wires exposed simultaneously to a sodium system.

3. Calculate S according to the following formula:

$$S = \sqrt{\frac{\sum_{i=1}^K S_i^2}{df}}$$

4. Obtain a $t_{0.95}$, using the df previously calculated, by referring to Table B.1.

5. Calculate F according to the following formula:

$$F = t_{0.95} \times S$$

6. This value for F will be used to evaluate subsequent data until sufficient additional data are available to warrant recalculation of F. Recalculation is warranted at 40, 60, and 120 degrees of freedom. Data which have been rejected according to the criteria in Section B.1.2 must be included in the recalculation.

B.1.2 Treatment of New Data

1. Calculate each result from a set of n_i replicate measurements made on a sample as follows

$$B_j = \frac{Y_j}{X_j}, j = 1 \text{ to } n_i$$

2. If an outlying result is suspected, proceed with step 3; if not, proceed with step 9.

3. Reorder the measurements, designating the X and Y values of the suspect result as X_1 and Y_1 .

4. Calculate $\hat{B}_R$ according to the following formula:

$$\hat{B}_R = \frac{\sum_{j=2}^{n_i} X_j Y_j}{\sum_{j=2}^{n_i} X_j^2}$$

5. Using the F calculated in step 5 of Section B.1.1, calculate the limits of acceptance for Y_1 according to the following formula:

TABLE B-1

Values of t at the 95% Confidence Level

<u>df</u>	<u>t_{0.95}</u>
25	2.060
26	2.056
27	2.052
28	2.048
29	2.045
30	2.042
40	2.021
60	2.000
120	1.980

$$s_1^2 = 3202.57 - \frac{3746082.83}{1171.49} = 4.862$$

2nd Set of Wires (i = 2)

j	1	2	3	4	5	6	7	8	9	10
X _j	16.5	15.3	19.3	25.8	21.1	21.6	20.0	19.3	21.1	22.3
Y _j	13.0	11.3	14.8	19.4	16.5	16.9	15.8	15.3	15.2	17.5

$$\Sigma X_j^2 = 4171.23$$

$$\Sigma Y_j^2 = 2470.97$$

$$(\Sigma X_j Y_j)^2 = 10297681.00$$

$$s_2^2 = 2470.97 - \frac{10297681}{4171.23} = 2.230$$

3rd Set of Wires (i = 3)

j	1	2	3	4	5	6	7	8	9	10	11	12
X _j	14.9	17.0	20.6	20.0	20.4	16.2	23.4	22.6	24.9	17.8	23.8	22.4
Y _j	7.0	8.6	11.0	11.3	11.0	9.1	12.6	12.0	13.9	9.7	13.6	13.2

$$\Sigma X_j^2 = 5077.34$$

$$\Sigma Y_j^2 = 1524.72$$

$$(\Sigma X_j Y_j)^2 = 7723341.228$$

$$s_3^2 = 1524.72 - \frac{7723341.228}{5077.34} = 3.581$$

$$df = 9 + 10 + 12 - 3 = 28$$

$$s = \sqrt{\frac{4.862 + 2.230 + 3.581}{28}} = 0.6174$$

Table B.1 indicates that for a df of 28, $t_{0.95}$ has the value 2.048, therefore:

$$F = 2.048 \times 0.6174 = 1.264$$

The values obtained on subsequent sets of vanadium wires are given below:

Set 4 (i = 4)			Set 5 (i = 5)		
<u>i</u>	<u>X</u>	<u>Y</u>	<u>i</u>	<u>X</u>	<u>Y</u>
1	13.0	14.5	1	23.4	14.1
2	13.1	14.7	2	22.7	13.5
3	18.6	21.5	3	27.3	15.7
4	16.7	19.8	4	77.8	45.1
5	13.0	19.8	5	26.7	15.4
			6	79.9	46.2

<u>Step 1</u>	<u>B</u>	<u>Step 1</u>	<u>B</u>
1	1.11	1	0.602
2	1.12	2	0.595
3	1.16	3	0.575
4	1.19	4	0.580
5	1.52	5	0.577
		6	0.578

Step 2			Step 2		
The data for X_5 and Y_5 lead to a result which apparently is an outlier. Proceed to step 3.			No apparent outlier. Therefore, proceed to Step 9.		

Step 3			Step 3		
Rearrange the data			Omit.		
<u>X</u>	<u>Y</u>				
1	13.0	19.8			
2	13.0	14.5			
3	13.1	14.7			
4	18.6	21.5			
5	16.7	19.8			

Step 4

$$\hat{B}_R = \frac{\sum_{j=2}^{n_i} X_j Y_j}{\sum_{j=2}^{n_i} X_j^2} = \frac{1111.63}{965.46}$$

$$= 1.151$$

Step 5

Calculate limits of Y_1 :

Confidence limits on $Y_1 =$

$$\hat{B}_R X_1 \pm F \sqrt{1 + \frac{X_1^2}{\sum_{j=2}^{n_i} X_j^2}}$$

$$= 1.151 \times 13.0$$

$$\pm 1.264 \sqrt{1 + \frac{169}{965.46}}$$

$$= 14.96 \pm 1.37$$

Therefore, Y_1 should lie between 13.7 and 15.4.

Step 6

Since $Y_1 = 19.8$, which is outside the limits calculated in Step 5, proceed with Step 7. Retain both X_1 and Y_1 for subsequent calculations of F.

Step 4 Omit.

Step 5 Omit.

Step 6 Omit.

Step 7 (Section 1.1)

Calculate confidence limits:

Confidence limits on B =

$$\begin{aligned}\hat{B}_R \pm F \sqrt{\frac{1}{\sum_{j=2}^{n-1} X_j^2}} \\ = 1.15 \pm 1.264 \sqrt{\frac{1}{965.46}} \\ = 1.15 \pm 0.04\end{aligned}$$

Step 8

Report result as 1.15 ± 0.04

Step 9 Omit.

Step 10 Omit.

Step 11 Omit.

Step 7 Omit.

Step 8 Omit.

Step 9 Calculate $\hat{B}$.

$$\begin{aligned}\hat{B} &= \frac{\sum XY}{\sum X^2} \\ &= \frac{8676.34}{14957.88} \\ &= 0.580\end{aligned}$$

Step 10 Calculate confidence limits:

Confidence limits on B

$$\begin{aligned}&= \hat{B} \pm F \sqrt{\frac{1}{\sum X^2}} \\ &= 0.580 \pm 0.264 \sqrt{\frac{1}{41957.88}} \\ &= 0.58 \pm 0.01\end{aligned}$$

Step 11

Report result as 0.58 ± 0.01 .

B.1.4 Discussion

All calculations required by the procedures in this manual are of the following general form:

$$\frac{Y}{X} = B$$

where

Y = an analytical measurement of a constituent in the sample multiplied by appropriate constants (e.g., aliquot size, calibration factor, etc.)

X = a measurement of the sample weight or volume, and

B = the concentration of the constituent in the sample.

Furthermore, the error in Y generally is larger than the error in X. In such cases the statistical treatment suggested by Snedecor and Cochran* is applicable. In this treatment, based on the linear regression theory, it is assumed that for all observations the errors in measuring Y_i are identically and independently normally distributed with means 0 and variances σ^2 .

Letting x_{ij} , y_{ij} be the j th of n_i observations on X_i and Y_i in the i th sample, for which it is known that $Y_i = B_i X_i$, the maximum likelihood estimate of B_i is

$$\hat{B}_i = \frac{\sum_{j=1}^{n_i} x_{ij} y_{ij}}{\sum_{j=1}^{n_i} x_{ij}^2}.$$

This estimate of B_i is normally distributed with mean B_i and variance

$\sigma^2 / \sum_{j=1}^{n_i} x_{ij}^2$. In the i th sample, σ^2 is estimated by

$$\sum_{j=1}^{n_i} (y_{ij} - \hat{B}_i x_{ij})^2 / (n_i - 1).$$

If K samples are present, these estimates are pooled to give

$$\begin{aligned} S^2 &= \frac{\sum_{i=1}^K \sum_{j=1}^{n_i} (y_{ij} - \hat{B}_i x_{ij})^2}{\left(\sum_{i=1}^K n_i - K \right)} \\ &= \frac{\sum_{i=1}^K \left(\sum_{j=1}^{n_i} y_{ij}^2 - \frac{\left(\sum_{j=1}^{n_i} x_{ij} y_{ij} \right)^2}{\sum_{j=1}^{n_i} x_{ij}^2} \right)}{df} \\ &= \sum_{i=1}^K S_i^2 / df, \text{ where } df = \sum_{i=1}^K n_i - K. \end{aligned}$$

* Snedecor and Cochran, "Statistical Methods," 6th Ed., Chap. 6, The Iowa State Univ. Press, Ames, Iowa (1967).

This estimate of σ^2 is distributed as a chi-square variable divided by its degrees of freedom.

We can now construct 95% confidence limits on B_i from the fact that the quantity

$$(\hat{B}_i - B_i) / \sqrt{S^2 / \sum_{j=1}^{n_i} x_{ij}^2}$$

follows the t distribution with df degrees of freedom.

For a given value of X, say x_* , a 95% confidence prediction interval on y can be constructed since $y - \hat{B}_i x_*$ is normally distributed

with 0 mean and variance $\sigma^2 \left(1 + x_*^2 / \sum_{j=1}^{n_i} x_{ij}^2 \right)$; and thus,

$$(y - \hat{B}_i x_*) / \left(S \sqrt{1 + x_*^2 / \sum_{j=1}^{n_i} x_{ij}^2} \right)$$

is t-distributed with df degrees of freedom. If there is a suspect x_* , y_* observation in sample i, y_* can be tested for possible measurement error by constructing, from the remaining observations, a prediction interval on y for the given x_* .

B.2 RECOMMENDED TREATMENT FOR SMALL NUMBERS OF OBSERVATION USING RANGE STATISTICS ^{**,†}

The manner in which the range method may be used for reporting and for rejecting results is given below.

B.2.1 Presentation of Results

$$\text{Result} = \bar{x} \pm wf$$

where

- $\bar{x}$ = the arithmetic mean of the group of individual determinations,
- w = the range of determinations, i.e., the largest value minus the smallest value,
- f = a multiplier, obtained from Table B-2, which converts the range to a 95% confidence limit.

^{**} ASTM E-178, "Recommended Practice for Dealing with Outlying Observations".

[†] R. B. Dean and W. J. Dixon, *Anal. Chem.* **23**, 636 (1951).

TABLE B-2. Confidence Factors and Rejection Quotients

Number of Observations n	Confidence Factor f	Rejection Quotient Q	Number of Observations n	Confidence Factor f	Rejection Quotient Q
2	6.4	-	6	0.40	0.56
3	1.3	0.94	7	0.33	0.51
4	0.72	0.76	8	0.29	0.47
5	0.51	0.64	9	0.26	0.44
			10	0.23	0.41

B.2.2 Rejection Test

If one of the values is suspected to be grossly in error and there is no experimental or other obvious reason for rejecting it, then the following rejection test should be applied:

1. Label the suspected value x_1 and arrange the rest of the values by magnitude in ascending or descending order.
2. Calculate r appropriate to n according to the equation:

$$r = \frac{|x_1 - x_2|}{|x_1 - x_n|}$$

where

$|x_1 - x_2|$ = absolute difference between the doubtful value and its nearest neighbor
 $|x_1 - x_n|$ = w , the range
 n = number of determinations

3. If $r < Q$, retain the suspected value (Q is tabulated in Table B-2).
4. If $r \geq Q$ and $n \geq 6$, reject the suspected value.
5. If $r \geq Q$ and $N < 6$, perform enough additional determinations to make $n \geq 6$ and repeat the test on the enlarged group.
6. If a value is rejected, compute $\bar{x} \pm wf$ on the basis of the reduced number of values. In addition, report all of the values and note which one was rejected.

As an example, consider three determinations: 4.0, 5.0, and 9.0. The value 9.0, although suspect, cannot be rejected because of insufficient data; thus, three more analyses are performed, yielding the values 4.0, 5.0, and 6.0. Then,

$$\left(r = \left| \frac{9.0-6.0}{9.0-4.0} \right| = 0.60 \right) > (Q = 0.560)$$

and the value 9.0 would be rejected. On the basis of the five valid determinations, the result $= 4.8 \pm (2.0)(0.51) = 4.8 \pm 1.0$ would be reported. However, the values obtained in all six determinations would be listed. On the other hand, if the second set of three determinations had yielded values of 3.0, 5.0, and 6.0, then

$$\left(r = \left| \frac{9.0-6.0}{9.0-3.0} \right| = 0.50 \right) < (Q = 0.560)$$

Consequently, all values would be retained, and the result $5.3 \pm (6.0)(0.40) = 5.3 \pm 2.4$ would be reported.

Appendix C

MERCURY TEST AND CLEANING PROCEDURE

C.1 TEST PROCEDURE

The procedures specified for the determination of hydrogen and oxygen in sodium (Sections 5 and 11) require the use of Hg that has been tested to establish that its oxygen-and hydrogen-bearing impurity levels (especially moisture) are within tolerable limits. To effect the requisite test, the following procedure is recommended.

Amalgamate 1 g of sodium with 20 ml of mercury and agitate for 3 min. Allow a minimum of 2 min for the insoluble residue to reach the surface. Drain 5 ml of the residue-free amalgam into each of two precleaned funnels, A and B. Add 5 ml of the mercury to be tested to one funnel (A) and 100 ml to the other (B). Agitate for 5 min, allow a minimum of 2 min for the insoluble residue to reach the surface, and drain all but approximately 0.3 ml of the dilute amalgam from the funnels into waste containers. This allows any moisture present in the mercury under test to be reacted with sodium amalgam. The two funnels are then rinsed with five 10-ml portions of mercury (the mercury under test may be used); agitating for 5 min, allowing to settle 2 min, and draining all but approximately 0.3 ml, each time. Determine the sodium content of the residue from each funnel, after the last rinse, by flame photometry as in Section 11. The maximum acceptable difference between the sodium contents of vessels A and B is a ratio of 1 to 2. Should a given supply of mercury fail this test, it must be either (a) cleaned (the procedure described below is recommended) and retested until it meets specification or (b) replaced by a fresh supply, which in turn, must be tested to determine its adequacy.

C.2 CLEANING PROCEDURE

C.2.1 Apparatus

Mercury Scrubbing Apparatus. This apparatus is shown in Fig. C-1. It consists of a stainless steel storage tank for dirty mercury and a glass column, 4-cm dia by 120 cm long, packed with 0.6-cm glass beads.

Gold Adhesion Filter. A satisfactory gold adhesion filter is manufactured by the Bethlehem Apparatus Co.

Reservoir. This reservoir may be a 15-liter stainless steel tank as shown in Fig. C-2.

C.2.2 Materials and Reagents

Nitric Acid. 2M.

Hydrochloric Acid. 3M

C.2.3 Procedure

1. Remove gross amounts of sodium from the mercury by allowing the amalgam to stand under 3M hydrochloric acid until hydrogen evolution ceases.

Fig. C-1

Typical Mercury Scrubbing Apparatus

Fig. C-2

Typical Mercury Reservoir

2. Separate the mercury from the aqueous solution by draining the mercury from a separatory funnel. Transfer the dry mercury to the storage tank. Leave the fill plug loose during storage to prevent the possible buildup of hydrogen pressure.

3. Connect a carboy of 2M nitric acid to the scrub column. Start the water aspirator and adjust the flow of acid to 50 ml/min.

4. Tighten the fill plug and pressurize the mercury storage tank to 25 psig with air. Adjust the flow of mercury into the column to about 50 ml/min.

5. Open the stopcock and allow the scrubbed mercury to drain into a clean, dry vessel as fast as it collects at the bottom of the column.

6. Pour the mercury into the reservoir of a gold adhesion filter. The mercury should be poured smoothly and near the edge of the reservoir to minimize the possibility of insoluble matter being carried to the apex of the filter.

7. Allow one minute for insoluble matter to reach the surface, then drain mercury through the filter at about 50 ml/min into a clean, dry vessel for transfer to the depressurized stainless steel reservoir.

8. After the cleaning has been completed, flush the scrub column with distilled water. Evacuate the head space of the reservoir then pressurize it with argon.

C.2.4 Safety Precautions

Because of the poisonous nature of mercury and its compounds, this procedure should be performed in a fume hood. Rubber gloves should be worn and spilled mercury cleaned up promptly. The atmosphere should be monitored frequently with a mercury-vapor detector.

Appendix D
DETERMINATION OF THE CHEMICAL ACTIVITY OF CARBON
IN SODIUM BY AN EQUILIBRATION METHOD USING Fe-12 WT% Mn TABS
(TENTATIVE)

D.1 PRINICPLE

A metal tab of Fe-12 wt% Mn is immersed in flowing sodium at 700 C until equilibrium with respect to carbon is reached. Subsequently, the carbon concentration in the tab is measured and the chemical activity of carbon is calculated.

D.2 SENSITIVITY AND PRECISION

This procedure is applicable for carbon activities in sodium in the range 0.002 to 0.3. The precision is expected to be within $\pm 10\%$ at activities > 0.01 .

D.3 APPARATUS

Equilibration Module. Fig. D-1 is a schematic drawing of the Specimen Equilibration Module for use on reactors and large sodium systems. This module shall conform to the requirements of RDT C 8-8. Fig. D-2 is a schematic drawing of a typical Specimen Equilibration Device for use on small experimental systems.

Carbon Analyzer. The LECO Carbon-Oxygen Determinator, manufactured by the Laboratory Equipment Corporation, has been found suitable for this application.

Forceps. Dissecting forceps.

D.4 MATERIALS

Standard Fe-12 wt% Mn Tabs, annealed, 5 mils thick x 1 inch wide x 1 inch long. Suitable 5-mil thick x 1-inch-wide strip stock has been supplied by the Materials Research Corporation.

Accelerator. Tin Metal Accelerator, LECO Catalog No. 25705, has been found satisfactory for this use.

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

Acetone. Reagent Grade.

Ethanol. Technical Grade, and absolute reagent grade.

D.5 PROCEDURE

D.5.1 Tab Preparation

1. Prepare tabs by cutting the standard Fe-12 wt% Mn strip stock into 1-in.-long lengths.

2. Scribe or punch identifying numbers on each tab.

Fig.D-1 SCHEMATIC of a TYPICAL SPECIMEN EQUILIBRATION MODULE

Fig. D-2

SCHEMATIC of a TYPICAL SPECIMEN EQUILIBRATION DEVICE

3. Hold a tab with clean dissecting forceps and carefully degrease it with acetone washes. After degreasing, the tab must be handled only with degreased tools.

4. Degrease the sample holder by washing it with acetone.

5. Mount the tabs in the sample holder.

D.5.2 Equilibration

1. Insert the sample holder into the sodium system.

2. After establishing sodium flow (minimum, 0.2 gal/min) through the equilibration device, equilibrate the tabs at $700 \pm 2^\circ\text{C}$ for at least 3 and for no more than 7 days.

D.5.3 Post-Exposure Treatment

1. Discontinue flow through the sample holder.

2. Cool the tabs quickly by forced air cooling of the loop section containing the holder. The temperature should be reduced from 700°C to 400°C or lower within 0.5 hour.

3. Remove the sample holder from the equilibration module or device.

4. Dissolve the sodium adhering to the holder in approximately 1000 ml of technical grade alcohol. (The large volume of alcohol prevents excessive heating.)

5. Rinse the holder and tabs with distilled water, reagent grade absolute ethyl alcohol, and then allow the tabs and tab holder to dry.

6. Remove the tabs from the holder and place them in a clean, dry glass vial.

D.5.4 Carbon Determination

1. Analyze 4 or 5 samples of NBS Type 335 Steel. For each determination, use approximately 0.7 g of tin accelerator.

2. Prepare a calibration curve of instrument meter units vs micrograms carbon.

3. Analyze approximately 0.5-g samples from a tab according to the procedure used for standardization.

4. From the calibration curve, determine the micrograms of carbon in each sample.

D.6 CALCULATIONS

1. Calculate the wt ppm carbon in the Fe-12 wt% Mn tab from the following formula:

$$A, \text{ wt ppm carbon in tab} = \frac{B}{C}$$

where

B = carbon in sample, μg

C = weight of sample, g

2. Calculate the chemical activity of carbon in the sodium from the following formula:

$$\text{Chemical Activity of Carbon} = \frac{A}{K - 0.264A}$$

K = 13,480 ppm C

D.7 SAFETY

The steps under Equilibration and Post-Exposure Treatment present hazards which should be controlled by locally-administered safety programs.

The laboratory operations present no unusual hazards except the safe handling of liter quantities of flammable organic liquids.

D.8 DISCUSSION

This entire procedure, excluding the equilibration time, requires about 4 hr.

Appendix E
DETERMINATION OF CHLORIDE IN SODIUM BY SPECIFIC ION ELECTRODE
(TENTATIVE)

E.1 PRINCIPLE

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

E.2 SENSITIVITY AND PRECISION

This method is suitable for the determination of 50 to 500 μg of chloride (1 to 10 ppm of chloride in a 50-g sample of sodium). The range can readily be adjusted upward. For chloride concentrations in the range of approximately 5 ppm, replicate determinations from the same sample are expected to agree within 20%.

E.3 APPARATUS

Digital Electrometer/pH meter. Suitable for use with the specific ion electrode. The Corning Model 101 instrument has been found suitable for this purpose.

pH Electrode. With double junction calomel reference electrode.

Chloride Specific Ion Electrode. The Orion Research, Inc., Model 92-17 Liquid Ion Exchange Membrane Electrode and Model 90-02 Counter Electrode has been found suitable.

Balance. A balance that is capable of weighing to ± 0.1 g is adequate.

Magnetic Stirrer, with Teflon-covered stirring bars.

E.4 MATERIALS AND REAGENTS

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

Concentrated Buffer. To approximately 150 ml of water, add 285 ml of reagent grade glacial acetic acid and 0.30 g reagent grade sodium citrate. Adjust the solution of pH 5.0 to 5.5 by addition of reagent grade NaOH pellets. Cool, dilute to 500 ml, and store in a polyethylene bottle.

Buffer. Dilute 100 ml of Concentrated Buffer to 1 liter with water.

Sodium Chloride Standard (1 mg Cl^-/ml). Dissolve 1.649 g reagent grade NaCl in Buffer and dilute to 1 liter with Buffer.

Chloride Working Standard (50 μg Cl^-/ml). Dilute 5 ml of Sodium Chloride Standard to 100 ml with Buffer. Prepare fresh on the day of use.

E.5 PROCEDURE

1. Obtain a distillation residue prepared by the method of Section 4. Use a tantalum cup.

2. Compute the sample weight from the information recorded on the distillation residue container (Section 4.4 step 23).
3. Rinse the cup with 10 ml of Buffer and two 5-ml portions of Buffer
4. Combine all washings and dilute to 25 ml with additional Buffer.
5. Prepare standard solutions containing 1, 2, 3, 5, 10, and 20 $\mu\text{g Cl}^-/\text{ml}$ 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.
6. Immerse the chloride specific ion electrode and its reference electrode in the standard solution containing 20 $\mu\text{g Cl}^-/\text{ml}$ while stirring the solution with a magnetic stirrer. Set the instrument zero to 200 and adjust the meter response to 200 by turning the "Calibrate" control.
7. Rinse the electrodes with Buffer, and immerse them in the standard containing 10 $\mu\text{g Cl}^-/\text{ml}$. Adjust the meter response to 100 by turning the "Slope" control.
8. Determine and record the meter response with the electrodes immersed in each other standard, in Buffer as a blank, and in the sample solution. Between each measurement, intersperse a recheck of the meter response to the 20 $\mu\text{g Cl}^-/\text{ml}$ standard. Rinse the electrodes with Buffer before each transfer to a new concentration.
9. From the measurements on the standards and blank, prepare a calibration curve of $\mu\text{g Cl}^-/\text{ml}$ vs meter response.
10. From the calibration curve and the measurement on the sample solution, determine the $\mu\text{g Cl}^-/\text{ml}$ of sample solution.

E.6 CALCULATIONS

$$\text{Chloride, ppm} = \frac{A \times B}{W}$$

where

A = Cl^- concentration in sample solution, $\mu\text{g}/\text{ml}$

B = volume of sample solution, ml

W = weight of sample, g

E.7 SAFETY

This procedure presents no unusual safety hazards.

E.8 DISCUSSION

This procedure takes approximately 1 hr.

Appendix F

VERIFICATION OF IDENTITY OF PURCHASED COVER GAS BY
GAS CHROMATOGRAPHY AND MASS SPECTROMETRY

These methods are intended to be used to verify the identity of as-purchased cover gas. They are not applicable to cover gas samples removed from a reactor or an experimental system.

F.1 GAS CHROMATOGRAPHIC METHOD

F.1.1 Principle

The gas being tested is uniquely defined by its relative retention time as measured gas chromatographically under controlled conditions.

F.1.2 Sensitivity and Precision

This is a "go-no-go" test which is adequate to verify the identity of samples of unused cover gas.

F.1.3 Apparatus

Gas Chromatograph. Any instrument which shows adequate response when tested with known mixtures may be used. Typical operating parameters are noted in the individual methods.

Gas Handling System. An apparatus suitable for preparing known dilutions of gas mixtures. A typical set-up is shown in Fig. F-1. This system consists of a rough vacuum pump, a mercury diffusion pump, vacuum and pressure measuring equipment, and a tubular manifold consisting of gas storage vessels and ports.

Syringe, 0.5-ml Valved, Gas-Type. Pressure-Lok syringes, manufactured by the Precision Sampling Corp., have been found satisfactory.

