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PACIFIC NORTHWEST LABORATORY
MANUAL OF PROCEDURES FOR THE ANALYSIS
OF METALLIC SODIUM

Second Revision
June, 1970

R.F. Keough, Editor

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PREFACE

This, the second revision of the manual describes the methods used for the chemical analysis of essentially non-radioactive sodium by the Systems Chemistry Section at Pacific Northwest Laboratory. It has two functions: first, to serve as a laboratory manual, and second, to provide a source of background information about the procedures to the chemically oriented scientists and engineers who submit samples.

Improvements in the analytical chemistry of sodium are being made continually and the methods included in this manual are undergoing evolutionary changes. Major revisions of some sections will be made as better methods become available or as procedures for additional impurities are developed. These revisions will be issued to known holders of the manual.

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June 1970

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OXYGEN DETERMINATION BY AMALGAMATION

INTRODUCTION

A knowledge of the oxygen content of sodium coolant is important because of the major role of oxygen in the corrosion of containment systems. An analytical method is required for oxygen levels in the range of 5 to 100 parts per million.

The two approaches commonly used for trace oxygen analysis in sodium involve the physical separation of sodium oxide from the free metal by either vacuum distillation (1) or mercury amalgamation (2,3). The methods are comparable in sensitivity, precision and accuracy. They are both indirect techniques and therefore subject to the same inherent problems associated with measuring a quantity related to oxygen rather than oxygen itself.

The amalgamation method was selected for use at the Pacific Northwest Laboratory because of the laboratory's need to handle a variety of samples from a large number of sources, most of which do not warrant the use of sophisticated vacuum distillation equipment, because of the simplicity of the equipment required and because of its wide general acceptance (4,5).

Actual quantitative measurement of the apparent oxygen content is usually accomplished through the hydrolysis of the residue followed by the titration of the resulting base or by the flame photometric measurement of sodium ion concentration. Base titration was selected for use because of the simplicity of the apparatus required and the lack of any clear demonstration of the superiority of one approach over the other.

The procedure described below achieves the separation of sodium metal from sodium oxide by the repeated batch extraction of the sample with mercury in a separatory funnel. The sodium is quantitatively drained off as liquid amalgam while the insoluble sodium oxide remains as a film floating on the mercury and adhering to the walls of the funnel. The oxide film is then dissolved in water and titrated with standard acid. The sample size is determined by reacting the sodium in the mercury from the extractions with excess acid and titrating the excess with standard base.

The separatory funnel contains some adsorbed water regardless of how vigorous the drying process used to prepare the glassware. Some or all of this water reacts with the amalgam to give sodium hydroxide which is separated with the sodium oxide and titrated. To correct for this glassware blank, the first amalgam from a sample is drained into a clean funnel where the amalgam reacts with adsorbed water. This "piggyback" blank is then processed along with the sample.

EXPERIMENTAL

Apparatus

The amalgamation is performed in an argon atmosphere glove box maintained at less than 1 ppm each of water and oxygen by a recirculating purification train (Figure 1-1). Wide mouth 125 ml separatory funnels of heavy wall glass and fitted with teflon stopcocks (Figure 1-2) are used for the extraction. The titration is done in the separatory funnel with a titration probe (Figure 1-3) which consists of an acid delivery tube from a motor driven buret, an argon sparge tube which stirs the solution and maintains a carbon dioxide free atmosphere, and a combination pH electrode.

Solutions

- A. Hydrochloric acid 4.35M - Dilute 1125 ml of concentrated hydrochloric acid to 3 liters with distilled water. Check titer against anhydrous sodium carbonate.
- B. Sodium hydroxide 4.35M - Dissolve 175 g of sodium hydroxide in sufficient water to make 1 liter of solution. Check titer against (A) above.
- C. Hydrochloric acid 0.0050M - Dilute 2.30 ml of (A) above to 2 liters.
- D. Thymol Blue - Dissolve 0.04 g of the sodium salt of thymolsulfonephthalein in 100 ml of water.
- E. Mercury - Clean triple distilled mercury or mercury from previous amalgamations by the procedure given in the Appendix.

Safety Precautions

Mercury poisoning is a hazard in this analysis. The argon from the glove box contains a high concentration of mercury vapor and must not be inhaled when opening the air lock. Do not allow box atmosphere to enter the room unless all ventilation systems are operating. The vacuum pump serving the glove box should exhaust into a fume hood. Handle mercury in a hood whenever possible and clean up spills immediately. Wash before eating or smoking. Store waste sodium in a metal can under Met-L-X (Ansul Company) until it can be disposed of by authorized personnel.

Procedure

1. Wipe the sample tube with cotton moistened with toluene to remove any film of grease or dust. Handle the clean sample by the ends to minimize contamination. Transfer the sample immediately to the glove box air lock.
2. Prepare the separatory funnels by washing with dilute hydrochloric acid, rinsing repeatedly with water and drying at 150° for several hours. Transfer the funnels directly from the oven to the vacuum air lock of the glove box. Quickly evacuate the air lock to an absolute pressure of 30 torr or less. Continue pumping overnight then pressurize the air lock with box atmosphere and take the sample and equipment into the glove box.
3. Analyses are performed in duplicate with a "piggyback" blank on