F.1.4 Materials and Reagents

Helium Gas, $\geq 99.995\%$ purity and verified as helium by mass spectrometry.

Argon Gas, $\geq 99.995\%$ purity and verified as argon by mass spectrometry.

Nitrogen Gas, $\geq 99.99\%$ purity and verified as nitrogen by mass spectrometry.

Krypton Gas, $\geq 99.9\%$ purity and verified as krypton by mass spectrometry. A lecture bottle is a suitable quantity.

Hydrogen Gas, $\geq 99.95\%$ purity and verified as hydrogen by mass spectrometry.

Oxygen Gas, $\geq 99.6\%$ purity and verified as oxygen by mass spectrometry.

Fig. F-1

TYPICAL GAS HANDLING SYSTEM

F.1.5 Procedure

Individual procedures are specified for the identification of nitrogen, helium, and argon.

F.1.5.1 Procedure for Identification of Nitrogen

1. Bring the gas chromatograph to stable operating condition. The following are typical operating parameters:

Column: A 3-ft by 1/4-in.-O.D. column packed with -60+80 mesh Linde Molecular Sieve 5A

Column temperature: 25 C

Carrier gas and flow rate: Helium at 60 ml/min

Detector: A thermal conductivity detector operated at 150 mA bridge current.

Sample size: 0.5 ml

2. Prepare, using the gas handling apparatus, an equimolar mixture of nitrogen and krypton at a final pressure of approximately 1 atm.

3. Obtain a 0.5-ml sample of the mixture from step 2 in the gas-tight syringe and inject the sample through the septum of the chromatograph.

4. Record and examine the chromatogram.

5. Adjust, if necessary, the operating parameters of the chromatograph until N_2 and Kr show adequate peak heights and peak separations.

If there is any doubt as to the identity of the individual peaks, obtain and inject a sample of pure N_2 and record its retention time.

6. Obtain a sampling vessel containing the gas to be tested.

7. If the gas sample is at approximately 1 atm and is contained in a vessel equipped with a septum, obtain a 0.5-ml gas sample in the gas-tight syringe. Otherwise, attach the sampling vessel to the gas handling apparatus and, by appropriate manipulations, obtain a sample at approximately 1 atm in an auxiliary vessel equipped with a septum, then obtain a 0.5-ml sample in the gas-tight syringe.

8. Inject the gas sample into the chromatograph septum and record the chromatogram.

9. If the chromatogram shows only one main peak and that peak occurs at the retention time for nitrogen, record that the sample has been identified as nitrogen. Otherwise, mark the sample as rejected pending further investigation.

F.1.5.2 Procedure for Helium

1. Bring the gas chromatograph to stable operating condition. The following are typical parameters:

Pre-column: A tube 3-in. long by 1/4-in. I.D., packed with CuO wire mesh and operated at 300 C.

Column: A 3-ft by 1/4-in.-O.D. column packed with -60+80 mesh Linde Molecular Sieve 5A.

Column temperature: 25 C

Carrier gas and flow rate: Ar at 60 ml/min.

Detector: A thermal conductivity detector operated at 100 mA bridge current.

Sample size: 0.5 ml

2. Prepare, using the gas handling apparatus, samples of pure helium and pure hydrogen each at a final pressure of approximately 1 atm.

3. Obtain a 0.5-ml sample of helium from step 2 in the gas-tight syringe and inject the sample through the septum of the chromatograph.

4. Record and examine the chromatogram.

5. Adjust, if necessary, the operating parameters of the chromatograph until a single major peak due to helium is observed. Record the He retention time.

6. Obtain a 0.5-ml sample of hydrogen from step 2 in the gas-tight syringe and inject the sample through the septum of the chromatograph.

7. Record and examine the chromatogram.

8. Adjust, if necessary, the operating parameters of the CuO pre-column until the chromatogram shows no major peak and only the disturbances due to pressure changes on injection of the sample.

9. Obtain a sampling vessel containing the gas to be tested.

10. If the gas sample is at approximately 1 atm and is contained in a vessel equipped with a septum, obtain a 0.5-ml gas sample in the gas-tight syringe. Otherwise, attach the sampling vessel to the gas handling apparatus and, by appropriate manipulations, obtain a sample at approximately 1 atm in an auxiliary vessel equipped with a septum. Then obtain a 0.5-ml sample in the gas-tight syringe.

11. Inject the gas sample into the chromatograph septum and record the chromatogram.

12. If the chromatogram shows only one main peak and that peak occurs at the retention time for helium, record that the sample has been identified as helium. Otherwise, mark the sample as rejected pending further investigation.

F.1.5.3 Procedure for Identification of Argon

1. Bring the chromatograph to stable operating condition.
The following are typical operating parameters:

Column: A 3-ft by 1/4-in.-OD column packed with -60+80 mesh
Linde Molecular Sieve 5A.

Column temperature: 25 C

Carrier gas and flow rate: Ar at 60 ml/min

Detector: A thermal conductivity detector operated at 100 mA
bridge current.

Sample size: 0.5 ml.

2. Prepare, using the gas handling apparatus, an equimolar
mixture of argon and oxygen at a final pressure of approximately 1 atm.

3. Obtain a 0.5-ml sample of the mixture from step 2 in the
gas-tight syringe and inject the sample through the septum of the chromatograph.

4. Record and examine the chromatogram.

5. Adjust, if necessary, the operating parameters of the chroma-
tograph until the single major peak due to oxygen is observed. Record the oxygen
retention time.

6. Obtain a sampling vessel containing the gas to be tested.

7. If the gas sample is at approximately 1 atm and is contained
in a vessel equipped with a septum, obtain a 0.5-ml gas sample in the gas-tight
syringe. Otherwise, attach the sampling vessel to the gas handling apparatus
and, by appropriate manipulations, obtain a sample at approximately 1 atm in an
auxiliary vessel equipped with a septum. Then, obtain a 0.5-ml sample in the gas-tight
syringe.

8. Inject the gas sample into the chromatograph and record
the chromatogram.

9. If the chromatogram shows no main peak and only the minor
peaks attributable to contamination during sampling, record that the sample has been
identified as argon. Otherwise, mark the sample as rejected pending further
investigation.

F.1.6 Calculations

The decisions required are based on visual examination of
chromatograms. No calculations are required.

F.1.7 Safety

These procedures require the usual safety precautions for handling eva-
cuated and pressurized glassware, gases in cylinders, and liquefied cryogenic gases.

F.1.8 Discussion

The central ideas and assumptions supporting all three identification
procedures are as follows:

1. It is possible to state the gas that is most difficult to distinguish from the gas under test (cover gas) namely krypton from nitrogen, hydrogen from helium, and oxygen from argon.

2. Each procedure has been shown to distinguish between the gas under test (cover gas) and its most-difficult-to-detect substitute.

3. Therefore, each procedure allows an unequivocal decision between the gas under test (the cover gas) vs. all other gases.

In the case of nitrogen, the retention time for nitrogen distinguishes it from all other gases.

In the case of helium, the two most seriously interfering gases are hydrogen and neon. Hydrogen is converted to H_2O by the pre-column, the resulting H_2O is retained by the molecular sieve, and no peak attributable to hydrogen appears in the chromatogram. The procedure does not protect against the inadvertent substitution of neon for helium. Neon is so expensive and in such short supply that protection against this substitution is considered to be unnecessary.

Each procedure, exclusive of sampling, requires approximately 1/2 hr.

F.2 MASS SPECTROMETRIC METHOD

F.2.1 Principle

The gas being tested is uniquely defined by its mass spectrum as measured under controlled conditions.

F.2.2 Sensitivity and Precision

This is a "go-no-go" test which is adequate to verify the identity of samples of unused cover gas.

F.2.3 Apparatus

Mass Spectrometer. The mass spectrometer may be any type commonly used for general gas analysis. The discontinued, but still widely available, Consolidated Electrodynamics Corp. Model 21-620 instrument, has been found satisfactory for this purpose. CEC instruments now are a product of the Instrument Products Division, E.I. du Pont de Nemours and Co., Inc.

Gas Handling System. As described in Section F.1.3

Syringe, 0.5-ml Valved, Gas-type. Pressure-Lok syringes, manufactured by the Precision Sampling Corp., have been found satisfactory.

F.2.4 Materials and Reagents

Nitrogen Gas, $\geq 99.99\%$ purity

Helium Gas, $\geq 99.995\%$ purity

Argon Gas, $\geq$ 99.995% purity

F.2.5 Procedure

1. Bring the mass spectrometer to stable operating condition, either according to the manufacturer's specifications or according to the experience of the operator.

2. Calibrate the instrument by successively analyzing known standard samples of N_2 , He, and Ar. Record typical mass spectra for future reference.

NOTE: If the mass spectrometer has a history of stable operation, this step needs to be performed only infrequently.

3. Obtain a sampling vessel containing the gas to be tested.

4. Using the gas handling system, if necessary, and by the manipulation appropriate for the mass spectrometer being used, introduce a gas sample into the inlet system of the instrument.

5. Obtain and record a mass spectrum of the gas under test.

6. If the mass spectrum of the sample matches the spectrum of the appropriate standard, record that the identity of the sample has been verified. Otherwise, mark the sample as rejected pending further investigation and record whatever tentative identification is possible from the spectrum of the rejected sample.

F.2.6 Calculations

The decisions required are based on visual examination of mass spectra. No calculations are required.

F.2.7 Safety

This procedure requires the usual safety precautions for handling evacuated glassware, gases in cylinders, and liquefied cryogenic gases.

F.2.8 Discussion

Each analysis, exclusive of sampling, requires 1/2 to 1 hr.

Appendix G
VERIFICATION OF PURITY OF PURCHASED COVER GAS
(TENTATIVE)

The impurities, oxygen and moisture are best determined individually by commercially-available monitors. The other impurities, H_2 , N_2 , CH_4 , CO_2 , CO , total hydrocarbons (as methane), Ne, Kr, and Xe are conveniently determined by gas chromatography. The various techniques are covered in separate sections below.

G.1 DETERMINATION OF OXYGEN IN NITROGEN, HELIUM, OR ARGON

G.1.1 Principle

Oxygen is determined from a measurement of the electrolysis current in a commercial electrolytic oxygen analyzer.

G.1.2 Sensitivity and Precision

The detection limit is approximately 0.1 ppm oxygen. The reproducibility is expected to be $\pm 10\%$ relative.

G.1. Apparatus

Electrolytic Oxygen Analyzer. This type of instrument ordinarily uses a silver cathode and a lead or cadmium anode in an alkaline electrolyte. Instruments manufactured by Beckman Instruments, Inc., by the Manufacturers Engineering and Equipment Company, and by Lockwood and McLorie, Inc. have been found suitable.

G.1.4 Materials and Reagents

Standard Gas Mixture. A cylinder of helium containing 4 to 6 ppm of oxygen and purchased with a certified analysis from the vendor.

G.1.5 Procedure

1. Pass the standard gas mixture through the oxygen analyzer while operating the analyzer according to the manufacturer's specifications. Typically, these call for a gas flow of 100 ml/min until the meter readout is stable for at least 1 hour.

2. Record the indicated analysis of the standard gas and verify that the oxygen analyzer is in calibration.

3. Obtain a sample of the gas to be analyzed. Typically, this will be as compressed gas in a cylinder or in a cryogenic sampler, type TTU-131/E (described in MIL-S-27626). (Quantities of gas up to 3 cubic feet will be used in this analysis.)

4. Pass the gas sample through the oxygen analyzer operating as in step 1, above.

5. Record the indicated oxygen content of the sample.

G.1.6 Calculations

Ordinarily, the analyzer is calibrated to read ppm oxygen directly, and no calculations are required.

G.1.7 Safety

This procedure requires the usual safety precautions for handling compressed gases in cylinders.

G.1.8 Discussion

This procedure, excluding sampling time, takes 3 to 4 hours.

G.2 DETERMINATION OF MOISTURE IN NITROGEN, HELIUM, OR ARGON

G.2.1 Principle

Moisture is determined from a measurement of the electrolysis current through, or the capacitance of, the sensing element of a commercial hygrometer.

G.2.2 Sensitivity and Precision

The detection limit is approximately 1 ppm H₂O. The reproducibility of measurements is expected to be $\pm 10\%$.

G.2.3 Apparatus

Hygrometer, Continuous Recording. Two instruments are needed. Available hygrometers operate on the following principles:

1. Measurement of the electrolysis current due to moisture absorbed in a film of P₂O₅ deposited between a pair of electrodes. Instruments manufactured by Beckman Instruments, Inc., by the Manufacturers Engineering and Equipment Company, and by the E. I. du Pont de Nemours and Co., Inc., Instrument Products Division (formerly Consolidated Electrodynamics Corporation) have been found suitable.

2. Measurement of the capacitance, which varies with the moisture absorbed by the aluminum oxide layer, of an aluminum-aluminum oxide-gold capacitor. Instruments manufactured by Panametrics, a subsidiary of the Esterline Corporation, have been found satisfactory.

G.2.4 Materials and Reagents

No special materials or reagents are needed for this procedure.

G.2.5 Procedure

1. Obtain a sample of the gas to be analyzed. Typically, this will be as compressed gas in a cylinder or in a cryogenic sampler, Type TTU-131/E (described in MIL-S-27626). (Up to 3 cubic feet of gas may be used in this analysis.)

2. Connect two hygrometers in parallel to the source of gas to be analyzed.
3. Operate each hygrometer according to the manufacturer's specifications.
4. When the readings have stabilized, record the moisture content of the gas as indicated by each instrument.
5. If the two moisture contents show a spread of 10% or less of the higher reading, record the average of the two readings as the moisture content of the gas. Otherwise, mark the sample for further investigation, and either (1) obtain a third hygrometer which has recently been calibrated, or (2) return one or both of the hygrometers to the manufacturer(s) for re-calibration.

G.2.6 Calculations

In some cases, hygrometers are calibrated to read ppm moisture directly, in which case no calculations are required. Others are supplied by the manufacturer with calibration curves which are used to determine the moisture content.

G.2.7 Safety

This procedure requires the usual safety precautions for handling compressed gases in cylinders.

G.2.8 Discussion

This procedure, excluding sampling time, takes 2 to 4 hours.

This procedure specifies that the manufacturer's calibrations of their instruments will be accepted and that malfunction of an instrument will be detected by noting disagreement between the simultaneous readings of two instruments monitoring the same gas stream.

A more stringent alternative would be the requirement that each laboratory be prepared to calibrate its hygrometers. Published discussions of the difficulties that will be encountered in implementing that approach make it appear unreasonable to require such capability on the part of each analytical laboratory. For example, see A. Wexler, "Calibration of Humidity-Measuring Instruments at the National Bureau of Standards," Instrument Society of America Transactions, 7, 356-362 (1968).

G.3 DETERMINATION OF H_2 , N_2 , CH_4 , CO_2 , CO , TOTAL HYDROCARBONS (AS METHANE), Kr , Xe , AND Ne , IN NITROGEN, HELIUM, OR ARGON

G.3.1 Principle

The specified impurities are determined by standard gas chromatographic techniques employing a helium ionization detector or a flame ionization detector.

G.3.2 Sensitivity and Precision

The practical detection limit is approximately 0.005 ppm for Xe , approximately 0.1 ppm for N_2 , CH_4 , CO_2 , Kr , or CO , and approximately 0.5 ppm for H_2 or Ne .

The reproducibility is $\pm 10\%$ on replicate determinations when the concentration of a specific contaminant is greater than ten times its detection limit.

G.3.3 Apparatus

Gas Chromatographs. The procedures of this section make stringent demands on the sensitivity and versatility of the gas chromatograph. The Varian Aerograph Series 1200 instrument has been found suitable when a flame ionization detector is used.

For the other determinations, the Varian Aerograph Model 1732 instrument, equipped as described below, has been found suitable. The gas chromatograph should be a dual-column, dual-helium-ionization-detector instrument with a 0 to 500-V power supply. The column oven should operate from 25 to 300 C, and have auxiliary provision for operation down to 0 C. The sample introduction system should have the capability of splitting the sample into two approximately equal and precisely reproducible fractions. The preferred recorder is a two-pen strip-chart potentiometric recorder with 1-mV span.

Helium Purifier, to further purify the carrier gas. An Electron Technology, Inc. Model SLM-1 apparatus has been found satisfactory.

Gas Sampling Loop. The loop should have a known volume, approximately 10 ml, and should be detachable. See Fig. G-1.

Xenon Gas Trap. A modified 10 ml gas sampling loop containing 10 to 20 3-mm glass beads held in place at the lower end of the loop by glass wool plugs.

Glass Handling System. An apparatus suitable for preparing known dilutions of gas mixtures. A typical set up is shown in Fig. G-2. This system consists of a rough vacuum pump, a mercury diffusion pump, vacuum and pressure measuring equipment, and a tubular manifold consisting of gas storage vessels and ports.

Regulators. Diffusion-resistant metal-diaphragm regulators which are evacuable without damage and which are purchased with a vendor's helium leak rate certification should be used to avoid contaminating standard gases and gas samples. The Matheson Gas Products Two-Stage Metal-Diaphragm Regulator-Model 3104 has been found satisfactory.

G.3.4 Materials and Reagents

Helium Gas, $\geq 99.995\%$ purity, for carrier gas after further purification.

Helium Gas, $\geq 99.999\%$ purity, for preparation of standard mixtures.

Helium Gas Containing 6% Hydrogen, for carrier gas in measurements using the flame ionization detector.

Fig. G-1 Typical Gas Sampling Loop

Fig. G-2

TYPICAL GAS HANDLING SYSTEM

Hydrogen Gas, $\geq$ 99.95% purity.

Carbon Dioxide Gas, $\geq$ 99.99% purity.

Carbon Monoxide Gas, $\geq$ 99.5% purity.

Methane Gas, $\geq$ 99.5% purity.

Krypton Gas, $\geq$ 99.9% purity. A lecture bottle is a suitable quantity.

Xenon Gas, $\geq$ 99.9% purity. A lecture bottle is a suitable quantity.

Neon Gas, $\geq$ 99.99% purity. A lecture bottle is a suitable quantity.

Methanation Catalyst. A mixed metal oxide catalyst sieved to -60+80 mesh. Katalco 11-2, a product of Katalco Corporation, 180 N. Michigan Avenue, Chicago, Illinois, has been found suitable.

G.3.5 Procedure

Individual or group procedures for the various impurities are given below.

G.3.5.1 Determination of Ne and H_2 in N_2 , He, or Ar

1. Bring the gas chromatograph to stable operation. Typical operating parameters are a He carrier gas flow of 40 ml/min through a 20-ft x 1/8-in.-O.D. Linde Molecular Sieve 5A column maintained at 0 C.
2. Prepare, using the gas handling system, two or more standards of He containing Ne and H_2 at levels bracketing the acceptance limits for these impurities.

3. Using the gas handling system, fill a 10-ml sample loop with each standard at NTP* successively, and elute the standard sample through the chromatograph. Record the chromatograms.

NOTE: The neon response will show a "reversed peak" due to its high ionization potential in comparison with helium. A preferred practice is to operate the recorder zeroed at mid-scale. Switching polarity of recorder response between peaks is not recommended.

4. Prepare calibration curves of peak height vs ppm H_2 and vs ppm Ne.

5. Obtain a sampling vessel containing the gas to be analyzed. Typically, the sample will be contained in a 1-liter stainless steel or glass sampling bulb or in a cryogenic sampler, type TTU-131/E (described in MIL-S-27626).

6. Attach the sampling vessel to the gas handling system and transfer an uncontaminated sample to a 10-ml sample loop at NTP.

*NTP is an abbreviation for "normal temperature and pressure" and means some convenient temperature and pressure (e.g., 25 C and 745 mm Hg absolute) to which all gas samples will be adjusted.

7. Elute the sample through the chromatograph and record the chromatogram.

8. By reference to the calibration curves, determine ppm H_2 and ppm Ne in the sample from the peak heights in the chromatogram.

G.3.5.2 Determination of N_2 in He or Ar

1. Bring the gas chromatograph to stable operation. Typical operating parameters are a He carrier gas flow of 40 ml/min through a 20-ft x 1/8-in.-O.D. Linde Molecular Sieve 5A column maintained at approximately 25 C.

2. Prepare, using the gas handling system, two or more standards of He containing N_2 at levels bracketing the acceptance limit for N_2 .

3. Using the gas handling system, successively fill a 10-ml sample loop with each standard at NTP, and elute the standard sample through the chromatograph. Record the chromatogram.

4. Prepare a calibration curve of peak height vs ppm N_2 .

5. Obtain a sampling vessel containing the gas to be analyzed. Typically, the sample will be contained in a 1-liter stainless steel or glass sampling bulb or in a cryogenic sampler, type TTU-131/E (described in MIL-S-27626).

6. Attach the sampling vessel to the gas handling system and transfer an uncontaminated sample to a 10-ml sample loop at NTP.

7. Elute the sample through the chromatograph and record the chromatogram.

8. By reference to the calibration curve, determine ppm N_2 in the sample from the peak height in the chromatogram.

G.3.5.3 Determination of Hydrocarbon Gases (as Methane) in Nitrogen, Helium, or Argon

1. Establish stable operation of the flame ionization detector with the carrier gas. Typically, the carrier gas flow rate is 20 ml/min.

2. Prepare, using the gas handling system, two or more standards of helium containing methane at levels bracketing the acceptance limit.

3. Using the gas handling system, successively fill a 10-ml sample loop with each standard and elute the standard gas through the flame ionization detector and record the change in voltage.

4. Prepare a calibration curve of voltage change vs ppm CH_4 .

5. Obtain a sampling vessel containing the gas to be analyzed. Typically the sample will be contained in a 1-liter stainless steel

or glass sampling bulb or in a cryogenic sampler, type TTU-131/E (described in MIL-S-27626).

6. Attach the sampling vessel to the gas handling system and transfer an uncontaminated sample to a 10-ml sample loop at NTP.

7. Elute the sample through the flame ionization detector and record the change in voltage.

8. By reference to the calibration curve, determine ppm hydrocarbon gases (as CH₄) in the sample.

G.3.5.4 Determination of CO, CH₄, and CO₂ in N₂, He, or Ar.

1. Bring the gas chromatograph to stable operation. Typical operating parameters are a He-6% H₂ carrier gas flow of 20 ml/min through an 8-ft. x 1/8-in.-O.D. Porapak Q column maintained at 0 C, then through a 4-in. x 1/4-in.-O.D. column packed with -20+40 mesh mixed metal oxide catalyst (Katalco 11-2, or equivalent) at 400 C, and finally through the flame ionization detector.

2. Prepare, using the gas handling system, two or more standards of He containing each impurity to be determined at levels bracketing their acceptance limits.

3. Using the gas handling system, successively fill a 10-ml sample loop with each standard and elute the standard sample through the chromatograph. Record the chromatograms. The elution order is CO, CH₄, and CO₂.

4. Prepare calibration curves of peak height vs ppm of each impurity.

5. Obtain a sampling vessel containing the gas to be analyzed. Typically the sample will be contained in a 1-liter stainless steel or glass sampling bulb or in a cryogenic sampler, type TTU-131/E (described in MIL-S-27626).

6. Attach the sampling vessel to the gas handling system and transfer an uncontaminated sample to a 10-ml sample loop at NTP.

7. Elute the sample through the chromatograph and record the chromatogram.

8. By reference to the calibration curves, determine ppm CO, ppm CH₄, and ppm CO₂ in the sample from the peak heights in the chromatogram.

G.3.5.4 Determination of Kr in He or Ar

1. Bring the gas chromatograph to stable operation. Typical operating parameters are a He carrier gas flow of 40 ml/min through a 20-ft-long x 1/8-in.-O.D. Linde Molecular Sieve 5A column maintained at 15 C.

2. Prepare, using the gas handling system, two or more standards of He containing Kr at levels bracketing the acceptance limit for Kr.

3. Using the gas handling system, successively fill a 10-ml sample loop with each standard at NTP and elute the standard sample through the chromatograph. Record the chromatogram.

4. Prepare a calibration curve of peak height *vs* ppm Kr.

5. Obtain a sampling vessel containing the gas to be analyzed. Typically, the sample will be contained in a 1-liter stainless steel or glass sampling bulb or in a cryogenic sampler, type TTU-131/E (described in MIL-S-27626).

6. Attach the sampling vessel to the gas handling system and transfer an uncontaminated sample to a 10-ml sample loop at NTP.

7. Elute the sample through the chromatograph and record the chromatogram.

8. By reference to the calibration curve, determine ppm Kr in the sample from the peak height in the chromatogram.

G.3.5.5 Determination of Xe in He or Ar

1. Bring the gas chromatograph to stable operation. Typical operating parameters are a He carrier gas flow of 40 ml/min through a 3-ft-long x 1/8-in.-O.D. column packed with -40+50 mesh Linde Molecular Sieve 5A maintained at 0C. The helium ionization detector is operated at 400 volts and its temperature is maintained at 50C. The electrometer range is set at 10^{-9} amp, full scale. The attenuator is set on the X2 scale.

2. Prepare, using the gas handling system, two or more standards of He containing Xe at levels bracketing 0.1 ppm Xe.

3. Attach the Xe gas trap to the gas handling system, evacuate the trap, the manifold, and a spare 1 liter gas storage vessel to 10^{-3} torr. Isolate the trap and storage vessel from the manifold and valve off the vacuum pump.

4. Pressurize the manifold to approximately 800 torr with a standard gas mixture. Isolate the manifold and record the pressure.

5. Open the Xe gas trap stopcock for one second, then close it.

6. Chill the trap in liquid nitrogen for 15 to 20 minutes. Pump the manifold down to 10^{-3} torr, valve off the vacuum pump, and open the stopcock to the spare storage vessel.

7. Open and close the Xe gas trap stopcock. Remove the liquid nitrogen and allow the trap to warm to room temperature.

-
8. Remove the trap from the manifold, connect it to the chromatograph, and heat the trap for 2 min with a heat gun.
  9. Elute the sample through the chromatograph. Record the chromatogram.
  10. Repeat steps 3 through 9 for each standard gas mixture.
  11. Prepare a calibration curve of peak height *vs* ppm Xe.
  12. Obtain a sampling vessel containing the gas to be analyzed. Typically, the sample will be contained in a 1-liter stainless steel or glass sampling bulb or in a cryogenic sampler, type TTU-131/E (described in MIL-S-27626).
  13. Attach the sampling vessel to the gas handling system.
  14. Attach a Xe gas trap to the gas handling system. Use the trap from step 3.
  15. Evacuate the trap and manifold to 10^{-3} torr. Valve off the vacuum pump, and isolate the trap from the manifold.
  16. Fill the manifold with sample gas to the same pressure used for the standard gas mixtures. Isolate the manifold.
  17. Open the Xe gas trap stopcock for one second, then close it.
  18. Chill the trap in liquid nitrogen for 15 to 20 min.
  19. Pump the manifold and a spare 1 liter-gas storage vessel down to 10^{-3} torr and valve off the vacuum pump.
  20. Open and close the Xe gas trap stopcock.
  21. Remove the liquid nitrogen bath and allow the trap to warm to room temperature. Close the stopcock to the 1 liter-gas storage vessel.
  22. Pump the manifold down to 10^{-3} torr and valve it off.
  23. Repeat steps 16 through 22 three more times and then repeat steps 16 through 21.
  24. Remove the Xe gas trap from the manifold. At this point the trap contains essentially all of the Xe from five 10-ml portions of sample gas, and about 12 torr pressure of the base gas of the sample gas.
  25. Attach the trap to the inlet system of the chromatograph and warm the trap with a heat gun for 2 to 3 min.

26. Elute the sample and record the chromatogram.

27. From the height of the Xe peak in the chromatogram, determine a corresponding Xe concentration from the calibration curve. Report the concentration of Xe in the cover gas as one-fifth of the value indicated from the calibration curve.

G.3.6 Calculations

No special calculations are required.

G.3.7 Safety

These procedures require the usual safety precautions for handling compressed gases in cylinders, for handling evacuated and pressurized glass vessels, and for handling cryogenic liquids.

G.3.8 Discussion

The estimated time to perform all of the analyses in Section G.3 is 2 to 3 days.

Because of the relatively high sensitivities required, it is not recommended that any other type of detector be substituted when the helium ionization detector is specified.

Appendix H

H. DETERMINATION OF CARBON IN PURCHASED SODIUM
BY THE TOTAL CONSUMPTION OXYACIDIC FLUX METHOD

H.1 PRINCIPLE

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 flashed into a gas chromatograph for measurement.

H.2 SENSITIVITY AND PRECISION

This method is suitable for the determination of 5 to 10,000 μg carbon in sodium, 0.5 to 1000 ppm of carbon in a 10-g sample of sodium. The range can be adjusted by recalibration of the chromatograph.

For carbon concentrations in the range 0.5 to 10 ppm, replicate determinations from the same bypass sample are expected to agree within 0.5 ppm at the 95% confidence level. This estimate of precision is based on recent EBR-II experience.

H.3 APPARATUS

Analytical System. The analytical system consists of the following equipment whose relationships are shown in the block diagram of Fig. H-1:

Gas Supply and Purification Tube. The tube (Fig. H-2) consists of a quartz tube containing CuO (which is heated to $750 \pm 10^\circ\text{C}$ by a tube furnace), Ascarite, and BaO , and through which helium and oxygen are passed. The gas supply pressure is approximately 3 psig. The gases are supplied from gas cylinders equipped with valve-controlled flow meters.

Inert-Atmosphere Glovebox. The box must have a purification system capable of controlling the impurity level of the box atmosphere. For this analysis, the carbon monoxide, carbon dioxide, and hydrocarbon gases (calculated as methane) of the atmosphere must each be <1 ppm, and oxygen and moisture <20 ppm (see Appendix A). All sampling and transfer operations must be performed in this box. The box should also be equipped with (1) a balance (± 0.05 g); (2) 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); (3) a powder horn; (4) holders for reaction bottles, shield tubes, and tools; and (5) wrenches for opening the sampler.

Combustion Tube. The combustion tube shown in Fig. H-3 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. A 45° 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 overtightening or undertightening and extends the life of the lead gasket to several months of use. Organic sealing gaskets, greases, or cements must not be used in

Fig. H-1

Block Diagram of a Typical Analytical System

Fig. H-2 Typical Gas Purification Tube

Fig. H-3 Typical Combustion Tube

or between the purification and combustion tubes, though they may be used elsewhere.

The gas line enters the combustion tube through the entrance-port flange.

During use, the metal port is located inside the glove box, the quartz section penetrates the box wall and is heated by two tube furnaces outside the box. The combustion tube is packed with copper oxide. The copper oxide section of the tube is heated to 600 ± 10 C and the reaction zone is heated to 950 ± 10 C.

A heat shield, Fig. H-4, is placed in the graded-seal section to prevent radiation and convective heating from damaging the port-cover lead gasket. If the shield is not used, the temperature of the metal port becomes too high to allow handling, and the lead gasket could melt.

Carbon Dioxide Trap. This trap is 3/16-in.-OD stainless steel U-shaped tube 5-in. high containing 40 to 60 mesh Molecular Sieve 5A. Provision to heat the trap rapidly to approximately 300 C to desorb the CO_2 is included. The SKC, Inc. Model 215 Component Concentrator has been found suitable for this application. A 3/16-in.-OD thin wall trap must be substituted for the one supplied with the instrument. The trap is heated by direct application of a low-voltage, high-current electrical source.

Carbon Dioxide Measurement System. This system consists of the carbon dioxide trap, listed above, and a gas chromatograph, as shown in Fig. H-5. The gas chromatograph should be suitable for the detection of 0.1 μg of carbon as CO_2 . A Beckman Series E Analyzer equipped with a recorder having a 1-mV span was found suitable for this application by the originator of the method. This chromatograph contains a 6-ft x 1/4-in.-OD column packed with Porapak Q maintained at 60 C and a standard two-filament thermal conductivity detector, which is operated with helium carrier gas at 100 cc/min.

Train Gas Composition and Volume Measurement System. This system (Fig. H-5) consists of an oxygen sensor enclosed in a glass adaptor, followed by a wet-test meter. A Beckman Model 778 polarographic oxygen analyzer was found suitable for this application by the originator of the method.

H.4 MATERIALS AND REAGENTS

Helium Gas.

Oxygen Gas. High purity.

Barium Oxide. 10 to 20 mesh

Ascarite. 8 to 20 mesh

Quartz Wool. Preignited in oxygen at 1000 C for 2 hr.

Quartz Fiber. Cut to 1- to 2-cm lengths. Ignited as above

Fig. H-4 TYPICAL HEAT-SHIELD

Fig. H-5 TYPICAL CO₂ MEASUREMENT SYSTEM

Fig. H-6

TYPICAL TRAIN-GAS COMPOSITION & VOLUME MEASUREMENT

Copper. Light turnings, reagent grade.

Potassium Dichromate. Reagent grade. Reagent grade $K_2Cr_2O_7$ contains from 5 to 10 ppm of carbon. This is readily removed by ignition for one hour at 700 C.

Molecular Sieve 5A. 40 to 60 mesh.

H.5 PREPARATION OF APPARATUS

1. Clean the quartz purification tube (Fig. H-2) with detergents, rinse, and then etch inside for 5 min at room temperature with reagent grade 48% HF. Care must be taken to prevent etching of the ground-joint and graded-seal at the outlet end. Rinse the tube with distilled water to remove HF and then with reagent grade acetone. After evaporation of the acetone, heat the quartz portion of the tube to red heat by means of an oxyhydrogen (not oxygen-hydrocarbon) flame.

2. Place a piece of quartz wool (preignited in oxygen at 1000 C for 2 hr) inside the purification tube at the outlet end. Then, pack the tube with barium oxide to a length of 20 cm, lightly tapping to pack; add Ascarite (8 to 20 mesh) to give a bed length of 25 cm and 1.5-cm barrier of preignited quartz wool.

3. Next, pack pure copper turnings into the tube to give a bed length of 33 cm. Place the section containing copper into a tube furnace and heat to 600 ± 10 C. Pass a 50% oxygen-helium mixture through the tube at 80 to 100 ml/min for 16 to 24 hr. After the CuO bed appears entirely black, stop the helium flow and pass pure oxygen over the CuO for an additional 8 hr.

4. Connect the outlet of the purification tube (1/8-in Kovar tubing) to a flexible 1/8-in.-OD copper tube by a 1/8-in. Swagelok coupling.

5. Prepare the quartz combustion tube (Fig. H-3) in a manner similar to the purification tube, by a 5-min etch with 48% HF (care must be taken to prevent HF contact with the graded seal), a distilled water rinse, an acetone rinse, and finally by heating the quartz portion only to red heat with an oxy-hydrogen flame.

6. After cleaning, pack the small diameter section of the combustion tube with pure copper turnings. Convert the copper to copper oxide as described for the purification tube in step H.5.3.

7. Etch the shield-boat and reaction bottles shown in Fig. H-7 by immersion in 48% HF for 5 min at room temperature, rinse with distilled water, and then with reagent grade acetone.

8. Etch the heat shield (Fig. H-4) in the same way before platinizing. To platinize the shield, mount it in a glass lathe or some device to allow rotation at 10 to 20 rpm. Prepare a solution of 10 g of platinic chloride in 50 ml of 2N HCl. Using a Beckman aspirator burner (for flame spectrophotometry) and hydrogen-oxygen gases, aspirate the platinic chloride into the burner while playing the flame on the quartz discs of the shield as it is rotated. Coat both front and back surfaces with platinum until they are opaque. Flame the shield to bright red heat with an oxy-hydrogen burner. Cool and place in the heated zone of the combustion tube. In the graded-seal-zone place three or four wads of aluminum foil to act as a temporary heat shield.

Fig. H-7

TYPICAL REACTION BOTTLE & SHIELD-BOAT

Ignite the quartz heat shield at 950 to 1000 C for 2 to 4 hours in oxygen. Remove the aluminum-foil wads.

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

H.6 CALIBRATION OF CHROMATOGRAPH

1. Fill a glass calibration vessel with standard gas (0.25% CO₂ in He) at known temperature and pressure and insert it into the train between the combustion tube exit and the manual flow-switching valve.

Alternatively, inject known amounts of carbon dioxide into the combustion train through a septum in a tee before the combustion tube.

2. Trap the standards from a stream of helium flowing at 100 ml/min.

3. After trapping, heat the CO₂ trap and obtain the CO₂ chromatogram.

4. Repeat the procedure, with adjustments on the chromatograph attenuator, until the desired calibration is achieved. Prepare a graph of peak height or area vs μg of C.

H.7 PROCEDURE

H.7.1 Preparation of Reaction Bottle

1. Flush the entire system including purification train, combustion train, and train-gas composition and measurement line with helium flowing at 100 ml/min.

2. Adjust the controllers for the copper oxide furnaces. Purification furnace 750 ± 10 C. Combustion tube 600 ± 10 C.

3. When the oxygen analyzer indicates <1% O₂, open the combustion-tube port. To avoid oxygen contamination of the glove box atmosphere, the combustion-tube port should never be opened if the train-gas composition is above 1% O₂.

4. Place a clean shield-boat and reaction bottle (Fig. H-7) in the reaction zone using a clean forceps. Then place the heat shield in the graded seal section. (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 by use of point contacts only).

5. Close the combustion-tube port, and set the reaction-zone furnace controller so that a temperature of 950 ± 10 C is attained.

6. Replace the helium with oxygen flowing at 100 ml/min.

7. After ignition for 1 hr at 950 ± 10 C, replace the oxygen with helium flowing at 100 ml/min and then turn off the reaction-zone furnace. Open the furnace to cool down. To save time, the furnace can be cooled with a fan.

8. Make up a mixture of preignited quartz fiber and $K_2Cr_2O_7$ (0.5% fiber by weight) and store in a glass bottle or powder horn.

9. When the furnace has cooled to $<150\text{ C}$ and the oxygen analyzer indicates $<1\% O_2$, pull the heat shield, reaction bottle, and shield-boat out into the metal port. (The reaction bottle is always handled with a clean steel rod which has been bent to fit the loop on the end of the bottle).

10. Grip the bottle around its center with a pair of fitted tongs and, holding its mouth up, pour $130 \pm 10\text{ g}$ of the $K_2Cr_2O_7$ plus quartz fiber mixture into the bottle. (This amount is easily estimated by volume if the approximate volume has been predetermined by dummy runs outside the glove box).

11. Replace the bottle with the flux in the reaction zone. Replace the heat shield in the graded-seal section. Close the port. Heat the reaction zone in oxygen for $1-1/2\text{ hr}$ at $790 \pm 10\text{ C}$. The bottle should lie with the rear indentation on the bottom.

12. After $1-1/2\text{ hr}$ replace the O_2 flow by helium and cool the reaction zone to 150 C . (The flux must be cooled down below 500 C to stop liberation of oxygen. Otherwise, the train-gas composition will remain above $1\% O_2$ at a helium flow of 100 ml/min for an unacceptable period of time).

13. Open the port and pull the reaction bottle and shield-boat into the metal port so that the bottle can be lifted up.

Proceed with Section H.7.2 when running a blank, or with Section H.7.3 when running a sample.

H.7.2 Operational Blank

An operational blank is to be obtained with each batch of samples, and also when (a) changes are made in the system or reagents or, (b) discrepant results are observed.

The operational blanks consists of (a) performing the steps of Section H.7.1 (Preparation of Reaction Bottle), (b) carrying out dummy manipulations comparable to those of Section H.7.3, and (c) continuing the steps of Section H.7.4 (Combustion). Thus, this blank contains all the steps and manipulations involved in running a sample, except for the actual addition of sodium.

H.7.3 Sample Handling

1. Obtain a group of 10-g overflow samples in quartz cups by the method of Section 3.2. Open the sample vessel in the glove box, using the appropriate tools.

2. Using the special clean tongs, remove one quartz cup containing sodium and place it on the V-shaped sample holder on the balance pan. Obtain the weight of sodium. (The quartz sample cups have been

preignited and weighed before insertion in the sample vessel).

3. Grasp the reaction bottle with the special fitted tongs and hold with the mouth up and the bottle slanted. Insert the sample cup mouth-down and gently work it to the back of the reaction bottle.

4. Replace the reaction bottle in the shield-boat and turn it so that the flux is above the 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). Gently shove the bottle into the heated zone so that the funnel-mouth of the shield-boat is firmly against the quartz wool at the entrance of the CuO bed. Also, make sure the reaction-bottle-mouth is firmly up against the funnel-outlet of the shield boat. Replace the heat shield in the graded seal section. Close the port.

H.7.4 Combustion

1. Switch the train-gas to the CO₂ trap.

2. Replace helium by O₂ at 100 ml/min. After the O₂ flow is started, obtain the initial wet-test meter reading.

3. As soon as the train gas is 95% O₂, heat the reaction zone to 400 C. At some point during heat-up, the sodium will ignite and burn to Na₂O. If the train-gas is less than 95% O₂, combustion will be delayed or erratic, and be accompanied by ejection of sodium oxide smoke, molten flux, and bits of burning sodium. If this occurs, reject the sample and start over.

4. If the sodium burns without significant ejection of materials from the reaction bottle, close the reaction-zone furnace and heat to 950 ± 10 C.

5. Maintain the furnace at 950 ± 10 C until 20 liters of O₂ have passed through the train, then cool the reaction-zone furnace. Replace the O₂ by helium and take a wet-test meter reading.

6. When the O₂ concentration has dropped to <1%, switch the CO₂ trap to the chromatograph.

7. As soon as the chromatograph has stabilized with the trap in the flow path, heat the trap to introduce the CO₂ into the chromatograph and obtain a chromatogram. Then switch the CO₂ trap back to the combustion-train flow path. Remove the heat shield and reaction bottle.

H.8 CALCULATIONS

From the calibration graph prepared in part H.6, calculate the concentration of carbon in sodium by the following formula:

$$\text{Carbon, ppm} = \frac{A - B}{W}$$

where,

A = weight of carbon in the sample, μg

B = weight of carbon in the blank, μg

W = weight of the sodium sample, g

H.9 SAFETY

Sodium. Normal precautions for handling sodium should be observed.

H.10 DISCUSSION

This procedure, exclusive of sampling, requires approximately 8 hr.

Appendix I
DETERMINATION OF PURITY OF PURCHASED SODIUM BY TITRATION

I.1 PRINCIPLE

Sodium hydroxide is produced by the hydrolysis of sodium metal; and sodium is determined by weight titration with a slight excess of hydrochloric acid, followed by a back-titration of the excess acid with sodium hydroxide.

I.2 SENSITIVITY AND PRECISION

Duplicate samples analyzed by this procedure should agree within 0.01%. The accuracy is primarily limited by the accuracy of the hydrochloric acid standardization and the technique of the analyst, but a total error of less than 0.02% is reasonable.

I.3 APPARATUS

Inert-Atmosphere Glovebox. Maintained at less than 2 ppm of oxygen and moisture. (See Appendix A).

Two Single-Pan Analytical Balances. With weight combinations within Class S tolerances. The weights should have a density of 7.8 g/cc (stainless Steel). All weighings should be to the nearest 0.1 mg.

Dissolution Vessel. This is made from a 500-ml cylindrical conventional polyethylene narrow-mouth bottle. Cut off the top of the bottle cleanly about 2 cm below the shoulder. Invert the cut-off top to serve as a funnel which will allow addition of methanol or water and escape of hydrogen.

Acid Weight Buret. A 125-ml polyethylene wash bottle is used.

10-ml Buret. With a reservoir protected from atmospheric carbon dioxide.

Glass Wool. Prepared by washing with acetone, soaking 1 to 2 minutes in 0.001 M hydrochloric acid, rinsing with water and drying at 120 to 150C.

Magnetic Stirrer, with stirring bars.

pH Meter.

Mason Jar (Optional). A screw-capped pint-size jar.

Safety Shield. For use during dissolution of sodium.

I.4 MATERIALS AND REAGENTS

Water. Boil double-deionized water for five minutes; transfer it to covered storage bottles while still hot. Prepare fresh for each use.

Sodium Hydroxide. Dilute 8 ml of saturated sodium hydroxide to 4 liters with the above water. Standardize against high-purity sulfamic acid. Store in a polyethylene bottle protected from carbon dioxide.

Ethyl Red Indicator Solution. Dissolve 0.1 g of ethyl red indicator (formula weight 454.36) in 100 ml of ethanol. 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.

Tris. Dry NBS Standard Reference Material 723 (99.969%), tris-(hydroxymethyl)-aminomethane, under vacuum for 24 hours at 70 C then store it in a desiccator over magnesium perchlorate.

Sulfamic Acid. Reagent grade. Dry at 110 to 120 C before use.

Hydrochloric Acid. Dilute 1150 ml of concentrated reagent grade hydrochloric acid to 4 liters with the above water.

Standardize the acid as follows: Fill the weight buret with hydrochloric acid and weigh it. Weigh a 250-ml beaker then add 10 to 11 g of tris. Reweigh the beaker and tris. Add 150 ml of water, a stirring bar and a drop of ethyl red indicator solution to the beaker. 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. Wash down the beaker walls with water. Reweigh the acid weight buret. Insert the pH electrodes into the beaker and back-titrate with standard sodium hydroxide to a pH of 4.2. Practice with commercial tris before using the expensive NBS standard material.

Store the standardized acid in well-capped bottles. Reconfirm the titer of the acid monthly.

Methanol. Neutral, reagent grade, acetone free.

I.5 PROCEDURE

I.5.1 Sample Preparation

Separate treatments are given below for the preparation of a bypass sample and an overflow sample.

I.5.1.1 Bypass sample

1. Obtain a sodium sample in a stainless steel bypass tube by the procedure described in Section 3.1.
2. Rinse the exterior of the tube with deionized water and methanol.
3. Dry the tube and transfer it into an inert-atmosphere box.
4. Cut off at least a one-inch section from the end of the tube with a tubing cutter. Discard the end section.
5. Cut off and weigh a section containing 5 to 6 g of sodium.
6. Proceed to step 1 of Section I.5.2 (Analysis) below.

I.5.1.2 Overflow-cup sample

1. Obtain a sodium sample weighing 5 to 6 g in a tantalum or glass overflow cup.
2. Open the overflow sampling device in the inert-atmosphere box and remove the cup.
3. Weigh the cup plus sample and record the weight.
4. Proceed to step 1 of Section I.5.2 (Analysis) below.

I.5.2 Analysis

1. Place a loose plug of glass wool in the neck-opening of the top of the dissolution vessel.
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 cold ethanol or Butyl Cellosolve, if necessary, to keep the reaction under control and to minimize spray.
3. After all the sodium is in solution, rinse any spray trapped by the glass wool and on the underside of the vessel top back into the dissolution vessel. Use a total of 100 to 150 ml of water for the rinses and the transfer in steps 3, 4, and 5. Discard the glass wool.
4. Remove the sample container from the vessel, using appropriate rinses to retain all of the sample in the dissolution vessel.
5. Quantitatively transfer the sample solution to a 400-ml beaker.
6. Fill the acid weight buret with the standardized hydrochloric acid and weigh it.
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 over-running the endpoint.
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.

A pH meter may be employed for the titration and the back-titration although the use of an indicator is satisfactory, particularly if a comparison solution is used.

9. Dry the sample tube or cup and weigh it in the inert-atmosphere box.

I.6 CALCULATIONS

I.6.1 Standardization of acid

The grams (in air) of hydrochloric acid equivalent to one gram (in vacuum) of sodium can be found from the following equation:

$$\text{Grams hydrochloric acid/gram sodium} = \frac{\frac{A}{B}}{\frac{(C)(D)(E)}{F} + \frac{(G)(H)}{1000}}$$

where

A = weight of hydrochloric acid, g

B = equivalent weight of sodium

C = weight of tris, g

D = purity of tris

E = buoyancy correction factor for tris in air, (1.007)

F = equivalent weight of tris

G = volume of sodium hydroxide, ml

H = normality of sodium hydroxide

I.6.2 Uncorrected percent sodium

Calculate the purity as percent of sodium in the sample uncorrected for potassium, using the following equation:

$$\text{Purity, calculated as percent sodium uncorrected for potassium} = \frac{\frac{A}{I} - \frac{(C)(H)(B)}{1000}}{(J)(E)(0.01)}$$

where

A = weight of hydrochloric acid, g

B = equivalent weight of sodium

E = buoyancy correction factor for sodium, (1.0015 if weighed in argon; 1.0016 if weighed in helium. See Discussion, I.8)

G = volume of sodium hydroxide, ml

H = normality of sodium hydroxide

I = concentration of hydrochloric acid, grams of hydrochloric acid/gram of sodium

J = uncorrected weight of sodium, g

Although a buoyancy correction is required in the calculation of sodium mass, no correction is needed for the stainless steel tubing because the density of the tubing 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 provide the information for calculating the buoyancy correction.

I.6.3 Corrected percent sodium

To correct for the higher equivalent weight of potassium:

Purity, calculated as percent sodium plus potassium = $[(K) (4 \times 10^{-5})] + L$

where

K = amount of potassium known to be in the sodium, ppm

L = percent sodium uncorrected for potassium

I.6.4 Buoyancy corrections

Reduction of weights to vacuum is accomplished according to the equation:

$$W_o = W_a [1 + 1 \times 10^{-5} + d_A (\frac{1}{d_s} - \frac{1}{d_w})]$$

where

W_o = weight of the sample in vacuum

W_a = apparent weight of the sample in an atmosphere

d_A = density of the atmosphere, g/cc

d_s = density of the sample, g/cc

d_w = density of the weights, g/cc

The constant, 1×10^{-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/cc.

For sodium weighed in argon, the buoyancy correction factor is 1.0015, based on:

density of argon = $(1.38)(0.0012) = 0.01656$ g/cc

density of sodium = 0.9684 g/cc

density of stainless weights = 7.8 g/cc

For sodium weighed in helium, the buoyancy correction factor is 1.00016 based on:

density of helium = 0.0001635 g/cc

density of sodium = 0.9684 g/cc

density of stainless weights = 7.8 g/cc

For tris weighed in air, the buoyancy correction factor is 1.007, based on:

density of air = 0.0012 g/cc

density of tris = 1.35 g/cc

density of stainless weights = 7.8 g/cc

I.7 SAFETY

The dissolution of sodium presents the slight possibility of a hydrogen explosion. This operation must be carried on behind a safety shield, and preferably in a metal hood.

I.8 DISCUSSION

This procedure, exclusive of sampling, takes 4 to 8 hr.

Tris 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.

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 ml of argon, for example, will increase the apparent sample weight by approximately 0.4 mg.

If an analytical balance with a capacity of at least 500 g is available in the laboratory, no weighings need be made in the inert-atmosphere box. Instead, transfer the sodium-filled cup or tube to a pint Mason 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 it. The apparent loss in weight of the jar is taken as the uncorrected weight of the sodium sample. For weighings made in this way, the buoyancy correction factor for sodium is 1.0016 if an argon-filled box is used; or it is 1.00002 if a helium-filled box is used. In calculating these factors, it was assumed that the balance weights were stainless steel of density 7.8 g/cc.

Appendix J

J. DETERMINATION OF PURITY AND POTASSIUM CONTENT OF PURCHASED SODIUM

Two of the determinations required for the acceptance of purchased sodium may be carried out on one overflow-cup sample by the procedures given below.

J.1 PRINCIPLE

A 50-g overflow-cup sample of sodium is dissolved in methanol and the solution is quantitatively transferred to a weight buret. To meet the precision required for the purity determination, weighed aliquants of the solution are taken for the determination of purity by weight titration and potassium by flame emission spectrophotometry.

J.2 SENSITIVITY AND PRECISION

Duplicate samples analyzed for purity by this procedure should agree within 0.01%. The accuracy is primarily limited by the accuracy of the hydrochloric acid standardization and the technique of the analyst, but a total error of less than 0.02% is reasonable.

The potassium method is suitable for the determination of 100 to 1000 μg of potassium (100 to 1000 ppm of potassium in a 1-g sample of sodium). The range can be extended downward by optimizing instrument parameters, using additional standards, and increasing the sample size. A detection limit of 4 to 10 μg of potassium can readily be attained. At the 100 ppm level, replicate samples are expected to agree within $\pm 5\%$.

J.3 APPARATUS

J.3.1 General Apparatus

Inert-Atmosphere Glovebox. Maintained at less than 2 ppm of oxygen and moisture. (See Appendix A.)

Two Single-Pan Analytical Balances. With weight combinations within Class S tolerances. The weights should have a density of 7.8 g/cc (stainless steel). All weighings should be to the nearest 0.1 mg. A 200-g capacity balance is placed in the inert-atmosphere box and a 1000-g capacity balance is used in the laboratory. By following the procedure for weighing sodium samples that is suggested in Section I.8, the balance in the inert-atmosphere box may be dispensed with.

Dissolution Vessel. This is made from a 1-liter cylindrical conventional polyethylene narrow-mouth bottle. Cut off the top of the bottle cleanly about 2 cm below the shoulder. Invert the cut-off top to serve as a funnel which will allow addition of methanol or water and escape of hydrogen.

Safety Shield. For use during dissolution of sodium.

Sample Weight Buret. A 1000-ml polyethylene wash bottle is used.

Glass Wool. Prepared by washing with acetone, soaking 1 to 2 minutes in 0.01 M hydrochloric acid, rinsing with water and drying at 120 to 150 C.

Magnetic Stirrer, with stirring bars.

Mason Jar (Optional). A screw-capped pint-size jar.

J.3.2 Purity Determination: Additional Apparatus

Acid Weight Buret. A 125-ml polyethylene was bottle is used.

10-ml Buret. With a reservoir protected from atmosphere carbon dioxide.

pH meter .

J.3.3 Potassium Determination: Additional Apparatus

Flame Spectrophotometer. This instrument should be a scanning spectrophotometer suitable for the determination of potassium at the 766.5 nm emission line. Typical specifications, except for the scanning feature, may be found in ASTM Method D 1428-64. A scanning instrument is preferred because automatic peak scanning offers the advantage of obtaining background correction with greater ease and precision than manual scanning procedures. The Perkin-Elmer Model 403 instrument has been found suitable.

Polypropylene Graduated Cylinders. 100-ml graduated cylinders are used as volumetric ware for samples and working standards.

J.4 MATERIALS AND REAGENTS

J.4.1 General Materials

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

Methanol. Redistill methanol from a quartz or borosilicate glass still and store it in polyethylene bottles.

Butyl Cellosolve. Purified ethylene glycol monobutyl ether. Ethanol or methanol may be substituted.

J.4.2 Purity Determination: Additional Materials and Reagents

Water. Boil double-deionized water for five minutes; transfer it to covered storage bottles while still hot. Prepare fresh for each use.

Sodium Hydroxide. Dilute 8 ml of saturated sodium hydroxide to 4 liters with the above water. Standardize against high-purity sulfamic acid. Store in a polyethylene bottle protected from carbon dioxide.

Ethyl Red Indicator Solution. Dissolve 0.1 g of ethyl red indicator (formula weight 454.36) in 100 ml of ethanol. 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.

Tris. Dry NBS Standard Reference Material 723 (99.969%), tris-(hydroxymethyl)-aminomethane, under vacuum for 24 hours at 70 C, then store it in a desiccator over magnesium perchlorate.

Sulfamic Acid. Reagent grade. Dry at 110 at 120 C before use.

Hydrochloric Acid. Dilute 1150 ml of concentrated reagent grade hydrochloric acid to 4 liters with the above water.

Standardize the acid as follows: Fill the weight buret with hydrochloric acid and weigh it. Weigh a 250-ml beaker, then add 10 to 11 g of tris. Reweigh the beaker and tris. Add 150 ml of water, a stirring bar and a drop of ethyl red indicator solution to the beaker. 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. Wash down the beaker walls with water. Reweigh the acid weight buret. Insert the pH electrodes into the beaker and back-titrate with standard sodium hydroxide to a pH of 4.2. Practice with commercial tris before using the expensive NBS standard material.

Store the standardized acid in well-capped bottles. Reconfirm the titer of the acid monthly.

J.4.3 Potassium Determination: Additional Materials and Reagents

Nitric Acid. Redistill nitric acid from a quartz still and store it in Teflon bottles after dilution to approximately 5M.

Bromocresol Green Indicator. Dissolve 0.04 g of bromocresol green in 100 ml of ethanol.

Potassium Standard Solution. Dissolve 0.24 g of KNO_3 , dried at 110 C in 100 ml of water to make a 1 mg/ml standard.

Sodium Carbonate. Select reagent grade anhydrous sodium carbonate for low potassium content.

J.5 PROCEDURE

J.5.1 Sample Preparation

1. Obtain a protected sodium sample weighing approximately 50 g in a tantalum overflow cup according to the procedure in Section 3.2.
2. Open the overflow-sampler transfer vessel in the inert-atmosphere box and remove the cup.
3. Weigh the cup plus sample in the inert-atmosphere box and record the weight.

4. Place a loose plug of glass wool in the neck-opening of the top of the dissolution vessel.

5. Take the sample from the inert-atmosphere box and slide it into 500 ml of cold methanol in the bottom of the dissolution vessel. Place the top of the vessel, with the neck down, and press the top into place. Cool the vessel in cold ethanol or Butyl Cellosolve, if necessary, to keep the reaction under control and to minimize spray. If necessary, add more methanol to complete dissolution of the sample.

6. After all the sodium is in solution, rinse into the vessel any spray trapped by the glass wool and on the vessel top with 100 to 150 ml of water. Discard the glass wool. The glass wool plug typically traps the equivalent of 0.1 to 0.2 mg of sodium, but occasionally traps much more.

7. Transfer the solution quantitatively to a weighed 1000-ml plastic wash bottle used as the sample weight buret.

8. Retrieve the overflow cup, rinse it, and add the rinsings to the wash bottle.

9. Dry the cup and weigh it in the inert-atmosphere box. Calculate the uncorrected weight of the sample by subtracting this weight from the weight obtained in step 3.

10. Swirl the solution in the sample weight buret to mix it, and allow the solution to cool to room temperature.

J.5.2 Purity Determination

NOTE: Perform steps 1 through 4 within the least possible elapsed time, preferably within 15 min. Otherwise, reweigh the sample weight buret before delivering any solution from it, and calculate the fraction of sample delivered accordingly.

1. Weigh the sample weight buret. Calculate the weight of the sodium sample solution by subtracting the weight of the empty sample weight buret.

2. Transfer a volume of sample equivalent to 5 to 6 grams of sodium to a 250-ml beaker.

3. Reweigh the sample weight buret.

4. Repeat steps 2 and 3 to dispense two more aliquants for the purity determination.

5. Calculate the grams of sodium in each aliquant of solution according to the formula:

$$\text{Aliquant weight} = \frac{W_1 - W_2}{W_S} \times W$$

where,

W_1 = weight of buret before dispensing aliquant, g

W_2 = weight of buret after dispensing aliquant, g

W_S = weight of solution containing the entire sample, g

W = uncorrected weight of the entire sample, g
(determined in step 9)

6. Proceed to step I.5.2.6. Omit step I.5.2.9, but carry out the rest of the procedure with each of the three aliquants of sodium solution. Use the aliquant weights from step 5 as the uncorrected weights of sodium samples.

7. Report the average of the three determinations of purity.

J.5.3 Potassium Determination

1. Transfer a volume of sample solution containing approximately 1 g of sodium to a 100-ml polypropylene mixing graduate.

2. Reweigh the sample weight buret.

3. Repeat steps 1 and 2 to dispense a second aliquant of solution.

4. Calculate the grams of sodium in each aliquant of solution as specified in step J.5.2.5.

5. Proceed to Section 17.5.2.

6. Report the average of the two determinations of potassium.

J.6 CALCULATIONS

J.6.1 Purity Determination

1. Refer to Section I.6

J.6.2 Potassium Determination

1. Refer to Section 17.6

J.7 SAFETY

The dissolution of sodium presents the slight possibility of a hydrogen explosion. This operation must be carried on behind a safety shield, and preferably in a metal hood.

J.8 DISCUSSION

Dissolution of the sample may take several hours or overnight. The purity determination requires 4 to 6 hr. The potassium determination requires about 4 hr.

Refer to Section I.8 for comments on the purity determination and to Section 17.8 for comments on the potassium determination.

Appendix K

K. DETERMINATION OF CALCIUM, LITHIUM, BORON, CHLORIDE,
AND URANIUM CONTENT OF PURCHASED SODIUM

Five of the determinations required for the acceptance of purchased sodium may be carried out on one distillation residue by the procedures given below.

K.1 PRINCIPLE

The distillation residue from a 50-g sample of sodium is dissolved in alkaline hydrogen peroxide and diluted to known volume. Aliquots of the solution are analyzed for calcium and lithium by atomic absorption and flame emission spectroscopy, for boron by spectrophotometry, for chloride by a specific ion electrode, and for uranium by fluorimetry.

K.2 SENSITIVITY AND PRECISION

The calcium method is suitable for the determination of 2.5 to 100 μg of calcium (1 to 25 ppm of calcium in a 4-g aliquot of sodium). The range for lithium is 1 to 6 μg (1 to 6 ppm of lithium in a 1 g aliquot of sodium). As the upper portion of the working range is approached, the precision for these two determinations is expected to approach 5 to 15%.

The boron method is suitable for the determination of 0.25 to 3.5 μg of boron (2.5 to 35 ppm of boron in a 0.1 g aliquot of sodium). For boron concentrations in the range 10 to 35 ppm, replicate determinations are expected to agree within 25%.

The chloride method is suitable for the determination of 20 to 200 μg of chloride (5 to 50 ppm of chloride in a 4-g aliquot of sodium). For chloride concentrations in the range of approximately 30 ppm, replicate determinations from the same sample are expected to agree within 20%.

For the uranium method, the detection limit is 0.1 μg of uranium (approximately 0.003 ppm in a 30-g aliquot of sodium). The precision of this analysis is approximately $\pm 10\%$, and the accuracy is approximately $\pm 15\%$.

K.3 APPARATUS

K.3.1 General Apparatus

Plastic Volumetric Flask, 25 ml.

Plastic Measuring Pipets, 5ml.

K.3.2 Calcium and Lithium Determinations: Additional Apparatus

Atomic Absorption Spectrophotometer. Any commercially-available grating instrument or laboratory-assembled equivalent instrument may be used. A Perkin-Elmer Model 303 instrument has been found suitable for this use.

Premix Burner. Air-acetylene triple-slot Belling head.

Hollow Cathode Lamp. For calcium.

K.3.3 Boron Determination: Additional Apparatus

Spectrophotometer, with matched 1-cm cells. The Beckman Model B instrument has been found to be suitable for this purpose.

Platinum Dishes.

Polyethylene Stirring Rods.

Centrifuge.

Polycarbonate Centrifuge Tubes.

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

K.3.4 Chloride Determination: Additional Apparatus

Digital Electrometer/pH meter. Suitable for use with the specific ion electrode. The Corning Model 101 instrument has been found suitable for this purpose.

pH Electrode. With double-junction calomel reference electrode.

Chloride Specific Ion Electrode. With double-junction calomel reference electrode. The Orion Research, Inc. Model 92-17 Liquid Ion Exchange Membrane Electrode and the Model 90-02 Counter Electrode have been found suitable for this application.

Magnetic Stirrer, with Teflon-covered stirring bars.

K.3.5 Uranium Determination: Additional Apparatus

Fluorophotometer. The 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.

Platinum Dishes. The platinum dishes are 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.

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

Meker-Type Burner.

Laboratory Centrifuge.

Centrifuge Cones, 15-ml capped type.

Pellet Press. This is a device to prepare 0.4-g pellets of flux.

K.4 MATERIALS AND REAGENTS

K.4.1 General Materials and Reagents

Hydrogen Peroxide, 30%. Reagent grade.

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

Sodium Hydroxide, 1M. Dissolve 40 g of reagent grade NaOH in 250 ml of water in a plastic beaker. Dilute to 1 liter and store in a polyethylene bottle.

K.4.2 Calcium and Lithium Determinations: Additional Materials and Reagents

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

Nitric Acid. Distill concentrated reagent-grade 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 thereby.

Redistilled Water. Distill ion-exchange water in a fused-silica still. Store in a polyethylene bottle.

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

Hydrochloric Acid-NaCl Solution. 2N HCl containing 200 µg/ml NaCl.

Standard Metal Solutions. (1 mg/ml) in 2N HCl containing 200 µg/ml NaCl. 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 NaCl as the sample. Solutions containing approximately 200 µg/ml NaCl normally result when a residue from the procedure in Section 15.1.5 is used. However, should experience show that the concentration of NaCl in the sample solutions differ from 200 ppm by ±25%, adjustments must be made.

Lanthanum Solution. Dissolve 1.17 g of La₂O₃ in 10 ml concentrated HCl and dilute to 1 liter with redistilled water. The analyst has considerable freedom in choosing the concentrations of the working standard solutions. If it becomes necessary or desirable, he may change the dilution volume of the sample solution and the concentration of lanthanum added.

Sodium Chloride. Check the specific batch used for Ca and Li.

Acetylene Gas. Purified, 99.6% min.

Air, Dry. Compressed gas in a cylinder, or a suitably-filtered lab supply.

K.4.3 Boron Determination: Additional Materials and Reagents

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

Curcumin-Acetic Acid. Dissolve 0.125 g of curcumin in 100 ml of reagent grade glacial acetic acid. (This reagent, stored in apolyethylene bottles, is stable for several months if kept in the dark.)

Sulfuric-Acetic Acid Reagent. Cautiously add 50 ml of reagent grade sulfuric acid (sp. gr. 1.84) to 50 ml of reagent grade glacial acetic acid with constant stirring.

Sodium Hydroxide Solution (10% w/v). Dissolve 10 g of reagent grade sodium hydroxide pellets in 100 ml of distilled water in a polyethylene beaker. Store in a polyethylene bottle.

Boron Standard Solution 1 mg B/ml. Dissolve 5.715 g reagent grade boric acid (H_3BO_3) in 500 ml of water and dilute to 1 liter. Store in a polyethylene bottle.

Boron Working Standard Solution, 10 $\mu\text{g B/ml}$. Dilute 10 ml of the Boron Standard Solution to 1 liter with water. Keep in a polyethylene bottle and prepare fresh on the day of use.

K.4.4 Chloride Determination: Additional Materials and Reagents

Concentrated Buffer. To approximately 150 ml of water, add 285 ml of reagent grade glacial acetic acid and 0.30 g reagent grade sodium citrate. Adjust the solution pH 5.0 to 5.5 by addition of reagent grade NaOH pellets. Cool, dilute to 500 ml, and store in a polyethylene bottle.

Buffer. Dilute 100 ml of Concentrated Buffer to 1 liter with water.

Sodium Chloride Standard (1 mg Cl^-/ml). Dissolve 1.649 g reagent grade NaCl in Buffer and dilute to 1 liter with Buffer.

Chloride Working Standard (50 $\mu\text{g Cl}^-/\text{ml}$). Dilute 5 ml of Sodium Chloride Standard to 100 ml with Buffer. Prepare fresh on the day of use.

K.4.5 Uranium Determination: Additional Materials and Reagents

NOTE: All reagents and glassware must be uranium free. .

Concentrated Nitric Acid. Reagent grade.

Nitric Acid, 2N. Add 130 ml of concentrated nitric acid to 500 ml of water and dilute to 1 liter.

Salting Solution. 1.9M aluminum nitrate, acid deficient, and 0.019M tetrapropyl ammonium nitrate. Dissolve 725 g of $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ in a minimum amount of water with the aid of heat. Slowly add 95 ml concentrated NH_4OH 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 one liter with deionized water.

Hexone (Methyl isobutyl ketone).

Flux 98% NaF-2% LiF (powder).

Uranium Standard Solution. 0.5 µg U/ml in 2N HNO₃.

K.5 PROCEDURE

K.5.1 Sample Preparation

1. Obtain a distillation residue from approximately 50 g of sodium according to the method of Section 4. Use a tantalum cup.
2. Record the weight of the filled and empty cup as marked on the transfer container.
3. Dissolve the distillation residue by adding 2.5 ml of 1M NaOH followed by 2.5 ml of 30% hydrogen peroxide to the cup. Dispense these reagents from a plastic pipet directed to wet the inner walls of the cup. Tilt and rotate the cup to rinse its inner surface.
4. Quantitatively transfer the solution to a 25-ml plastic volumetric flask by water rinses.
5. Dilute the solution to volume with water. This is the sample solution.

K.5.2 Calcium Determination

K.5.2.1 Determination in Solution from K.5.1

1. Introduce a 2-ml aliquot of the sample solution into a 10-ml volumetric flask.
2. Add 0.1 ml of lanthanum solution.
3. Dilute to volume with 2N HCl.
4. Proceed to Section 15.5 and carry out steps 10 through 15, using the directions for aqueous solutions.
5. Calculate the calcium concentration in the sample as follows:

$$\text{Calcium, ppm} = \frac{A \times F}{C - D}$$

where,

A = weight of Ca in the 2-ml aliquot of sample solution, µg

F = aliquot factor = 12.5

C = weight of sodium sample plus container, g

D = weight of empty container, g

K.5.2.2 Determination in Solution from J.5.3

1. Prepare a calcium working standard of 40 μg Ca/ml by diluting a portion of the 1 mg Ca/ml standard.
2. Obtain the sample solutions remaining after potassium has been determined according to Section J.5.3.
3. Pipet three 10-ml aliquots of the first sample solution into 15-ml beakers.
4. Calculate the grams of sodium per 10-ml aliquot from the previous measurements on the solution.
5. Add 0, 2, and 4 μl of Ca (0, 50, and 100 μl of Ca working standard) to the 10-ml aliquots of sample solution.
6. Adjust the atomic absorption spectrophotometer for determination of calcium. Typical instrument parameters are:
  1. Calcium lamp
  2. Wavelength setting : 422.7 nm
  3. Burner : triple-slot
  4. Oxidant and fuel : air-acetylene
7. Aspirate the three portions of sample solution and record the response.
8. Plot sample response as a function of concentration calcium added to the solution as shown in Figure K-1.
9. Draw a straight line through the plotted points, extend the line to the abscissa, and read μg Ca/ml of sample solution.
10. Calculate the calcium concentration as follows:
$$\text{Calcium, ppm} = \frac{A \times B}{W}$$

where

A = concentration of calcium, $\mu\text{g}/\text{ml}$

B = volume of solution = 10 ml

W = weight of sodium in the 10-ml aliquot, g
11. Carry out steps 3 through 10 using the second sample solution.
12. Report the average of the two determinations of calcium.

Fig. K-1

SAMPLE RESPONSE AS A FUNCTION
OF CALCIUM ADDITIONS

K.5.3 Lithium Determination

1. Introduce a 0.5-ml aliquot of the sample solution into a 10-ml volumetric flask.
2. Add 0.025 ml of lanthanum solution.
3. Dilute to volume with 2N HCl.
4. Proceed to Section 15.5 and carry out steps 10 through 15, using the directions for aqueous solutions.
5. Calculate the lithium concentration of the sample as follows:

$$\text{Lithium, ppm} = \frac{A \times F}{C - D}$$

where,

A = weight of Li in the 0.5-ml aliquot of sample solution, μg

F = aliquot factor = 50

C = weight of sodium sample plus container, g

D = weight of empty container, g

K.5.4 Boron Determination

NOTE: The use of borosilicate glassware should be avoided throughout this determination.

1. Transfer a 0.050-ml aliquot of the sample solution to a platinum dish.
2. Add 0.5 ml of 10% sodium hydroxide to the platinum dish.
3. Evaporate the solution in the platinum dish to dryness on a boiling water bath.
4. Add 1.5 ml of curcumin-acetic acid reagent and warm the platinum dish gently to dissolve the residue.
5. Cool the platinum dish to room temperature and add 1.5 ml of sulfuric acid-acetic acid reagent.
6. Proceed to Section 20.5 and carry out steps 7 through 15.
7. Calculate the boron concentration in the sample as follows:

$$\text{Boron, ppm} = \frac{A - B}{C - D} \times \frac{100}{R} \times F$$

where,

A = boron in the 0.050-ml aliquot of sample solution, μg

B = boron in the blank, μg

C = weight of sodium sample plus container, g

D = weight of empty container, g

R = percent recovery of boron in the procedure. Assume R to be 95, or determine it by carrying spiked samples through the distillation and analysis.

F = aliquot factor = 500

K.5.5 Chloride Determination

1. Transfer a 2-ml aliquot of the sample solution into a 10-ml volumetric flask.
2. Add 1 ml of Concentrated Buffer to the volumetric flask.
3. Dilute to volume with water.
4. Proceed to section E.5 and carry out steps 5 through 10.
5. Calculate the chloride concentration in the sample as follows:

$$\text{Chloride, ppm} = \frac{A \times B \times F}{C - D}$$

where,

A = Cl^- concentration in the buffered aliquot, $\mu\text{g/ml}$

B = volume of the buffered aliquot = 10 ml

F = aliquot factor = 12.5

C = weight of sodium sample plus container, g

D = weight of empty container, g

K.5.6 Uranium Determination

NOTE: All reagents and glassware used throughout this determination must be uranium-free.

1. Transfer 15 ml of the sample solution to a 30-ml beaker.
Add 5 ml of 2N HNO_3 .
2. Proceed to Section 21.5 and carry out steps 6 through 17.
3. Calculate the uranium concentration in the sample as follows:

$$\text{Uranium, ppm} = \frac{A \times F_1 \times F_2}{C - D}$$

where,

A = weight of uranium in a fused pellet sample, μg

F_1 = aliquot factor from splitting the hexone extract = 10

F_2 = aliquot factor from splitting the distillation residue = 1.667

C = weight of sodium sample plus container, g

D = weight of empty container, g

K.6 CALCULATIONS

For these determinations, the calculation steps have been incorporated into the procedures in Section K.5.

K.7 SAFETY

In addition to the demands of ordinary laboratory technique one should note the specific hazards involved in using acetylene gas, as discussed in Section 15.7.

K.8 DISCUSSION

These procedures, exclusive of sampling and distillation, require approximately 2 to 3 hr for the determination of chloride, and 1 hr for the determination of uranium.

Appendix L

L. PREPARATION OF SAMPLES FOR SHIPMENT OR STORAGE.

L.1 GENERAL REQUIREMENTS

General requirements for the preparation of components for shipment are defined in RDT F 7-2. That document, however, does not cover the special requirements for the shipment of sodium or of samples containing small amounts of radioactive materials. Department of Transportation (DOT) regulations covering surface transportation of hazardous materials are set forth in 49 CFR 170 to 179. Additional DOT regulations covering air shipment of hazardous materials are set forth in 14 CFR 103. Authoritative secondary sources for this information are: R. M. Graziano's Tariff No. 25 for surface shipments, and Official Air Transport Restricted Articles Tariff No. 6-D for air shipments.

Directions given in this procedure both will comply with current restrictions covering the acceptance and transportation of materials such as sodium samples, and will insure the chemical integrity of the samples. The shipping office of the site originating the samples must be made fully aware of the nature of the shipment and its packaging, for it is the responsibility of the shipping agent to certify that the shipment complies with the applicable DOT regulations.

Procedures which are specific to the types of samples collected for the application of the analytical methods specified in this Standard are given below.

L.2 SODIUM SAMPLES IN BYPASS SAMPLE VESSELS NOT EQUIPPED WITH SWAGelok OR CONOSEAL FITTINGS

1. Wrap the sample vessel in plastic.
2. Slide the plastic-enclosed vessel into an appropriate length of previously-cleaned iron pipe which is threaded at both ends.
3. Cap both ends of the pipe. Use Teflon tape on the threads to effect the seal.
4. Embed the capped pipe in expanded vermiculite contained in an appropriate container.
5. Seal the container and place a DOT yellow "Caution" seal on the side of the container.
6. Follow the additional procedures specified in RDT F 7-2, and in the applicable DOT regulations.

L.3 SODIUM SAMPLES IN OVERFLOW CUPS.

1. Enclose the cup or cups in a layer of aluminum foil. Add sufficient extra wrappings of crumpled aluminum foil to make a close fit in the iron pipe used for shipping.

2. Slide the aluminum-enclosed vessel into an appropriate length of previously-cleaned iron pipe which is threaded at both ends.

3. Separate multiple samples shipped in the same pipe with metal disks slightly less in diameter than the I.D. of the pipe. Place crumpled aluminum foil pads at both ends of the pipe to completely fill it.

4. Cap both ends of the pipe. Use Teflon tape to effect the seal.

5. Embed the capped pipe in expanded vermiculite in an approved shipping container.

6. Seal the container and place a DOT yellow "Caution" seal on the side of the container.

7. Follow the additional procedures specified in RDT F 7-2 and in the applicable DOT regulations.

L.4 RESIDUES FROM VACUUM DISTILLATION

1. Place a press-fitted cap on each distillation cup.

2. Enclose each capped cup in a layer of aluminum foil. Add sufficient extra wrappings of crumpled aluminum foil to make a close fit in the iron pipe used for shipping.

3. Slide the aluminum-enclosed vessel into an appropriate length of previously-cleaned iron pipe which is threaded at both ends.

4. Separate multiple samples shipped in the same pipe with metal disks slightly less in diameter than the I.D. of the pipe. Place crumpled aluminum foil pads at both ends of the pipe to completely fill it.

5. Cap both ends of the pipe. Use Teflon tape on the threads to effect the seal.

6. Embed the capped pipe in expanded vermiculite contained in an appropriate container.

7. Seal the container and place a DOT yellow "Caution" seal on the side of the container.

8. Follow the additional procedures specified in RDT F 7-2, and in the applicable DOT regulations.

L.5 EQUILIBRATED WIRES OR TABS

1. Slide wires or tabs (washed free of sodium and dried) into a glass or metal tube of appropriate outer diameter and length. This tube may be open at both ends or closed at one end. Should more than one wire or tab constitute a single aliquot, bundle the specimens together and mark them appropriately.

2. Stopper the open end(s) of the tube. Cork and rubber are suitable stopper materials.

3. Place the stoppered tube in a wooden or cardboard box of appropriate dimensions. If a glass tube is used, protect the tube from breakage by embedding it in a soft matrix (e.g. glass wool, cotton, expanded vermiculite, etc.) within the box.

4. Follow the additional procedures specified in RDT F 7-2, and in other applicable documents defined in that Standard.

L.6 SODIUM SAMPLES IN BYPASS SAMPLE VESSELS EQUIPPED WITH SWAGELOK OR CONOSEAL FITTINGS

1. Wrap in aluminum foil the sample vessel sealed at each end with either Swagelok or Conoseal Fittings.

2. Embed the aluminum foil-enclosed sample vessel in expanded vermiculite contained in an approved container.

3. Seal the container and place a DOT yellow "Caution" seal on the side of the container.

4. Follow the additional procedures specified in RDT F 7-2, and in the applicable DOT regulations.

L.7 GAS SAMPLES

Follow the procedures specified in RDT F 7-2, and in the applicable DOT regulations.

L.8 PROCEDURE FOR HANDLING RADIOACTIVE SODIUM SAMPLES

The DOT specifications allow shipment of specimens without shielding if the activity level at the exterior of the package is less than 200 mr/hr. In normal practice, sodium samples for analytical purposes should not be highly radioactive, and should fall within this category. By packaging in suitable interior containers and in small lots, it should be possible to meet DOT requirements for all shipments by carrying out the following steps:

1. Package the bypass, overflow cup, gas, or other type of sample as specified for nonradioactive samples in the sections above.

2. Place the iron pipes in the appropriate size of DOT-approved container for shipping. Packaging shall conform to 49 CFR 173.394.

3. Label the package according to 49 CFR 173.402, identifying both radioactive and other hazards.

L.9 STORAGE OF SAMPLES

The storage procedure to be used will depend on the type of sample and on whether or not protection from the atmosphere is required. Specific instructions for each condition are given below.

L.9.1 Equilibrated Wires

1. Place cleaned and dried wires in a capped metal or glass vial

that is properly marked for identification.

2. Store the vial in a convenient storage area.

L.9.2 Bypass Samples

1. Close each end of the sample tube with a Swagelok cap plug.

2. Store the closed tube in an inert-gas enclosure if protection from the atmosphere is required. Otherwise, place the sample in a storage area approved by local safety officials.

L.9.3 Overflow Cup Samples (Unprotected)

1. Wrap the cup in aluminum foil.
2. Place the cup into a cleaned piece of metal pipe which is closed at one end and threaded at the other end.
3. Cap the pipe. Use Teflon tape on the threads to effect the seal.
4. Mark the pipe for identification.
5. Store the pipe in an area approved by local safety officials.

L.9.4 Overflow Cup Samples (Protected)

1. Obtain the samples while they still are protected in a sealed sampler or transfer vessel.
2. Select a cleaned metal pipe, sealed at one end and threaded at the other.
3. Mark the pipe properly for identification of the samples.
4. Transfer pipe and protected samples into an inert-atmosphere box.
5. Remove the cups from the sampler and wrap each cup in aluminum foil.
6. Place the wrapped cup into the pipe and cap the pipe, using Teflon tape to effect the seal.
7. Store the pipe in an inert atmosphere.

L.9.5 Distillation Residues

1. Place a press-fitted cap on each distillation cup.
2. Wrap each capped cup in aluminum foil.
3. Place each wrapped cup into an appropriate length of cleaned metal pipe.

4. Cap both ends of the pipe. Use Teflon tape to effect the seal.

5. Mark the pipe for identification.

6. Store the pipe in a convenient storage area.

L.10 SAFETY

Vermiculite dust has been known to produce serious and persistent eye irritation. Handle vermiculite in an area free of strong drafts, and pour it slowly and carefully.

RDT STANDARD

UNITED STATES ATOMIC ENERGY COMMISSION
DIVISION OF REACTOR RESEARCH AND DEVELOPMENT

RDT F 3-40T, Amendment 2
DATE August 1974
PAGE 1 OF 38

METHODS FOR THE ANALYSIS OF SODIUM AND COVER GAS

AMENDMENT 2

This amendment forms a part of RDT F 3-40T
dated January 1973

1. Page ii, Table of Contents: Add:

34. Determination of Carbon in Sodium by an Equilibration Method Using Iron-Manganese Tabs

35. Determination of Hydrogen in Sodium by an Equilibration Method Using Scandium Tabs

Appendix N Recommended Values for the Solubilities of Oxygen and Hydrogen in Sodium

Appendix O Determination of Carbon, Hydrogen, and Oxygen in Sodium by a Simultaneous Equilibration Method Using Vanadium Wire, Scandium Tabs, and Iron-Manganese Tabs, Respectively

Appendix P Determination of Sulfur in Sodium

Delete: "Activity" from 12.
Appendix D
Appendix M (Amendment 1)

2. Page 4, 3.1.3: Renumber to 3.1.4.

3. Page 4: Add:

3.1.3 Materials and Reagents.

1. Methanol. Redistill methanol using a quartz or borosilicate glass still and store it in polyethylene bottles. Ethanol may be substituted for methanol.

2. Nitric Acid. Reagent grade nitric acid diluted 1 part reagent grade nitric acid plus 5 parts distilled water.

3. Water. Pass distilled water through a high quality mixed-bed ion exchange column and store it in a polyethylene bottle.
4. Page 4, 3.1.4, Step 1: Change "dilute nitric" to "1:5 nitric".
5. Page 6, Footnote a: Change to read:
^aAfter equilibrating first at 320°C (600°F) for 1 hour for all sampling temperatures below 320°C (600°F). See 3.1.6.
6. Page 7, 3.1.4, Step 8: In the third line at the top of the page, change "determined" to "determination".
7. Page 7, 3.1.4, Step 9: Add "De-energize sample heaters".
8. Page 7, 3.1.4, Step 10: Change to read:
  10. Cool the sample below the freezing point of sodium, <93°C (<200°F), as quickly as operational limitations will allow.
9. Page 7, 3.1.4, Step 11: Change to read:
  11. Close the inlet valve prior to freezing same, >121°C <162°C (>250°F <325°F), and after further cooling to insure that inlet and outlet lines are frozen, remove the sampling vessel.
10. Page 7, 3.1.4: Renumber to 3.1.5 and add "400°C" before "750°F" and add parentheses on 750°F in two places.
11. Page 7, 3.1.5: Renumber to 3.1.6 and change last paragraph to read:

The requirement given in Table 3-1 that for sampling at 230°C (450°F) the sample vessel be equilibrated for 1 hour at 320°C (600°F) and then for 5 hours at 230°C (450°F) arises from the fact that sodium does not appreciably wet stainless steel at 230°C (450°F).
12. Page 8, 3.2.2: In the second paragraph, second line, change "is expected to" to "should".
13. Page 9, Figure 3-2: Add a legend for Cup Holder and Sampling Cups, and show area of overflow sampler body below the liquid level line in cross-hatch.
14. Page 11, 3.2.2: Add (prior to 3.2.3):

Multipurpose Sampler. An alternate device for overflow sampling is the multipurpose sampler (MPS) shown in Fig. 3-4. This device, designed for use on FFTF, provides three types of sampling capability in one unit. Overflow sampling is done using the sampler insert shown in Fig. 3-5. The MPS operation for overflow sampling is identical to that described in 3.3 for metal equilibration sampling except the sample section is

Fig. 3-4. Multipurpose Sampler

Fig. 3-5. Overflow Insert for Multipurpose Sampler

operated at 540°C (1000°F) for four hours rather than the 750°C (1382°F) for up to 24 hours.

15. Page 11, Fig. 3-4 and Fig. 3-5: Add as shown on pages 3 and 4 of this amendment.
16. Page 11, 3.2.3.1, Steps 1 and 2: Change to read:
  1. Wash tantalum sampling cups successively with 1:10 hydrofluoric acid, aqua regia made with reagent grade acids, and finally with demineralized water. Wash titanium, quartz, and borosilicate glass cups successively with aqua regia and demineralized water.
  2. Dry the cup in an oven at 110°C (230°F) for 1 hour.
17. Page 13, 3.2.3.2, Step 2: Change to read:
  2. Dry the cup in an oven at 110°C (230°F) for 1 hour.
18. Page 15, 3.2.5: In first sentence on top of page, change to read:

If oxide, hydroxide, or carbonate formed . . . a blank flange.
19. Page 15, 3.3: Add:

3.3 Wire and Foil Equilibration Sampling. This procedure is required for the determination of oxygen by the vanadium wire method, hydrogen by the scandium foil method, and carbon by the Fe-12Mn method (Procedures 12, 34, 35 and Appendix O respectively).

3.3.1 Principle. A specimen of wire or metal foil is exposed to flowing sodium at 750°C (1382°F) for 4 to 24 hours. 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.

3.3.2 Apparatus. Two basic types of samples are in use for metal equilibration analyses. The specimen equilibration module is described in detail in Procedures 12, 34, and 35.

3.3.2.1 Multipurpose Sampler. An alternate sampler device, designed for FFTF use, is the multipurpose sampler (MPS) illustrated in Fig. 3-4. 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. 3-6.

3.3.2.2 Sample Transfer. Sample inserts are removed from the sample body by disconnecting the upper Grayloc fitting and removing the

Fig 3-6. Equilibrium Insert for Multipurpose Sampler

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.

3.3.2.3 Sampling System. The sampling system described in Fig. 3-3 is typical of those used with the multipurpose sampler. 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. 3-3.

3.3.3 Procedure.

3.3.3.1 Sample Preparation and Equilibration. The individual preparation requirements are presented in Procedures 12, 34, and 35 for handling vanadium wire, Fe-12Mn tabs, and scandium tabs respectively.

3.3.3.2 Equilibration.

1. Insert the sample holder into the sodium system.
2. Establish the required sodium flow. (For the MPS, a flow of at least 0.25 gpm is required. Normally, 0.3 to 0.4 gpm is used.)
3. Equilibrate the samples at the required flow rate for a minimum of 24 hours at $750 \pm 2^\circ\text{C}$ ($1382 \pm 5^\circ\text{F}$).

3.3.3.3 Post Exposure Treatment.

1. Turn off heaters.
2. Shut off sodium flow by closing inlet valves.
3. Pressurize the sampler with inert gas forcing sodium out of the sampler area.
4. Close outlet sodium valve.
5. Remove the sample holder from the sampler and transfer to an inert gas glovebox.
6. Clean off residual sodium and prepare for analysis as described in Procedures 12, 34, and 35.

3.3.4 Safety. The multipurpose sampler has been field tested for over 18 months without incident. The sampler is connected to the piping system with Conoseal fittings and has been used many times at system temperatures between 482°C to 621°C (900 to 1150°F) without leakage. The Grayloc fitting used in removing the sample has been broken and remade over 100 times with the sampler operated at temperatures of

538 to 760°C (1000 to 1400°F). No abnormal safety problems are involved in the MPS operation.

3.3.5 Discussion. Metal equilibration sampling requires from 4 to 24 hours at 750°C (1382°F) depending upon the element being determined. The total time required is approximately eight hours longer.

20. Page 19, Figure 4-3: Add "Glass" to "Borosilicate".
21. Page 23, 4.5: Under "Sodium Metal", add asterisk after "Met-L-X" and add the following footnote:

* Trade name for NaCl powder. Na₂CO₃ is preferred.
22. Page 25, Figure 5-1: Add "Glass" to "Borosilicate".
23. Page 47, 7.7.1, Step 10: Add "flux" after "dichromate".
24. Page 53, Figure 8-3: Add dimension line for 13-inch dimension on left side of ground flange.
25. Page 57, 8.7: In second paragraph, second line, correct spelling of "accumulate".
26. Page 60, Figure 9-2: Correct spelling of "auxiliary".
27. Page 63, 9.4: In Sulfuric Acid, underline "M" in "6M".
28. Page 67, 10.4: Correct spelling of "Epstein's" reagent, underline "M" in "4M" in Sulfuric Acid, and add hyphen to "Chloramine-T" in two places.
29. Page 72, 11.3: In Flame Photometer, delete "Method" from "ASTM Method D 1428".
30. Page 77, 12.: Delete "Activity" from title.
31. Page 77, 12.1: Change second sentence to read:

Subsequent measurement of the oxygen concentration in the wire is related to the concentration of active oxygen in sodium by means of the distribution coefficient.
32. Page 77, 12.2: Add:

The precision is expected to be within ± 10 percent.
33. Page 77, 12.4: Add:

Iron Chips. LECO accelerator part 501077 has been found to be satisfactory.

34. Page 82, 12.4: Add to "Electropolishing Solution":

Add the acid to the alcohol slowly, with stirring.

35. Page 84, 12.5.2.2: Correct spelling of "Temperature" in Step 4.
36. Page 96, 14.: Change Procedure 14 to read as given in this amendment (pages 12 to 13).
37. Page 100, 15.5, Step 3: Change "moisture" to "moisten".
38. Page 104, 16.4: In Hydrochloric Acid, correct spelling of "polyethylene".
39. Page 106, 16.5 Step 16: Change "12M HCl" to "12N HCl".
40. Page 109, 17.7: Change to read:

17.7 Safety. 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 which 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 eliminate 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.

41. Page 110, 18.4: In AMP/Cotton, underline "M" in 8M and delete "(distilled in quartz)".
43. Page 111, 18.5, Step 7: Delete "and not harmful".
44. Page 114, 19.3: Correct spelling of "Polyethylene".
45. Page 115, 19.4: In Reducing Solution, second line, correct spelling of "naphthol".
46. Page 120, 21.4: In Nitric Acid, underline "N" in 2N.
47. Page 122, 21.5, Step 13: Change "LiF" to "LiF".
48. Page 123, 22.4: In Nitric Acid, underline "N" in 2N.
49. Page 126, 22.5.3, Step 1: Underline "N" in 0.5N.
50. Page 129, 23.4: Delete "concentrated acid" from end of line.
51. Page 131, 24.2: Change second sentence to read:

Detection limits of the order of $1 \times 10^{-5} \mu\text{Ci/g}$ of sodium for isotopes with favorable branching ratios, (e.g., ^{54}Mn , ^{125}Sb) have been obtained in

EBR-II primary sodium.

52. Page 138, 26.6: Delete "of" from " μ Ci/g of Na".
53. Page 139, 27.4: In last line, correct spelling of "naphthalene".
54. Page 150, 29.1: Correct spelling of "spectrometry".
55. Page 160, Footnote: Change "745 mm Hg" to "745 Torr".
56. Page 186, C.2.3, Step 7: Correct spelling of "insoluble".
57. Page 187-191, Appendix D: Change to Procedure 34 to read as given in this amendment (pages 14 to 18).
58. Page 197, F.1.5.2: Change title to "Procedure for Identification of Helium".
59. Page 198, F.1.6: Change to read "None required".
60. Page 207, Footnote: Change "745 mm Hg" to "745 Torr".
61. Page 210, G.3.5.5 (Amendment 1), Step 1: In the fourth line, correct temperature to "0°C (32°F)".
62. Page 213, H.3: In Inert-Atmosphere Glovebox, correct spelling of "box" in sixth line and correct tolerance to "($\pm$ 0.05g)" in seventh line.
63. Page 217, H.4: Add:

Helium Gas, ultrapure.
Acetone, reagent grade.
64. Page 223, H.5, Step 9: Change "hydrogen-oxygen" to "oxyhydrogen".
65. Page 224, H.7.3, Step 1: Add "preignited and weighed" prior to "quartz cups".
66. Page 224, H.7.3, Step 2: Delete the last sentence in parentheses.
67. Page 227, I.3: In Glass Wool, underline "M" in 0.001M.
68. Page 227, I.4: Add:

Acetone, reagent grade.
Ethanol, neutral, reagent grade, acetone-free.
69. Page 235, J.3.3: Delete "Method" from ASTM D 1428.

70. Page 235, J.4.1: Add:

Acetone, reagent grade.
Ethanol, reagent grade.

In Butyl Cellosolve, correct spelling of "glycol".

71. Page 241, K.4.2: Change Sodium Chloride to read:

Sodium chloride, reagent grade. Check the specific batch used for Ca and Li content.

72. Page 253, L.10: Add after first sentence:

It is also a lung irritant.

73. Page 18-21 (Amendment 1), Appendix M: Change to Procedure 35 to read as given in this amendment (pages 19 to 23).

74. Appendix N: Add Appendix N as given in this amendment (pages 24 to 27).

75. Appendix O: Add Appendix O as given in this amendment (pages 28 to 31).

76. Appendix P: Add Appendix P as given in this amendment (pages 32 to 35).

77. Index: Add an Index as given in this amendment (pages 36 to 38).

14. DETERMINATION OF FLUORIDE IN SODIUM BY SPECIFIC ION ELECTRODE

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

14.2 Sensitivity and Precision. This method is suitable for the determination of 0.2 to 20 μg fluoride (0.01 to 1 ppm in a 25 g sample of sodium). The range can readily be adjusted upward. For fluoride concentrations in the range 0.02 to 1 ppm, replicate determinations from the same sample are expected to agree within 25 percent.

14.3 Apparatus.

1. pH Meter. Suitable for use with specific ion electrodes, with expanded scale.
2. pH Electrode. Combination glass and calomel or separate electrodes.
3. Fluoride Specific Ion Electrode. Orion 94-09A or equivalent.
4. Magnetic Stirrer.
5. Plastic Cups. Size and shape depends upon electrodes used. They should be small enough that 5 ml solution will make proper contact with electrodes and allow space for a small stirring bar.

14.4 Materials and Reagents.

1. Water. Pass distilled water through a high quality commercial mixed-bed ion exchange column. Store in a polyethylene bottle.
2. Total Ionic Strength Adjustment Buffer (TISAB). To approximately 500 ml water, add 57 ml reagent grade glacial acetic acid, 58 g reagent grade sodium chloride, and 4 g CDTA (cyclohexylene dinitrilo tetracetic acid) dissolved in 22 ml 1 N NaOH; cool to room temperature, titrate to $\text{pH } 5.3 \pm 0.2$ with 5 M NaOH, dilute to 1 liter with water.)
3. Sodium Fluoride Standard (1 mg F^-/ml). Dissolve 2.210 g reagent grade NaF in water and dilute to 1 liter. Store in plastic.
4. Fluoride Working Standard (0.01 mg F^-/ml). Dilute 10 ml of the sodium fluoride standard to 1 liter. Prepare fresh on the day of use.

14.5 Procedure.

1. Obtain a distillation residue by the method of Section 4. Use a Ni or stainless steel cup.

2. Compute the sample weight from information recorded on the distillation residue container (Section 4.4, step 23).
3. Rinse the cup with 3 ml of buffer solution and two 1 ml portions of buffer solution.
4. Combine all washings in a small plastic cup.
5. Prepare standards by adding 0.1, 0.25, 0.50 and 1.0 μg fluoride (10, 25, 50 and 100 λ of working standard) to 5 ml portions of buffer.
6. Immerse the fluoride specific ion electrode in each standard in turn, stirring with magnetic stirrer until the millivolt reading on the expanded scale of the meter is constant. Record the readings and plot on semi-log paper, with the F^- concentrations on the log scale.

NOTE: 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.

7. Make measurements on samples in the same manner as for standards.

14.6 Calculations.

$$\text{Fluoride, ppm} = \frac{\mu\text{g F}^-}{\text{Sample weight}}$$

- #### 14.7 Safety. This procedure presents no unusual safety hazards.

14.8 Discussion. Since ion activity in a solution is temperature dependent, temperature changes during measurement will appear as meter "drifting." This can be minimized by preventing the plastic cups from resting against the top of the magnetic stirrer. If suspended about one-fourth inch above the stirrer, the stirring action will be satisfactory and the temperature change will be insignificant.

A recorder is convenient for use in determining when the meter reading has stabilized.

34. DETERMINATION OF CARBON IN SODIUM BY AN EQUILIBRATION METHOD USING IRON-MANGANESE TABS

34.1 Principle. A metal tab of Fe-12Mn is immersed in flowing sodium at 750°C 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.

34.2 Sensitivity and Precision. This procedure is applicable for carbon activities in sodium in the range 0.002 to 0.3. The precision is expected to be within ± 10 percent for activities >0.01 .

34.3 Apparatus.

Equilibration Module. Fig. 34-1 is a schematic drawing of the specimen equilibration module for use on reactors and large sodium systems. This module shall conform to the requirements of RDT C 8-8. Fig. 34-2 is a schematic drawing of a typical specimen equilibration device for use on small experimental systems.

Carbon Determination Apparatus. This apparatus should be capable of determining 10 to 200 μg of carbon in 500 mg of ferrous alloy by the combustion technique. The LECO WR-12 Carbon Determinator or the LECO ELC-12, manufactured by the Laboratory Equipment Company have been found suitable with the ELC-12 providing better sensitivity for low carbon values.

Forceps. Dissecting forceps.

34.4 Materials.

Standard Fe-12Mn Tabs. Annealed, 5 mil thick x 1 inch wide x 1 inch long. Suitable 5 mil thick x 1 inch wide strip stock has been supplied by the Materials Research Corporation.

Accelerator. Tin Metal Accelerator, LECO Catalog No. 25705, has been found satisfactory for this use.

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

Acetone. Reagent grade.

Ethanol. Technical grade and absolute reagent grade.

34.5 Procedure.

34.5.1 Tab Preparation.

1. Prepare tabs by cutting the standard Fe-12Mn strip stock into 1 inch long lengths.

Fig. 34-1. Schematic of a Typical Specimen Equilibration Module

Fig. 34-2. Schematic of a Typical Specimen Equilibration Device

2. Scribe or punch identifying numbers on each tab.
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.
4. Degrease the sample holder by washing it with acetone.
5. Mount the tabs in the sample holder.

34.5.2 Equilibration.

1. Insert the sample holder into the sodium system.
2. After establishing sodium flow (minimum, 0.2 gal/min) through the equilibration device, equilibrate the tabs at $750 \pm 2^\circ\text{C}$ ($1382 \pm 5^\circ\text{F}$) for at least 1 and for no more than 7 days.

34.5.3 Post-Exposure Treatment.

1. Shut off sodium flow by closing inlet and outlet valves.
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.)
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.)
4. Remove the sample holder from the equilibration module or device.
5. Dissolve the sodium adhering to the holder in approximately 1000 ml of technical grade ethanol. (The large volume of alcohol prevents excessive heating.)
6. Rinse the holder and tabs with distilled water, reagent grade absolute ethyl alcohol, and then allow the tabs and tab holder to dry.
7. Remove the tabs from the holder and place them in a clean, dry glass vial.

34.5.4 Carbon Determination.

1. Analyze 4 or 5 samples of NBS Type 335 Steel. For each determination use approximately 0.7 g of tin accelerator.
2. Prepare a calibration curve of instrument meter units vs micrograms

carbon.

3. Analyze approximately 0.5 g samples from a tab according to the procedure used for standardization.
4. The 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.
5. From the calibration curve determine the micrograms of carbon in each sample.

34.6 Calculations.

1. Calculate the wt ppm carbon in the Fe-12Mn tab from the following formula:

$$A, \text{ wt ppm carbon in tab} = \frac{B}{C}$$

where

B = carbon in sample, μg
C = weight of sample, g.

2. Calculate the chemical activity of carbon in the sodium from the following formula:

$$\text{Chemical activity of carbon} = \frac{A}{K - (.862A)}$$

where

$$K = 17,881 \text{ ppm C.}$$

34.7 Safety. The steps under equilibration and post-exposure treatment present hazards which should be controlled by locally-administered safety programs.

The laboratory operations present no unusual hazards except the safe handling of liter quantities of flammable organic liquids.

34.8 Discussion. This entire procedure, excluding the equilibration time, requires about 4 hours.

35. DETERMINATION OF HYDROGEN IN SODIUM BY AN EQUILIBRATION METHOD USING SCANDIUM TABS

35.1 Principle. A scandium tab is immersed in flowing sodium at 750°C 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.

35.2 Sensitivity and Precision. This procedure is applicable for active hydrogen concentrations in sodium in the range 0.06 to 0.5 ppm. The precision is expected to be within ± 10 percent.

35.3 Apparatus.

Equilibration Module. Fig. 35-1 is a schematic drawing of the specimen equilibration module for use on reactors and large sodium systems. This module shall conform to the requirements of RDT C 8-8. Fig. 35-2 is a schematic drawing of typical specimen equilibration device for use on small experimental systems.

Hydrogen Determination Apparatus. This apparatus should be capable of determining 10 to 200 μg of hydrogen in 20 to 100 mg of scandium by vacuum or inert gas fusion or by the hot extraction technique. The LECO RH-1 Hydrogen Determinator, manufactured by the Laboratory Equipment Company has been found suitable.

Forceps. Dissecting forceps.

35.4 Materials.

Standard Scandium Tabs. 10 mil thick x 1/8 inch wide x 3/4 inch long, prepared from 99.9 percent scandium sheet. Suitable 10 mil x 2 inch wide sheet has been supplied by Research Chemicals, a Division of Nucor Corporation.

Accelerator. Iron metal accelerator, LECO Catalog No. 501-007, has been found satisfactory for this use.

Hydrogen Standard. Titanium analyzed sample, LECO Catalog No. 762-741 has been found suitable.

Ethanol. U.S.P. or reagent grade absolute ethanol.

35.5 Procedure.

35.5.1 Tab Preparation.

1. Store scandium stock in a dry inert atmosphere.

Fig. 35-1. Schematic of a Typical Specimen Equilibration Module

Fig. 35-2. Schematic of a Typical Specimen Equilibration Device

2. Handle stock material only with degreased forceps.
3. Prepare tabs by cutting stock material in box into 3/4 inch long x 1/8 inch wide strips.
4. Remove tabs from box.
5. Place the tabs in the sample holder previously degreased by washing with acetone.

35.5.2 Equilibration.

1. Insert the sample holder into the sodium system.
2. After establishing sodium flow (0.1 gal/min) minimum through the equilibration device, equilibrate the tabs at $750 \pm 2^\circ\text{C}$ ($1382 \pm 5^\circ\text{F}$) for 24 hours.

35.5.3 Post Exposure Treatment.

1. Shut off sodium flow by closing inlet and outlet valves.
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.)
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.)
4. Remove the sample holder from the equilibration module or device and transfer it to an inert gas glovebox.
5. Melt the sodium in the sampler holder by heating to 125°C (257°F). Remove the tabs from the holder.
6. Remove the tabs and holder from the inert atmosphere box and thoroughly wash each one individually with absolute ethanol to remove the bulk of the adherent sodium.
7. Place the tabs in fresh warm $\sim 60^\circ\text{C}$ ($\sim 140^\circ\text{F}$) alcohol for 0.5 to 1.0 hours.
8. Dry the tabs by gently heating $\sim 60^\circ\text{C}$ ($\sim 140^\circ\text{F}$) in a glass vial.

35.5.4 Hydrogen Determination.

1. Analyze 1 or 2 samples of the LECO titanium standard samples. For each determination use approximately 0.5 g of accelerator.

2. Prepare a calibration curve of instrument meter units vs. micrograms hydrogen.
3. Analyze each tab individually. The tab may be bent or cut in two pieces in order to facilitate analysis.
4. Place the tab in the ignition boat.
5. Melt the scandium in a flowing argon stream.
6. Pass the hydrogen-argon mixture through a molecular sieve column and measure the hydrogen using a thermal conductivity detector.
7. Alternately, a manometric hydrogen measurement may be used.
8. From the calibration curve, determine the micrograms of hydrogen in each sample.

35.6 Calculations.

1. Calculate the wt ppm hydrogen in the scandium from the following formula:

$$A, \text{ wt ppm hydrogen in tab} = \frac{B}{C}$$

where

B = hydrogen in sample, μg

C = weight of sample, g.

2. Calculate the hydrogen concentration in the sodium from the following formula:

$$\text{ppm H in Na} = .000156 A \text{ (ppm H in Sc).}$$

35.7 Safety. The steps under equilibration and post-exposure treatment present hazards which should be controlled by a locally-administered safety program.

The laboratory operations present no unusual hazards except the safe handling of liter quantities of flammable organic liquids.

35.8 Discussion. This entire procedure, excluding the equilibration time, requires about 6 hours.

APPENDIX N

RECOMMENDED VALUES FOR THE SOLUBILITIES OF OXYGEN AND HYDROGEN IN SODIUM

N.1 INTRODUCTION

Two elements of primary concern in sodium characterization on test loops and reactor systems are oxygen and hydrogen. Both are controlled by cold trap purification systems.

Methods for their measurement by both on-line meters and laboratory analyses are included in the preceding pages.

In order to establish a common basis for data comparison throughout the LMFBF community, the presently accepted solubility information is presented. As techniques for sodium sampling and analysis have become more sophisticated, the solubility data of different experimenters have converged and the absolute values have decreased for a given temperature. The most recent work is assessed and "best" values are specified.

N.2 DISCUSSION

N.2.1 Oxygen Solubility. Oxygen solubility has been measured by a number of investigators and several different reviewers have made correlations. The latest of these, and in our opinion the best, is that of Smith. He has combined his distillation results with those of Rutkauskas and Noden and Bagley's high temperature mercury amalgamation data to yield the equation

$$\log_{10} C_{\text{ppm}} = 7.0058 - 2820.1/T(^{\circ}\text{K})$$

which is similar to those obtained by Eichelberger and Noden. The difference between Smith's and Eichelberger's equation is not significant for most engineering purposes, but may be important in some thermodynamic calculations where high temperature solubility limits are required.

N.2.2 Hydrogen Solubility. Hydrogen solubility measurements have been in such poor agreement that the data of Meacham was taken as the standard. Recently, however, Vissers of Argonne National Laboratory have done additional solubility measurements in the low temperature region where Meacham's data was lacking. An equation combining Vissers' and Meacham's data is therefore recommended, since it is the most recent and the only low temperature work available.

$$\log_{10} C_{\text{ppm}} = 6.067 - 2880/T(^{\circ}\text{K})$$

Vissers' equation agrees well with the unpublished work of Rhode and Hissink.

N.2.3 Accuracy of Values. Since no accuracy of precision indications have been specified by the authors of the oxygen and hydrogen solubility curves, it is difficult for the user to assign error limits. The tabular values, Tables I and II, are computed to two or three significant figures implying an accuracy of 5 percent or better. This is undoubtedly optimistic; probably none of the equations yield results any closer than ± 10 percent from the true values.

Table I. Oxygen Solubility in Sodium

Temperature °F	Temperature °C	Solubility ppm	Temperature °F	Temperature °C	Solubility ppm
210	99	.27	610	321	182
220	104	.34	620	327	200
230	110	.44	630	332	220
240	116	.56	640	338	245
250	121	.71	650	343	270
260	127	.90	660	349	300
270	132	1.12	670	354	330
280	138	1.40	680	360	360
290	143	1.72	690	366	390
300	149	2.1	700	371	420
310	154	2.6	710	377	460
320	160	3.1	720	382	500
330	166	3.8	730	388	550
340	171	4.5	740	393	590
350	177	5.4	750	399	640
360	182	6.5	760	404	700
370	188	7.7	770	410	750
380	193	9.1	780	416	810
390	199	10.7	790	421	880
400	204	12.6	800	427	950
410	210	14.7	810	432	1020
420	216	17.2	820	438	1090
430	221	20.0	830	443	1170
440	227	23	840	449	1260
450	232	27	850	454	1350
460	238	30	860	460	1440
470	243	35	870	466	1540
480	249	40	880	471	1650
490	254	46	890	477	1760
500	260	52	900	482	1870
510	266	59	910	488	1990
520	271	67	920	493	2120
530	277	75	930	499	2250
540	282	85	940	504	2390
550	288	95	950	510	2500
560	293	107	960	516	2700
570	299	119	970	521	2900
580	304	133	980	527	3000
590	310	148	990	532	3200
600	316	164	1000	538	3400

Table II. Hydrogen Solubility in Sodium

Temperature °F	°C	Solubility ppm	Temperature °F	°C	Solubility ppm
210	99	.021	610	321	16.6
220	104	.027	620	327	18.4
230	110	.035	630	332	20
240	116	.045	640	338	23
250	121	.057	650	343	25
260	127	.073	660	349	27
270	132	.091	670	354	30
280	138	.114	680	360	33
290	143	.141	690	366	36
300	149	.174	700	371	39
310	154	.21	710	377	43
320	160	.26	720	382	47
330	166	.32	730	388	51
340	171	.38	740	393	56
350	177	.46	750	399	60
360	182	.55	760	404	65
370	188	.66	770	410	71
380	193	.78	780	416	77
390	199	.92	790	421	83
400	204	1.08	800	427	89
410	210	1.27	810	432	96
420	216	1.49	820	438	104
430	221	1.73	830	443	111
440	227	2.0	840	449	120
450	232	2.3	850	454	128
460	238	2.7	860	460	137
470	243	3.1	870	466	147
480	249	3.5	880	471	157
490	254	4.0	890	477	168
500	260	4.6	900	482	179
510	266	5.2	910	488	191
520	271	5.9	920	493	200
530	277	6.7	930	499	220
540	282	7.6	940	504	230
550	288	8.5	950	510	240
560	293	9.6	960	516	250
570	299	10.7	970	521	280
580	304	12.0	980	527	290
590	310	13.4	990	532	310
600	316	14.9	1000	538	330

APPENDIX O

DETERMINATION OF CARBON, HYDROGEN, AND OXYGEN IN SODIUM BY A SIMULTANEOUS EQUILIBRATION METHOD USING VANADIUM WIRE, SCANDIUM TABS, AND IRON-MANGANESE TABS, RESPECTIVELY

0.1 PRINCIPLE

Vanadium wire, scandium tabs, and Fe-12Mn tabs are immersed in flowing sodium at 750°C (1382°F) until the materials have equilibrated with the elements of interest. Twenty-four hours has been established as satisfactory for equilibrating the three materials. Subsequently, the concentration in the metal specimens is measured and the concentrations of active species of carbon, hydrogen, or oxygen is calculated.

0.2 SENSITIVITY AND PRECISION

This procedure is applicable for oxygen, hydrogen, and carbon in sodium in the ranges 0.1 to 15 ppm, 0.06 to 0.5 ppm, and 0.15 to 23* ppm, respectively. The precision is expected to be within ± 10 percent.

0.3 APPARATUS

Equilibration Module. Fig. O-1 is a schematic drawing of the multi-purpose sampler for use on reactors and large sodium systems. The sampler shall conform to the requirements of RDT C 8-8. Optional devices are shown in Procedures 12, 34, and 35.

Analyzers. The LECO Carbon-Oxygen Determinator and LECO Hydrogen Determinator have been found suitable for the analysis function. Other inert-gas or vacuum-fusion apparatus should also prove satisfactory.

Electropolishing Apparatus. This apparatus consists of a 3 to 4 cm diameter by 7 cm long hollow platinum or tantalum cathode plus a 6.0 to 7.5 V low-impedance d-c power supply.

Forceps. Dissecting forceps.

0.4 MATERIALS

Accelerator. Iron metal accelerator, LECO Catalog No. 501-077, has been found satisfactory for this use.

Accelerator. Tin metal accelerator, LECO Catalog No. 25705, has been found satisfactory for this use.

*Using Longson-Thorby carbon solubility, $\log S_C \text{ ppm} = 7.2 - \frac{5445}{T (^{\circ}\text{K})}$

Fig. 0-1. Multipurpose Sampler

Carbon Standard. National Bureau of Standards Type 335 Steel (0.1 percent carbon) has been found suitable.

Electropolishing Solution. This solution is composed of 80 percent by volume absolute methanol - 20 percent by volume concentrated sulfuric acid. Add the acid to the alcohol slowly with stirring.

Ethanol. U.S.P. or reagent grade absolute ethanol.

High-Purity Vanadium Wire. 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 ppm total metallic impurities (Ti + Zr + Hf shall be <20 ppm), <300 ppm total of oxygen, nitrogen, hydrogen, and carbon (none of which shall be >150 ppm). 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 under the conditions described in paragraph A2.8 of ASTM A 510, which states in part:

"One end of the specimen is clamped in a vise or bending machine, the jaws of which are rounded to a specific radius, and the wire is bent back and forth at a uniform rate through a total of 180°. Each 90° movement in either direction is counted as one bend."

Hydrogen Standard. Titanium analyzed sample, LECO Catalog No. 762-741 has been found suitable.

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

Oxygen Standards. Approximately 100 ppm and 300 ppm oxygen in steel. LECO Oxygen Standards, Stock Numbers 501-645 and 501-646 have been found satisfactory.

Standard Fe-12Mn Tabs. Annealed, 5 mil thick x 1 inch wide x 1 inch long. Suitable 5 mil thick x 1 inch wide strip stock has been supplied by the Materials Research Corporation.

Standard Scandium Tabs. 10 mil thick x 1/8 inch wide x 3/4 inch long, prepared from 99.9 percent scandium sheet. Suitable 10 mil x 2 inch wide sheet has been supplied by Research Chemicals, a Division of Nucor Corporation.

0.5 PROCEDURE

0.5.1 Sample Preparation and Equilibration. The individual preparation requirements are presented in Procedures 12, 34, and 35 for handling vanadium wire, Fe-12Mn tabs, and scandium tabs respectively.

0.5.2 Equilibration.

1. Insert the sample holder into the sodium system.
2. Establish the required sodium flow. (For the MPS, a flow of at least 0.25 gpm is required. Normally 0.3 to 0.4 gpm is used.)
3. Equilibrate the samples at the required flow rate for a minimum of 24 hours at $750 \pm 2^{\circ}\text{C}$ ($1382 \pm 5^{\circ}\text{F}$).

0.5.3 Post Exposure Treatment.

1. Turn off heaters.
2. Shut off sodium flow by closing inlet valves.
3. Pressurize the sampler with inert gas forcing sodium out of the sampler area.
4. Close outlet sodium valve.
5. Remove the sample holder from the sampler and transfer to an inert gas glovebox.
6. Clean off residual sodium and prepare for analysis as described in Procedures 12, 34, and 35.

0.5.4 Final Determination. Carry out the instructions for each individual sample material as described in Procedures 12, 34 and 35.

0.6 CALCULATIONS

Follow the calculational formulas included in Procedures 12, 34 and 35.

APPENDIX P

DETERMINATION OF SULFUR IN SODIUM

P.1 PRINCIPLE

Sodium metal is dissolved in an alcohol-water solution. Sulfur is distilled from the acidified solution as hydrogen sulfide and the sulfide measured colorimetrically as methylene blue.

P.2 SENSITIVITY AND PRECISION

The detection limit is 1 μg sulfur (0.2 ppm in a 5 g sample.) Determinations on replicate samples are expected to agree within 25 percent at the 5 μg level.

P.3 APPARATUS

Distillation apparatus. See Fig. P-1.

Argon supply.

Spectrophotometer. A grating instrument equipped with 4 cm or 5 cm cells.

Inert atmosphere glove box.

Safety shield. Lucite plate with stand to protect analyst during dissolution of sodium.

Syringe. At least 1/2 ml capacity, with steel needle to penetrate rubber stopper of sulfide standard storage vessel.

P.4 MATERIALS AND REAGENTS

Water. Distilled or deionized.

Hydrochloric Acid. Reagent grade, approximately 1:4.

Ethanol. Reagent grade, absolute.

Sodium hydroxide. Reagent grade, 0.1 N.

Thymol blue. 0.05% in methanol or ethanol.

Mixed acid. 250 ml conc. HCl and 25 ml conc. H_3PO_4 diluted to 500 ml.

"Diamine" solution. Dissolve 0.6 g N,N-dimethyl-p-phenylene-diamine sulfate (Eastman #1333) in 200 ml of cool sulfuric acid (diluted 2 parts conc. sulfuric acid to 1 part water), add 1.1 g ferric chloride dissolved in 40 ml 1:1 HCl, and dilute to 250 ml.

Fig. P-1. Distillation Apparatus

Sulfate standard, 200 ppm. Wash crystals of sodium sulfide ($\text{Na}_2\text{S} \cdot 9 \text{H}_2\text{O}$) with water and blot dry. Dissolve 150 mg sodium sulfide in 100 ml of 0.1 N NaOH. 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.

P.5 PROCEDURE

1. Working in the inert atmosphere glove box, place a weighed 1 to 3 gram sodium sample into the dissolution flask. Cover the flask tightly with aluminum foil. (Note: If a section of bypass tubing is used, the weight of sodium may be estimated with sufficient accuracy by measurement of the length. A fresh cut should be made at each end of the tube section and the tubing should have recently been cleaned with toluene or should be filed bright before cutting.
2. Prepare the apparatus by flushing thoroughly with dilute HCl, then water. Rinse the reservoir with a few milliliters of ethanol. Turn on the condenser cooling water. Turn on the argon purge and adjust to about 1000 ml/min. Place 25 to 75 ml (depending upon sample size) absolute ethanol in the reservoir.
3. Transfer the flask from the glovebox and attach quickly to the apparatus, minimizing the amount of air entering the flask. Purge with argon for 5 minutes.
4. Put the safety shield in place.
5. Place an ice bath under the dissolution flask. Adjust the argon purge to about 250 ml/min.
6. Slowly drain the alcohol from the reservoir onto the sodium. Do not allow air to enter the flask. When the sodium is nearly dissolved, the reaction will slow considerably. The ice may then be removed. Put 50 ml water in the reservoir. Add water from the reservoir into the flask, a little at a time, keeping the reaction proceeding smoothly and slowly until the sodium is all dissolved.
7. When the reaction is complete, add the remaining water. Dry the outside of the flask.
8. Place 5 ml 0.1 N NaOH in a plastic test tube and attach as a gas scrubber.
9. Add to the reservoir 3 drops thymol blue indicator and an amount of mixed acid to neutralize the NaOH in the flask (7-1/4 ml per gram of sodium) plus 3 ml excess.
10. With the argon purge at about 250 ml/min, drain the acid from the reservoir into the flask. Follow with about 5 ml water. The indicator should color the solution a flesh pink. If no pink color is present, add more acid.

11. Place a heating mantle under the flask and heat for 10 to 15 minutes or until the solution is refluxing at the rate of one or two drops per second. Then turn off the heat and continue the argon purge for a total of 30 minutes.
12. Remove the scrubber and note the volume of solution. If the volume 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, too high a setting on the heating mantle variac, or excessive argon purge during refluxing.
13. Place the scrub solution in a 25 ml graduate, add water to 21 ml, transfer to a 50 ml beaker containing a stirring bar and add 4 ml diamine solution while stirring. Wait 15 minutes, read vs. water in a 4 cm cell at 750 mu. By comparison with the standard curve, determine μg sulfur.

P.6 PREPARATION OF STANDARD CURVE

Remove about 1/2 ml sulfide standard solution from the storage flask with a syringe and place it in a small dry test tube. Immediately pipet 0, 10, 25, and 50 lambda aliquots into beakers containing 5 ml 0.1 N NaOH. Add 16 ml water to each, then 4 ml diamine solution, while stirring. After 15 minutes, read in 4 cm cells versus water at 750 mu. Plot optical density versus μg sulfide.

P.7 DETERMINATION OF YIELD

Prepare a sample as in step 1. Prepare the apparatus as in step 2 but do not place ethanol in the reservoir. Place 2 ml ethanol in a 5 ml beaker and pipet 25 lambda of sulfide standard into this. Transfer to the reservoir with 3 ml alcohol rinse. Continue as in steps 3, 4, and 5 above. Carefully drain the alcohol from the reservoir into the flask, rinsing with another 2 ml alcohol. Make sure that the alcohol contacts the sodium sample. Allow a few minutes for reaction. Then add 25 ml to 75 ml alcohol to the reservoir and continue the analysis as in steps 6 - 13.

By comparison with the standard curve, determine μg sulfide recovered, then calculate yield:

$$\text{Yield} = \frac{\mu\text{g S found in spiked sample} - \mu\text{g S found in sample}}{\mu\text{g S in spike}}$$

P.8 CALCULATION OF PPM S IN SODIUM SAMPLE

$$\text{ppm S in sample} = \frac{\mu\text{g}}{\text{g sample} \times \text{yield}}$$

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MASTER

RDT Standard

CLEANING and CLEANLINESS REQUIREMENTS FOR NUCLEAR REACTOR COMPONENTS

March 1969

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Division of Reactor Development and Technology
United States Atomic Energy Commission

CLEANING AND CLEANLINESS
REQUIREMENTS FOR NUCLEAR REACTOR COMPONENTS

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CLEANING AND CLEANLINESS
REQUIREMENTS FOR NUCLEAR REACTOR COMPONENTS

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1.   SCOPE

1.1   This standard covers minimum requirements for cleaning and cleanliness of vessels, heat exchangers, pumps, piping, valves and other fabricated components for nuclear service. The standard does not cover cleaning of reactor fuel elements, in-place cleaning of installed systems or components or mill products.

1.2   The supplier furnishing components that meet the cleanliness requirements of this standard shall be responsible for ensuring that all items furnished by his subcontractors conform to the requirements of this standard.

2.   APPLICABLE DOCUMENTS

2.1   The following documents are a part of this standard to the extent specified:

RDT-F2-2	(March 1969) Quality Control System Requirements
RDT-F7-2	(March 1969) Preparations for Sealing, Packaging, Packing and Marking of Components for Shipment and Storage
USAS A11.1-1965	Practice for Industrial Lighting
ASTM D 512-67	Tests for Chloride Ion in Industrial Water and Industrial Waste Water
ASTM D 1125-64	Tests for Electrical Conductivity of Industrial Water and Industrial Waste Water
ASTM D 1192-64	Specification for Equipment for Sampling Industrial Water and Steam

2. APPLICABLE DOCUMENTS (Cont'd)

ASTM D 1293-65	Tests for pH of Industrial Water and Industrial Waste Water	•
26 CFR-212	Code of Federal Regulations - Title 26, Internal Revenue, Chapter 212, Denaturing of Alcohol and Rum	

3. REQUIREMENTS

3.1 Definitions - For the purposes of this standard, the following definitions are applicable:

- (a) Chemical Reagents. All reagents referred to in this standard shall be of technical grade or better unless otherwise specified.
- (b) Clean Room. A room into which conditioned and filtered air is passed and maintained at a slight positive pressure and in which a high degree of housekeeping is exercised so that production and assembly work can be carried on under clean conditions.
- (c) Clean Area. (1) a clean space located in a clean building; or (2) a clean tent or partitioned area with a filtered air supply; or (3) a clean plastic bag or sleeve pressurized with dry filtered air or inert gas; or (4) an enclosed space where the area is inherently clean and the air is free of foreign particles.
- (d) Component. A part, combination of parts, subassembly or complete assembly.
- (e) Contamination. Grit, metal particles, oil, grease, slag, scale, film and fiber.
- (f) Coolant Surfaces. Those surfaces that are exposed to reactor coolant.

3. REQUIREMENTS (Cont'd)

- (g) Corrosion-Resistant Material. Materials, such as chromium-nickel stainless steel, nickel-base and cobalt-base alloys, and precipitation-hardened stainless steel, that inherently resist oxidation or chemical attack in air, water and the operating environment.
- (h) Crevice. Any narrow opening in a surface or any open juncture between mating surfaces in which dirt or liquids can be trapped and not readily removed; including the annular space in threaded connections, socket weld assemblies, tube-to-tube sheet joints, tube-to-tube support joints, grooves and press-fit joints.
- (i) Denatured Alcohol. Ethyl alcohol that has been denatured in accordance with formula 23A of 26CFR-212.
- (j) Critical Surfaces. Surfaces, such as small orifices, bearings, bellows, journals, seating surfaces and tubing of thickness equal to or less than 1/8 in., which when corroded or otherwise roughened can impair the function or cause the component to become inoperable.
- (k) Filter Cloth. Cloth through which flushing water is passed to determine the acceptability of a flush. A bleached cotton fabric of "nainsook" (muslin) construction that weighs between 2.8 and 3.2 oz. per square yard (when new) and has approximately 80 to 100 yarns per inch in both the warp and fill directions.
- (l) Final Cleaned Surface. The surface condition after all surface finishing and cleaning operations have been performed prior to placing the surface in service.

(m) Flushes.

- (1) Once-Through. Where water is introduced, flushed through a component under pressure at a prescribed velocity, and discharged from an outlet through a filter cloth.
- (2) Recirculating. Where a single batch of water is recirculated under pressure at a prescribed velocity in a closed path through a strainer in the flushing system.
- (3) Proof. A flush to demonstrate that a component is free of gross contaminants.

(n) Inaccessible Areas. Areas or openings in a component that are not readily accessible for cleaning or inspection during or after fabricating, and where dirt, liquids or other contaminants may be trapped during fabrication.(o) Noncorrosion-Resistant Material. Materials, such as martensitic chromium stainless steels, carbon steels and low-alloy steels that inherently do not resist oxidation or chemical attack in air or water.(p) Rust. Corrosion products, consisting largely of hydrous ferric oxide, formed on the surface of iron and iron-base alloys. Such oxides may vary in color from red to black and may form a loosely adherent heavy covering to a tightly adherent light film. Pitting or general surface roughening may or may not be present.(q) Water Grades. The requirements for the various water grades to be used in conjunction with this standard are summarized in Table 1.

TABLE 1. WATER GRADES^{ab}

Property	Grade		
	A	B	C
Chloride, maximum ppm	0.1	1.0	25.0
Conductivity, maximum micromhos/cm	2.5	20.0	400.0
pH range	6.0 to 8.0	6.0 to 8.0	6.0 to 8.0
Visual clarity	No turbidity, oil or sediment		

^a Power plant condensate and distilled water may meet the requirements for Grade B water. Demineralized water may meet the requirements for Grade A water. Where water has been subjected to possible CO₂ absorption, such as when retained in storage tanks, the pH requirement may be lowered to 5.8 to compensate for CO₂ pickup. Where a particular grade of water is specified in this standard (such as rinse with Grade C) it shall be understood that the use of the next higher grade is acceptable (such as rinse with Grade A or B).

^b For referee purposes, water property determinations shall be made in accordance with the ASTM standards listed in paragraph 2.1.

3.2 Cleanliness and Cleaning

3.2.1 General - The fabrication of components shall be conducted so as to facilitate cleaning and inspection for cleanliness and to minimize contamination during fabrication. Surfaces shall be clean and shall be maintained in a clean condition up to and including assembly into the component. Components supplied in accordance with this standard shall be suitable for installation into nuclear systems without additional cleaning. Components which do not meet the requirements of this standard shall be subject to rejection.

3.2.2 Cleaning Procedures - When required by the purchaser, the supplier shall submit detailed in-process and final cleaning procedures to the purchaser for approval, which shall include:

- (1) The general cleaning procedures to be employed;
- (2) Descriptions and drawings designating inaccessible areas and critical surfaces involved;
- (3) Specific cleaning methods to be employed for inaccessible areas and critical surfaces;
- (4) Precautions to be taken before, during and after assembly to maintain cleanliness of incoming materials, components and the completed item through final preparation for delivery;
- (5) Required purity levels of cleaning reagents, solvents and lubricants;
- (6) Flushing procedures, where proof flushing is required by the purchaser;
- (7) Quality control and inspection procedures to be employed during and after cleaning operations and fabrication, to ensure that the purchaser's requirements have been met;
- (8) Acceptance standards for contamination and rust on components and equipment where such criteria are not contained in this standard;
- (9) Drying methods to be employed on cleaned equipment;
- (10) Inhibitors employed for minimizing corrosion when applicable and procedures for their removal;
- (11) Base metal or metals covered by the procedure;
- (12) Application tests which are necessary prior to the cleaning operation to avoid deliterious effects on components or assemblies containing differing materials;
- (13) Precautions to be taken during the cleaning operation to avoid deliterious effects on components or assemblies containing differing materials, e.g., swelling of elastomers, etc.;
- (14) A list and description which specifically identifies the equipment to be used such as cleaning tanks, spray systems, air compressors, filters, drying ovens, tumblers, sand blasting units, etc.

3.2.3 Acceptance Criteria for Cleanliness

Unless otherwise specified, components shall be clean to the extent that no contamination of any surface is visible to a person with normal visual acuity, natural or corrected. Lighting in inspection areas shall provide a lighting level of at least 100 foot candles on surfaces being inspected (Reference USAS All.1). A wiping technique shall be used to determine the cleanliness of surfaces of components that cannot be visually inspected because of inaccessibility or geometry. The cleanliness of the surfaces shall be evaluated by wiping with a clean lint-free cloth, either dry or moistened (but not saturated) with alcohol or acetone. Where chemical reagents are used in the wipe cloth to test for cleanliness, they should not contain more than 30 ppm non-volatile residue. Appearance of contaminants on the cloth shall be cause for rejection. Components that do not meet these requirements shall be recleaned.

3.2.3.1 Rust-Surfaces not Exposed to Liquid Metals

- (1) Temper Films - Irridescent temper films resulting from heat treatment and tightly adherent black oxide films that occur on the backside of welds need not be removed.
- (2) Rust on Critical Surfaces - If rusting occurs on critical surfaces or surfaces that will be exposed to reactor coolants, the surface shall be cleaned to remove the rust or rust-producing condition and any visible surface contamination. Its complete removal shall be checked for residual contamination by the wet cloth test. This test consists of covering or wrapping the area in question with a clean cloth that has been moistened with Grade A water. If no rust occurs within 6 hours, the surface shall be considered satisfactory. If, after the wet cloth test, there are rust spots that can be removed by wiping with a clean dry cloth, and corrosion pits are not visible, the surface shall be considered acceptable when all

rust has been removed. The occurrence of rust on clean corrosion-resistant material may indicate that something is wrong with the material (for example, improper heat treatment or material composition), and the cause of the rust should be determined.

- (3) Rust on Non-Critical Surfaces - Thin films of rust are acceptable on noncritical corrosion resistant material surfaces (those surfaces not included in 3.2.3.1(2), provided there is no visible evidence of corrosion pitting and the total area involved does not exceed 1% of the estimated total surface of the components.

Thin films of rust are defined as superficially corroded areas of red, brown or black discoloration. The rust observed may be either localized or general; that is, the rust may be present in spots or streaks or as a continuous film. Where localized rusting is involved, the total included area (the rusted area plus the included unrusted area) shall be used to determine the percentage involved rather than the actual area observed. These films of rust are not necessarily adherent. In many cases, it may be possible to remove the rust by rubbing with a clean dry cloth.

- (4) Pitting - The following criteria shall be used to determine if pitting has occurred, and the presence of one or more of these conditions shall provide the basis for rejection or repair.

These criteria are:

- (a) The presence of pit-like indications in which the voids are visible;
- (b) The buildup of corrosion products in a circular manner outlining the area of the pits (actual void of pit may not be visible); this type of buildup is usually considerably thicker than the surrounding rust and is almost always associated with pitting;
- (c) The presence of annular rings of discoloration surrounding the core of the pit (these rings do not usually show any visible thickness; however, they are generally of different colors).

- (5) Rust on Non-Corrosion Resistant Materials - Acceptance criteria for rust on carbon and low-alloy steels shall be specified by the purchaser. Slight rusting is occasionally observed in the neighborhood of backup rings, socket weld joints, canopy welds and similar parts, where welding slag entrapment causes rusting as a result of exposure to water. Unless otherwise specified, rust observed in such areas should not normally be considered detrimental provided the rust occurring in such areas is uniform in appearance and shows no visible thickness. Such forms of rust usually do not extend more than 1/2 inch from the area where slag entrapment has occurred.

3.2.3.2 Rust-Surfaces Exposed to Liquid Metals

The final cleaned surface shall be free of pitting, corrosion products and oxides, except that irridescent temper films resulting from heat treatment and tightly adherent black oxide films that occur on the back side of welds need not be removed.

3.2.4 Clean Room and Clean Area

3.2.4.1 Requirement for Use - A clean room or clean area shall be employed starting with that stage of fabrication where final critical surfaces or surfaces that will be exposed to reactor coolant are no longer accessible for further cleaning or inspection.

3.2.4.2 Clean Room - The clean room shall consist of a complete enclosure in which windows and doors are tight fitting. The air supplied to these rooms shall be clean and filtered to obtain the amount of cleanliness as could be expected in a normal business office. The walls may be constructed of standard structural materials and shall be painted to minimize dirt pickup and facilitate cleaning. Personnel working continuously in such areas shall wear clean coveralls or smocks without pockets, buttons or badges and similar items. Where dirt may be brought in from the outside, preventive measures

3.2.4.2 Clean Room (Cont'd)

such as shoe covers, shall be employed. In general, the room shall be free of dirt and debris and shall be maintained in a condition comparable to that which is normally expected in a business office or home. Any more stringent requirements than those stated herein shall be specified by the purchaser.

3.2.4.3 Clean Area - Where it is impractical to provide a clean room, the same type of operation may be performed in areas temporarily established for a specific job. These are called clean areas.

3.2.5 Water Used for Engineering Tests

Unless otherwise specified by the purchaser, Grade A, B or C water may be used for engineering tests conducted at water temperatures below 150 F (e.g., hydrostatic and performance tests). When Grade C water is used, it shall be drained immediately after completion of the test. The component shall then be flushed immediately with Grade A or B water.

Grade A or B water shall be employed for engineering tests above 150 F and the Grade B minimum purity shall be maintained throughout the tests except for the following:

- (1) For liquid metal system components, engineering tests at water temperatures above 150 F shall employ Grade A water. The effluent water may be permitted to degrade to a maximum conductivity of 5 micromohos per cm. After completion of the test, the component shall be thoroughly dried to ensure the complete removal of all water.
- (2) Grade C water may be used for such tests on nickel-chromium-iron alloy (alloy 600) items (where Grade C water is used, the component shall be drained and flushed with Grade A or B water).

3.2.6 Precautions

3.2.6.1 - For unstabilized austenitic stainless steel which may have been sensitized by exposure to temperatures in the range 800 F to 1600 F, precautions shall be taken to avoid intergranular attack in the sensitized region, e.g., attack by oxidizing agents such as nitric acid and attack by halide bearing environments such as salt air.

3.2.6.2 Welding and Brazing - Precautions shall be taken to control spatter and to remove smoke produced by welding and brazing operations. Anti-spatter and rust-preventive compounds shall be removed from the joint preparation and for at least 1-inch back from the joint preparation to avoid contamination of the weld. Flux, weld spatter and other contaminants shall be removed immediately after completion of the weld.

3.2.6.3 Exposure to Contaminated Atmospheres - Metals and components shall be protected from the general shop atmosphere, or other contaminated atmospheres such as salt air or blowing dust, insofar as possible during fabrication and temporary storage.

3.2.6.4 Heating - Precautions shall be taken to prevent contamination of surfaces prior to and during heat treatment, welding, hot forming and other high temperature operations. Quenching shall be performed with Grade C water or better.

3.2.6.5 Use of Lubricants - A lubricant may be employed during machining, fabrication and assembly operations provided the lubricant does not contaminate any crevices or inaccessible areas that cannot be subsequently cleaned. In those cases where machining, fabrication or assembly must be performed on components containing crevices and normal precautions will not prevent entry of lubricant into these crevices, only Grade A or B water or a lubricant approved by the purchaser shall be used. The lubricant or water shall be removed immediately following the operation in which it is used. Only Grade A water or a lubricant approved by the purchaser may be used for liquid metal system components.

3.2.6.6 Mercury Restrictions - Manometers, vacuum pumps, or other instrumentation or equipment containing mercury or mercury compounds shall not be used.

3.2.6.7 Handling of Components - In general, cleaned surfaces may be handled with clean hands; however, in final-production handling of critical surfaces, clean lint-free gloves shall be used. Handling equipment in contact with internal surfaces shall be made of corrosion-resistant or chromium plated steels.

3.2.6.8 Exclusion of Foreign Materials - During fabrication, extreme care shall be taken to prevent contamination by foreign material. Temporary plugs or seals conforming to RDT F7-2 shall be installed to keep contaminants out of the clean component during subsequent fabrication and storage. Precautions shall be taken to prevent temporary plugs, seals or other items from being inadvertently left in the component. Special attention shall be given to clothing worn while working on clean components in which there are openings. Precautions shall be taken to eliminate the possibility of accidental loss of articles such as buttons, badges, jewelry, pencils, pens, coins, spectacles, dentures, hearing aids, respiratory filters, tools and other objects in the component. An inventory control shall be instituted for all tools, cleaning clothes and equipment small enough to fit inside component openings. Where necessary, these articles should be attached to the user or a fixed object by a lanyard and shall be accounted for at all times.

3.2.6.9 Lead, Sulfur and Aluminum - Lead or lead compounds, sulfur or sulfur compounds, or materials containing lead or sulfur as a basic chemical constituent shall not be used in direct contact with the final cleaned surface of nickel base alloys.

Aluminum shall not be used either as soft pads or hammers to reduce marring during assembly and handling of nickel-base or stainless steel alloy components. Aluminum pipe caps and seals shall not be used on stainless steel or nickel-base alloy components. Zinc shall not be allowed to come in contact with final cleaned stainless steel.

3.2.6.10 Pipe Joint Compounds and Sealers - Pipe joint compounds, teflon tape or sealers, other than colloidal graphite in isopropanol (neolube or equivalent) to prevent galling, shall not be used in making up temporary or permanent joints of flushing systems or other attachments to the component unless approved by the purchaser. Teflon-inserted jam nuts may be used to seal threaded connections only in temporarily installed support systems and under the following conditions:

- (a) At ambient temperatures with pressures up to 3750 psig;
- (b) At temperatures less than 300 F with pressures up to 2000 psig.

3.2.6.11 Corrosion Inhibitors - Corrosion inhibitors shall not be allowed to come in contact with materials intended for coolant surfaces; however, inhibitors may be employed for minimizing corrosion of metals and parts intended for noncritical applications during fabrication, shipment and storage and installation.

3.2.6.12 Paint on Corrosion-Resistant Materials - Painting of corrosion-resistant materials is prohibited. If paint has been inadvertently applied to corrosion-resistant materials, it shall be removed by rinsing in acetone, denatured alcohol or Freon PCA (or its equivalent). If these methods fail, the paint shall be removed by simple mechanical cleaning using stainless steel tools or brushes. Following mechanical cleaning, the component shall be washed with Grade A water.

3.2.7 - Cleaning Process

3.2.7.1 Cleaning agents and solvents shall be technical grade or better. Unless otherwise approved by the purchaser, halogenated cleaning agents and solvents shall not be permitted on austenitic stainless steels.

3.2.7.2 Safety - Some of the materials required for use in this standard are hazardous. Every precaution shall be taken to protect personnel from materials that may present fire hazards, cause burns and skin irritations, or have a toxic effect when breathed. Local safety organizations shall be consulted for specific instructions.

3.2.7.3 Mechanical Cleaning - Mechanical cleaning shall be performed in such a manner that particles will fall away from the equipment to preclude particles from entering the component. Where mechanical cleaning cannot be performed in a manner that particles fall away from the equipment, a vacuum hose or dirt catcher shall be employed. A vacuum hose may also be employed near the work to remove fine airborne particles. Completed components shall be cleaned as required to remove any particles resulting from operations such as grinding, polishing, filing, deburring and brushing.

- (1) Mechanical cleaning tools such as grinding, polishing, filing, deburring and brushing tools shall be clean and shall not have been used on aluminum, copper, lead or materials containing lead or lead compounds, or other low melting point materials. Separate sets of tools shall be maintained and used as follows:
  - (a) One set of tools shall be used on carbon and low alloy steels only
  - (b) One set of tools shall be used on corrosion resistant materials only.

In order to preclude contamination of corrosion resistant materials with free iron, these tools shall not have been previously used on carbon or low alloy steel materials. These sets of tools shall be clearly marked to identify their intended use in accordance with a system specified by the activity performing work and shall be segregated according to their intended use.

- (2) Grinding and Polishing - Grinding and polishing shall be performed with resin or rubber bonded aluminum oxide or silicon carbide grinding wheels or discs that will assure a cleanly cut surface. Only resin-bonded aluminum-oxide grinding tools shall be used on stainless steels.
- (3) Brushing - Brushing shall be performed with clean, corrosion resistant steel brushes. Power-operated wire brushes shall not be used on seal membranes or seal welds. Power driven wire brushes shall not be used for cleaning components which will be liquid penetrant inspected unless the brushed surfaces are ground or machined prior to liquid penetrant inspection.
- (4) Filing and Deburring - Filing and deburring shall be performed with carbide or tool steel tools.
- (5) Abrasive Blasting - Abrasive blasting shall be used only when approved by the purchaser. Surfaces which have been cleaned by abrasive blasting shall be subsequently acid cleaned.
- (6) Tumbling - Tumbling may be used only when approved by the purchaser. In order to preclude obscuring material defects, tumbling shall not be used on surfaces which are subsequently to be liquid penetrant inspected, except when followed by machining or grinding. The tumbling equipment shall be thoroughly cleaned of materials used in previous operations. After the tumbling operation, the surfaces shall be cleaned with a tampico or stainless steel brush, rinsed with Grade C or better water, and then rinsed with Grade A water.

3.2.7.4 Degreasing - Surfaces containing no crevices or inaccessible areas may be cleaned and degreased by any of the following procedures. Surfaces containing crevices shall be cleaned using only unused or redistilled acetone, or alcahol.

3.2.7.4 Degreasing (Cont'd)

- (1) Vapor Degreasing - Vapor degreasing may be used on surfaces containing no crevices, or inaccessible or non-drainable areas and shall be accomplished by the following methods.

- (a) All components that enter the degreaser shall be dry.
- (b) Components shall be loaded onto racks in the condensing zone so that they do not touch each other, and in such a manner as to ensure complete draining of solvents.
- (c) Maintain baths as follows:

Perchloroethylene, operate at 250 to 260 F

Trichloroethylene, operate at 185 to 195 F

Note: These baths shall contain a neutral inhibitor to prevent acid formation due to hydrolysis. Periodic testing for alkalinity is required. Other types of inhibitors are not permitted.

- (d) Change solvent when boiling point of perchloroethylene exceeds 260 F or the boiling point of trichloroethylene exceeds 195 F. Earlier dumping may be necessary if cleanliness standards are not attained.
  - (e) Lower or raise components in the degreaser at a rate not to exceed 12 inches per minute, and immerse in vapor phase. Spray with clean solvent during immersion time. Keep the spray nozzle at least one foot below the vapor line during spraying.
  - (f) Allow the item to remain in the vapor until condensation ceases (3 to 5 minutes). Components shall be completely dry before removing from degreaser.
- (2) Degreasing by Immersion or Wiping - Degreasing of components that have no inaccessible areas or crevices may be performed by immersion in solvent or by wiping with a clean wiping cloth that has been saturated with the solvent (perchloroethylene, trichloroethylene, unused or redistilled acetone, ethanol, isopropanol or Freon PCA or its equivalent). Dry in accordance with Section 3.2.8.

-
- (3) Degreasing of Crevices and Inaccessible Areas - Parts of surfaces that contain crevices or inaccessible areas shall be degreased only by immersion in unused or redistilled acetone, ethanol, isopropanol, or Freon PCA or its equivalent. Dry in accordance with Section 3.2.8.

3.2.7.5 Trisodium-Phosphate Detergent Cleaning (Degreasing) -

Trisodium-phosphate detergent cleaning may be used on surfaces that do not contain crevices or inaccessible areas and shall be accomplished as follows:

- (1) Remove heavy dirt by either scrubbing with a non-shedding bristle brush and a solution of up to one fluid ounce of non-ionic detergent (polyethyleneglycol-monalkylaryl ether) per gallon of Grade A, B or C water, or by immersing the surfaces in a hot (approximately 160 to 180 F) solution consisting of 7 to 10 ozs. of trisodium-phosphate and up to 1 fluid ounce of the non-ionic detergent per gallon for about 20 minutes. Agitate and use brush as necessary. Permissible non-ionic detergents are Triton X, Igepal, Alconox or equivalent.
- (2) Rinse components thoroughly in hot (120 F minimum) Grade A or B water. Grade C water may be used for initial rinsing; however, such a rinse shall be followed by a final rinse with Grade B or A water. The final rinse of liquid metal system components shall be with Grade A water.
- (3) Dry components in accordance with Section 3.2.8.

3.2.7.6 Acid Cleaning Requirements

- (1) Restrictions - Components that have crevices or inaccessible areas shall not be acid cleaned. Hardened steels and age-hardenable stainless steel, such as 17-4 PH, that contain nitrided surfaces shall not be acid cleaned. Non-metallic parts shall not be acid cleaned. Austenitic stainless steel weldments and materials that have not been solution annealed shall not be acid cleaned.

- (2) Conditions and Precautions - Acid cleaning shall not be used as a standard procedure and when necessary, shall be done only after purchaser approval. Any acid cleaning shall be governed by the following conditions:
- (a) Subsequent to grit or vapor blasting provided the surfaces cannot be ground and/or polished after blasting
  - (b) Where there are surfaces with hot rolled or heavy heat treatment scale that cannot be removed by blasting, grinding and polishing
  - (c) To remove non-corrosion-resistant material embedded in the surface of corrosion resistant material
- (3) All components shall be degreased prior to acid cleaning by the appropriate method in accordance with this standard. The surfaces shall be free from grease, oil and foreign matter to ensure adequate surface contact by the acid and to prevent introduction of contaminants into the acid bath.
- (4) Tubular products with an internal diameter less than 1/2 inch shall be given special attention during acid cleaning since restricted movement of the acid within the small diameter may accelerate corrosion and cause pitting. Therefore, tubular products of this size shall have the acid within its small diameter replaced at least once every minute during the entire immersion period. This may be done by raising the product out of the acid bath to allow the acid within the small diameter to drain out, after which the product is immersed again for another minute.
- (5) Types 403 and 410 non-corrosion-resistant steel shall have bearing surfaces masked off during the acid cleaning operation of the whole part. Special attention shall be given to bearing surfaces during acid cleaning in order to ensure against

(5) Cont'd

the formation of excessively rough surfaces and harmful crevices which might arise from insufficient agitation or actual contact of the surfaces with other components.

(6) Procedure

- (a) Immerse metals and components in acid solution in accordance with conditions listed in Table 2 for the particular metal involved.
- (b) If the treatment does not remove scale completely, the scale may be loosened or removed by means of grinding or grit blasting subject to requirements of 3.2.7 after which the components may be recleaned in acid.
- (c) Some means of agitation shall be provided, especially around components that contain small pockets or recessed areas in which the acid content could become depleted and thereby cause pitting.
- (d) After acid cleaning has been completed, the component shall be initially rinsed in flowing Grade C water, followed by a neutralizing wash in 5% by volume ammonia or 0.75% by weight trisodium phosphate (Na_3PO_4) solution of 4 to 6 oz. of Na_2CO_3 per gallon and then thoroughly rinsed in Grade A or B water. The components shall not be permitted to dry after the initial rinse or after the neutralizing wash. The ammonia neutralizing wash shall not be used for brass or bronze materials.

3.2.8 Drying Requirements

Drying may be accomplished by still or forced clean, dry, oil-free air or inert gas; a drying oven; or evacuation. Dew point of air or inert gas shall be as specified in the cleaning procedure (3.2.2).

Drying in preparation for delivery shall be in accordance with RDT F7-2.

3.2.8 Drying Requirements (Cont'd)

When using evacuation, care should be exercised to prevent evacuating pump lubricant from contaminating the surfaces of the metal being dried. When forced air is used, it shall be passed through a trap to remove oil and water and a clean filter to remove dirt particles before using. There shall be no water marks visible on any dried surface.

TABLE 2. ACID CLEANING METHODS

<u>Material</u>		<u>Acid Treatment</u> ^a
Type 304 ^b ELC	Stainless Steel	Treatment A
" 304 ^b	" "	Nitric acid (1.42 sp gr), 150 parts by volume
" 308 ^b	" "	Hydrofluoric acid (60%), 15 parts by volume
" 309 ^b	" "	Water, 835 parts by volume
" 316 ^b	" "	Temperature of solution, 120 to 130 F
" 347 ^b	" "	Time of immersion, 15 minutes
" 321 ^b	" "	
Precipitation hardened corrosion-resistant steel		
Cobalt-base alloys		
Hard Chromium plate		
Type 410	Stainless Steel	Treatment C
Type 403	" "	Same as Treatment A except that the time of immersion is 5 minutes
Nickel-Chromium-Iron alloys		Treatment D
		Same as Treatment A except that the temperature is between 70 and 100 F
Nickel and nickel-Copper alloys		Treatment E
		Sulphuric acid (1.83 sp gr), 95 parts by volume
		Water, 1000 parts by volume
		Sodium nitrate (crude), 1/2 lb per gallon
		Temperature of solution, 180 to 190 F
		Time of immersion, 30 minutes
Copper		Treatment F
Copper-nickel 30-70		Sulphuric acid (1.83 sp gr), 70 parts by volume
		Sodium dichromate, 2% by weight
Brass		Water, 1000 parts by volume
Bronze		Temperature of solution, 100 to 125 F
Nickel-copper alloys		Time of immersion, 30 minutes

TABLE 2. ACID CLEANING METHODS (Cont'd)

Carbon and low-alloy steel	Treatment G
	Hydrochloric acid (1.18 sp gr), 11 parts by volume
	Water, 89 parts by volume
	Inhibitor ^c , 0.3 to 0.5 % by weight
	Temperature, 120 to 150 F Time of immersion, 10 - 20 minutes

^aThe acid solutions shall be tested at frequent planned intervals by immersing scrap base metal of the type being cleaned in the solution for 20 minutes. If pitting is evident, the acid composition shall be adjusted by the addition of inhibitor to preclude pitting. After the adjustment the tests should be repeated.

^bTreatment A may be used if the items are solution annealed.

^cDowell A-73, dibutylthiourea, diethylthiourea, or their equivalents are recommended. The supplier shall obtain the approval of the purchaser before using any equivalent.

4. COMPONENT PROOF FLUSHING

4.1 Applicability These provisions apply to flushing components by the vendor when proof flushing with water is required by the applicable purchase document. The requirements and cleanliness criteria for the use of filter cloths specified herein apply only to the final flushes to demonstrate that the component is free of particulates.

4.2 Water Purity The purity of each grade of water used for flushing is defined in 3.1(q).

- (1) Water to be used for flushing shall be checked for cleanliness prior to use by filtering approximately 20 gallons of water through a filter cloth, see 3.1(k). The resulting cloth shall be completely free from foreign material. This check shall be performed immediately prior to starting the flush, and the filter cloth shall be as near as practicable to where the flush water enters the system (that is, downstream of all hoses, pipes and fittings).

- (2) The grade of water for flushing shall be as approved by the purchaser
- (3) Flushing procedures shall be sequenced and care taken to preclude flushing material from other parts of the system into large, low-velocity flow regions, such as steam generators, unless otherwise approved by the purchaser.

4.3 Filter Cloths and Strainers   A filter cloth (supported by a strainer or other appropriate means), shall be used to filter the exit water from a once-through flush, see 3.1(m)(1). An installed 30 to 50 mesh corrosion resistant strainer should be used for recirculating flushes.

Where practicable, the filtering area of the cloth through which flush water is passed shall be no larger than about 1 square foot. Cloths of larger areas are to be avoided because they reduce the density of deposit and may result in a false appearance of cleanliness.

4.4 Velocity of Flushes   The velocity of the flush shall be as specified in the detailed system flushing procedures, and if practicable, shall be equal to or slightly greater than the normal operating flow rate for the component.

4.5 Duration of Flushes   Flushes shall be of duration or quantity of water as specified in detailed flushing procedures. Flushes shall be repeated until two successive filter cloths or strainers meet the applicable clean cloth or clean strainer criteria specified in 4.6.1 and 4.6.2.

4.6 Flushing Acceptance Criteria   The acceptance criteria for flushing of components shall be in accordance with either Type I or Type II, as specified by the purchaser.

4.6.1 - Type I Flush Acceptance Criteria

Type I flush acceptance criteria shall be as follows:

- (1) The general appearance of the filter cloth shall be that of a clean white wet cloth showing no more than slight speckling and no more than slight soiling or staining of any kind from rust or dirt.
- (2) There shall be no particles on the cloth larger than 1/32 in. in any dimension, except that fine hair-like slivers or thin flakes (much less than 1/32 in. thick) may have a major dimension up to 1/16 in.
- (3) Readily apparent quantities of unusual impurities in the exit flush water or on the cloth, such as resin particles, abrasive grit, or other foreign matter, shall be reason for non-acceptance of the flush.

4.6.2 - Type II Flush Acceptance Criteria

- (1) The general appearance of the filter cloth shall be that of a clean white wet cloth showing no more than slight speckling and no more than slight soiling or staining of any kind from rust or dirt.
- (2) The strainer shall contain no particles larger than 1/16 in. in any dimension; except that fine hair-like slivers or thin flakes (much less than 1/16 in. thick) may have a major dimension up to 1/8 in.
- (3) Readily apparent quantities of oil, brazing flux, pipe dope or sealers, preservatives, or other foreign matter on the strainer or in the flush water after recirculation shall be reason for non-acceptance of the flush.

4.6.3 - Drying

Following proof flushing, components shall be dried in accordance with 3.2.8.

5. QUALITY ASSURANCE PROGRAM

5.1 Unless otherwise specified, the provisions of F2-2 "Quality Control System Requirements" shall apply in the application of the requirements of this standard.

5.2 Except as otherwise waived, facility certification shall be granted by the purchaser prior to cleaning of components.

5.3 Cleaning procedures required by 3.2.2 shall be subject to review and approval by the purchaser.

5.4 Monitoring of clean rooms, clean areas and cleaning operations and facilities, to verify that the cleanliness is in compliance with the provisions of this standard is a requirement of this standard.

5.5 Records - The supplier shall maintain a current and complete file of all records of inspection, examination and monitoring data pertaining to cleaning, clean room and clean area operation.

5.6 Access - The purchaser or his agent shall have access to any area where work associated with component cleanliness is performed and to all records pertaining to the cleaning or cleanliness of components under the contract.

6. PREPARATION FOR DELIVERY

Packaging for delivery of equipment cleaned in accordance with this standard shall meet the requirements of RDT F7-2 unless otherwise specified.

Components shall be prepared for delivery as soon as practical after cleaning, drying and examination. Rust preventive or organic material shall not be added to internal surfaces of components fabricated for liquid metal application.

6. PREPARATION FOR DELIVERY (Cont'd)

The number of removable items such as dessicant bags, pipe plugs, etc., shall be noted so that an accounting can be made in the field to prevent inadvertently introducing such items in a system. Warning notices shall be placed on the shipping container or component to specify the location and quantity of dessicants in the component, location of humidity indication cards, location of gas bottle and pressure gage, type of inert gas and location of gas bleeders.

Components shall be capable of being reinspected at destination to assure conformance to the requirements of this standard. Components that do not meet the requirements of this standard shall be rejected.

Please file in drawer

R D T S T A N D A R D

UNITED STATES ATOMIC ENERGY COMMISSION
DIVISION OF REACTOR DEVELOPMENT AND TECHNOLOGY

RDT F 3-40T

Date May 1973

Page 1 of 22

METHODS FOR THE ANALYSIS OF SODIUM AND COVER GAS

A M E N D M E N T 1

This amendment forms a part of RDT F 3-40T
dated January 1973

1. Page ii, Table of Contents: Add:

	<u>Page</u>
32. DETERMINATION OF OXYGEN IN SODIUM BY THE ELECTROCHEMICAL OXYGEN METER - AMENDMENT 1	4
33. DETERMINATION OF THE PLUGGING ("SATURATION") TEMPERATURE OF SODIUM - AMENDMENT 1	8
APPENDIX M DETERMINATION OF THE CHEMICAL ACTIVITY OF HYDROGEN IN SODIUM BY AN EQUILIBRATION METHOD USING SCANDIUM TABS - AMENDMENT 1	19
2. Page 2, 2.1, RDT Standards. Add:

RDT A 1-5T Purity Requirements for Operating Sodium Reactor Systems

RDT C 8-5T Electrochemical Oxygen Meter for Service in Liquid Sodium

RDT E 4-19T Plugging Temperature Indicator Assembly for Sodium Service
3. Page 210-212, G.3.5.5 Determination of Xe in He or Ar. Change to read:

G.3.5.5 *Determination of Xe in He or Ar*

  1. Bring the gas chromatograph to stable operation.
Typical operating parameters are a He carrier gas flow of 40 ml/min through a 3-ft-long x 1/8-in.-O.D. column packed with -40+50 mesh Linde Molecular Sieve 5A maintained at 0.C. The helium ionization detector is operated at 300 volts and its temperatures is maintained at 50 C. The electrometer range is set at 10⁻⁹ amp, full scale. The attenuator is set on the X2 scale.
  2. Prepare, using the gas handling system, two or more standards of He containing Xe at levels bracketing 0.1 ppm Xe.

3. Attach the Xe gas trap to the gas handling system, evacuate the trap and manifold to 10^{-3} torr. Isolate the trap and storage vessel from the manifold and valve off the vacuum pump.

4. Pressurize the manifold to approximately 800 torr with a standard gas mixture. Isolate the manifold and record the pressure.

5. Open the Xe gas trap stopcock for one second, then close it.

6. Chill the trap in liquid nitrogen for 15 to 20 minutes. Pump the manifold down to 10^{-3} torr and valve off the vacuum pump.

7. Open the Xe gas trap stopcock. Pump the manifold and Xe gas trap down to a pressure of 1 torr. Close the Xe gas trap stopcock.

8. Remove the trap from the manifold, connect it to the chromatograph, and heat the trap for 2 min with a heat gun.

9. Elute the sample through the chromatograph. Record the chromatogram.

10. Repeat steps 3 through 9 for each standard gas mixture.

11. Prepare a calibration curve of peak height vs ppm Xe.

12. Obtain a sampling vessel containing the gas to be analyzed. Typically, the sample will be contained in a 1-liter stainless steel or glass sampling bulb or in a cryogenic sampler, type TTU-131/E (described in MIL-S-27626).

13. Attach the sampling vessel to the gas handling system.

14. Attach a Xe gas trap to the gas handling system. Use the trap from step 3.

15. Evacuate the trap and manifold to 10^{-3} torr. Valve off the vacuum pump, and isolate the trap from the manifold.

16. Fill the manifold with sample gas to the same pressure used for the standard gas mixtures. Isolate the manifold.

17. Open the Xe gas trap stopcock for one second, then close it.

18. Chill the trap in liquid nitrogen for 15 to 20 min.

19. Pump the manifold down to 10^{-3} torr and valve off the vacuum pump.

20. Open the Xe gas trap stopcock. Pump the manifold and the Xe gas trap down to a pressure of 1 torr. Close the Xe gas trap stopcock.

21. Remove the liquid nitrogen bath and allow the trap to warm to room temperature.

22. Pump the manifold down to 10^{-3} torr and valve it off.

23. Repeat steps 16 and 22 three more times and then repeat steps 16 through 21.

24. Remove the Xe gas trap from the manifold. At this point, the trap contains essentially all of the Xe from five 10-ml portions of sample gas, and about 4 torr pressure of the base gas of the sample gas.

25. Attach the trap to the inlet system of the chromatograph and warm the trap with a heat gun for 2 to 3 min.

26. Elute the sample and record the chromatogram.

27. From the height of the Xe peak in the chromatogram, determine a corresponding Xe concentration from the calibration curve. Report the concentration of Xe in the cover gas as one-fifth of the value indicated from the calibration device.

4. Add Section 32. Determination of Oxygen in Sodium by the Electrochemical Oxygen Meter.

32. DETERMINATION OF OXYGEN IN SODIUM
BY THE ELECTROCHEMICAL OXYGEN METER

32.1 PRINCIPLE

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, after calibration, as a continuous, on-line measure of the oxygen activity in the sodium.

32.2 SENSITIVITY AND PRECISION

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 volts. In actual practice the meter has been used to measure active oxygen as low as 0.01 ppm with a precision and accuracy of $\pm 20\%$.

32.3 APPARATUS

A schematic representation of a typical oxygen meter is shown in Fig. 32-1. The meter, components, controls, and instrumentation shall conform to the requirements for Type I meters as set forth in RDT Standard C 8-5T "Electrochemical Oxygen Meter for Service in Liquid Sodium." In addition, temperature control of the electrolyte tube shall be ± 1 at 400C.

32.4 PROCEDURE

32.4.1 Calibration

1. With the sodium system under steady state conditions (i.e. constant sodium, cold-trap, and meter temperatures), prepare and equilibrate a set of vanadium wires according to the procedure given in Section 12.5.1.
2. Record the meter readings, either continuously or every half hour, during the wire equilibration.
3. Withdraw the vanadium wires from the system and determine their oxygen content according to the procedure given in Section 12.5.2.
4. Determine the oxygen concentration in the sodium according to the procedure given in Section 12.6.
5. Readjust the cold-trap temperature, if practical, to produce a factor of 2 change in oxygen concentration and repeat step 1 through 4 at least once more.
6. Construct a calibration curve by plotting the log of the oxygen

OXYGEN METER SCHEMATIC

Fig. 32-1

concentration as established by the wires against the average meter voltage obtained during the equilibration. Alternatively, the above data may be used to establish an equation of the form:

$$E = K_1 - K_2 \log A$$

where E = meter reading (2)

K_1 & K_2 = experimentally determined constants for the meter

A = concentration of oxygen in sodium (ppm)

32.4.2 Measurement

1. Establish that the meter temperature is within $\pm 10^\circ\text{C}$, of the temperature used to calibrate the meter. (See Discussion)
2. Record the meter reading.
3. Establish the concentration of oxygen in the sodium by referring to the calibration curve or to the calibration equation.

32.5 SAFETY

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.

Once the meter has been demonstrated to be leak-tight, the only precaution which must be taken to assume that the cooling fins are maintained at a temperature well below ($>10^\circ\text{C}$) 100°C . To prevent damage to the ceramic electrolyte, the temperature of the sodium in contact with the electrolyte should be changed gradually.

32.6 DISCUSSION

The stipulation that all meter readings must be made within $\pm 10^\circ\text{C}$ of the calibration temperature is based on the following assumptions:

- a. that the temperature coefficient of the meter is $\pm 3 \text{ mV}/^\circ\text{F}$,
- b. that the desired precision of the measurement of the oxygen concentration is $\pm 10\%$.
- c. that 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.

The entire calibration procedure, excluding the actual time for wire equilibration takes 6-8 hours. The entire measurement procedure can be accomplished in a matter of minutes.

5. Add Section 33. Determination of the Plugging ("Saturation") Temperature of Sodium.

33. DETERMINATION OF THE PLUGGING ("SATURATION")
TEMPERATURE OF SODIUM

33.1 PRINCIPLE

The plugging ("saturation") temperature is measured by carrying out a specified set of manipulations of a plugging temperature indicator assembly to produce deposition of precipitated solids in a specially designed apparatus. Ideally, the plugging ("saturation") temperature equals the true saturation temperature for impurities; but, in practice, it is a semi-empirical quantity which also is dependent on several factors; these factors are enumerated below in the discussion section.

33.2 SENSITIVITY AND PRECISION

Consecutive measurements of the plugging ("saturation") temperature performed by the same operator usually agree within 5 F. Similar measurements by different operators may vary by as much as 10 F.

33.3 APPARATUS

Plugging Temperature Indicator (PTI) Assembly for Sodium Service, as specified in RDT E 4-19. The general features of this assembly are described below.

An isometric view of a typical modular version of the PTI assembly is shown in Fig. 33-1. Sodium enters the module through the bottom pipe, passes through a valve and through a flow meter into the tube side of the heat exchanger. It reverses flow at the bottom, passes through the plugging orifice, up through the shell side of the heat exchanger, and exits the module through the top of the front face. The piping inside the module is 1/4" SCH 40 Type 304 SS. The module is contained in a frame with dimensions of 11" x 30" x 32". A schematic drawing of the typical plugging temperature indicator is shown in Fig. 33-2. The bottom orifice plate geometry is shown in Fig. 33-3, and it should be noted that there are four 0.052 inch diameter holes arranged on a bolt circle of 0.187 inch plus a center hole of 1/8 inch diameter. The center hole is normally plugged with a long rod, the clearing device, as shown in Fig. 33-2. This rod is attached at the opposite end to an iron thimble which is actuated by a solenoid. When the solenoid is energized "out" the tip of the rod moves out of the axial hole and permits flow of sodium through this central hole. This provides bypass flow in the unlikely event that the other four holes become totally plugged and flow cannot be restored by stopping the cooling air flow.

The outside of the heat exchanger is cooled by a high-performance fan capable of delivering 100 scfm air. This air passes over 0.6 square foot of surface and is nominally capable of removing 2000 BTU/hr for an

Fig. 33-1 Typical Modular Version of a Plugging Temperature Indicator Assembly

Fig. 33-2 Schematic of a Typical Plugging Temperature Indicator

ORIFICE PLATE

MATERIAL: TYPE 304 SS

CLEARING DEVICE

Fig. 33-3 Orifice Plate and Clearing Device Detail

inlet sodium temperature of 1200°F. For the procedures of this method, it has been assumed that the PTI assembly is permanently connected to the sodium system, typically as in Fig. 33.4.

Two-Pen Strip-Chart Recorder-Controller, suitable for recording the sodium temperature and flowrate in the PTI; and for the automatic mode, with high-low limit switches actuated by the flowrate pen.

Temperature Control Panel. The temperature of the sodium at the orifice plate of the PTI must be varied either manually or automatically in a well-controlled manner. Typically, the operator must have available controls that:

- a. start and stop the blower motor,
- b. reset the position of the damper in the airstream from the blower,
- c. change the power output of the heater on the PTI.

33.4 PROCEDURE

1. Start the run with the PTI at 500 to 600 F, or well above (100 F or more) the cold trap and the probable plugging ("saturation") temperature. If the system is operating at less than 500 F (e.g. during startup), start the run with the PTI at system temperature.

2. Adjust the sodium flow to a convenient rate which is not less than 0.1 gal/min. Whenever possible, valves close to and in series with the orifice flow should be at least 75% open. Hence, auxiliary valving to achieve major flow control is desirable.

3. Reduce the temperature of the PTI to 400 F as rapidly as desired and then at a rate of <2 F/min from 400 to 325 F, <1 F/min from 325 to 300 F, <1/2 F/min below 300 F. Incremental temperature decreases as large as 20 F may be used, provided that the average cooling rates specified are maintained.

4. If a sodium flow decrease of at least 25% and preferably of 50% is observed while the temperature of the PTI is being reduced, proceed to step 5. Record the temperature of any flow decreases of <25% (see Discussion, Section 33.7). If a temperature of 230 F is reached before a 25% decrease in flow is observed, proceed to step 11.

5. Follow steps 6a through 8a for automatically controlled PTI's. Follow steps 6b through 8b for manually controlled PTI's.

Fig. 33-4

Typical Installation of PTI Assembly

6a. Adjust the sodium-flow limit switches to flows above and below the partially plugged flow of step 4 or step 12, and within 0.04 gpm of that value and observe the time required for one cycle of flow oscillation.

7a. Adjust the limit switches to produce a flow cycle time between 30 and 90 minutes. The oscillation cycle time and amplitude may change spontaneously, but they need not be readjusted unless the time exceeds 5 hours or the flow rate falls outside the range of 20% to 90% of bare orifice flow.

8a. Record at least 5 flow oscillations. Proceed to step 9.

6b. Stop the cooling and begin a heat-up at a rate of ~ 3 F/min. and record the temperature at which flow increases sharply. This is the unplugging temperature. (Incremental temperature increases as large as 20 F may be used provided that the average heating rate does not exceed 3 F/min.

7b. Resume cooling at the rate specified for the applicable temperature range. Record the temperature at which flow decreases sharply. This is the plugging temperature.

8b. Repeat steps 6b and 7b to produce at least four additional oscillations in flow. Proceed to step 9.

9. Calculate the plugging ("saturation") temperature. If this temperature has either (1) exceeded the maximum plugging ("saturation") temperature allowable for that system, or (2) unexpectedly increased by 20 F, then take the appropriate actions as specified in RDT A 1-5 "Purity Requirements for Operating Sodium Reactor Systems". If not, continue flow oscillations.

10. Periodically calculate the plugging ("saturation") temperature using the last 5 flow oscillations. If the calculated temperature exceeds the maximum plugging ("saturation") temperature allowable for that system, take the appropriate actions as specified in RDT A 1-5 "Purity Requirements for Operating Sodium Reactor Systems". If the calculated temperature changes by more than 15 F [but does not exceed the maximum plugging ("saturation") temperature allowable for that system), proceed to step 1 immediately. If a change of this magnitude is not observed, proceed to step 1 every 24 hours. Do not proceed to step 11 unless a PTI temperature of 230 F is reached.

11. Hold the temperature at 230 ± 10 F. If no flow decrease is recorded after 3 hours, report "Plugging ("saturation") temperature below 275 F". If no flow decrease is recorded after 15 hours, report "Plugging ("saturation") temperature below 260 F".

12. If a 25% flow decrease occurs while the PTI is in the continuous non-plugging mode of operation, proceed to step 5. If not, proceed to step 13.

13. Proceed to step 1 after 96 hours (or sooner if specified in the system operation manual).

33.5 Calculations

The strip chart record of a typical plugging run is shown in Fig. 33-6. Points U are individual unplugging temperatures and points P, individual plugging temperature.

For five or more cycles, find the average plugging temperature, $\bar{P}$, and the average unplugging temperature, $\bar{U}$.

then,

$$\text{Plugging ("Saturation") Temperature} = \frac{\bar{P} + \bar{U}}{2}$$

33.6 Safety

Local safety regulations governing the operation of components on sodium systems should be adhered to.

33.7 Discussion

During the course of a PTI run, minor flow decreases (<25%) may be observed. The impurities causing these flow decreases are probably present in such small quantities that oscillatory operation of the PTI is not possible. However, it is desirable to keep track of these high temperature breaks to establish whether or not the system is changing. Hence, it is recommended that occasionally a complete profile be run, even though the system is so clean that no oscillatory mode of operation can be attained.

The temperature range between the plugging and the unplugging temperature is dependent on the deposition-dissolution kinetics of the system. These kinetics are affected by such factors as orifice design, power input to heaters, cooling efficiencies, length of oscillation period, and the temperature at which a plug is formed. Often, plugging ("saturation") temperatures determined from PTI runs having a temperature range of 80 F will be reproducible within 5 F. Thus, to get a true statement of the reproducibility of a given PTI, it will be necessary to make consecutive runs on an unchanging system.

Fig. 33-6

Example of Plugging Run

Because the deposition kinetics for impurities in sodium are relatively slow compared to typical heating and cooling rates, it is possible to encounter relatively large degrees of supercooling, particularly at "high" plugging ("saturation") temperatures. This can easily lead to the deposition of a total plug of the orifice and a flow stoppage. To restore flow, increase the temperature of the PTI above the saturation temperature by 100 F or more. The precipitate will dissolve and flow will restart. Alternatively, for systems equipped with a cleaning device, energize the solenoid to lift the rod from the central 1/8" diameter hole in the orifice plate. When flow through the peripheral holes is achieved, deenergize the solenoid, adjust the temperature, and continue oscillation. It is wise to restore flow as soon as possible since the longer the precipitate remains on the plate, the more difficult it becomes to remove it.

6. Add Appendix M. Determination of the Hydrogen Activity in Sodium by an Equilibration Method Using Scandium Tabs.

Appendix M

DETERMINATION OF HYDROGEN ACTIVITY IN SODIUM
BY AN EQUILIBRATION METHOD USING SCANDIUM TABS
(TENTATIVE)

M.1 PRINCIPLE

A scandium tab is immersed in flowing sodium at 750 C until equilibrium with respect to hydrogen is reached. Subsequently, the hydrogen concentration in the tab is measured and the chemical activity of hydrogen is calculated.

M.2 SENSITIVITY AND PRECISION

This procedure is applicable for hydrogen concentrations in sodium in the range 0.06 to 0.5 ppm. The precision is expected to be within $\pm 10\%$.

M.3 APPARATUS

Equilibration Module. Fig. M-1 is a schematic drawing of the Specimen Equilibration Module for use on reactors and large sodium systems. This module shall conform to the requirements of RDT C 8-8. Fig. M-2 is a schematic drawing of typical Specimen Equilibration Device for use on small experimental systems.

Hydrogen Analyzer. The LECO Hydrogen Determinator, manufactured by the Laboratory Equipment Corporation, has been found suitable for this application.

Forceps. Dissecting forceps.

M.4 MATERIALS

Standard Scandium Tabs. 10 mils thick x 1/8" inch wide x 3/4" inch long, prepared from 99.9% scandium sheet. Suitable 10 mil x 2 inch wide sheet has been supplied by Research Chemicals, a Division of Nucor Corporation

Accelerator. Iron metal accelerator, LECO Catalog No. 501-077, has been found satisfactory for this use.

Hydrogen Standard. Titanium analyzed sample, LECO Catalog No. 762-741 has been found suitable.

Ethanol. U.S.P. or reagent grade absolute ethanol.

M.5 PROCEDURE

M.5.1 Tab Preparation

Fig.M-1 SCHEMATIC of a TYPICAL SPECIMEN EQUILIBRATION MODULE

Fig. M-2

SCHEMATIC of a TYPICAL SPECIMEN EQUILIBRATION DEVICE

1. Store scandium stock in a dry inert atmosphere.
2. Handle stock material only with degreased forceps.
3. Prepare tabs by cutting stock material in box into 3/4 inch long x 1/8 inch wide strips.
4. Remove tabs from box.
5. Place the tabs in the sample holder previously degreased by washing with acetone.

5.2 Equilibration

1. Insert the sample holder into the sodium system.
2. After establishing sodium flow (minimum 0.1 gal/min) through the equilibration device, equilibrate the tabs at 750 ± 2 C for 72 hours.

M.5.3 Post Exposure Treatment

1. Shut off sodium flow by closing inlet and outlet valves.
2. Pressurize the equilibration device with inert gas, open the drain valve and drain the sodium from the equilibration device. (If drainage at 750C is prohibited by local safety practices, cool the sodium in the device at a rate of 50 C/min down to 500 C before draining the sodium.)
3. Cool the tabs quickly by forced air cooling of the loop section containing the holder. (Allow no more than an over-night cooling while maintaining a positive inert gas pressure during this period.)
4. Remove the sample holder from the equilibration module or device and transfer it immediately to an inert gas glovebox.
5. Melt the sodium in the sampler holder by heating to 125 C. Remove the tabs from the holder.
6. Remove the tabs and holder from the inert atmosphere box and thoroughly wash each one individually with absolute ethanol to remove the bulk of the adherent sodium.
7. Place the tabs in fresh warm (~ 60 C) alcohol for 0.5 to 1.0 hours.
8. Dry the tabs by gently heating (~ 60 C) in a glass vial.

5.4 Hydrogen Determination

1. Analyze 1 or 2 samples of the LECO titanium standard samples. For each determination use approximately 0.5 g of accelerator.

2. Analyze each tab individually. The tab may be bent or cut in two pieces in order to facilitate analysis.

M.6 CALCULATIONS

1. Calculate the wt ppm hydrogen in the scandium from the following formula

$$A, \text{ wt ppm hydrogen in tab} = \frac{B}{C}$$

where B = hydrogen in sample, μg

C = weight of sample, g

2. Calculate the hydrogen concentration in the sodium from the following formula

$$\text{ppm H in Na} = .000156 A (\text{ppm H in Sc})$$

M.7 SAFETY

The steps under equilibration and post-exposure treatment present hazards which should be controlled by locally-administered safety program.

The laboratory operations present no unusual hazards except the safe handling of liter quantities of flammable organic liquids.

M.8 DISCUSSION

This entire procedure, excluding the equilibration time, requires about 6 hours.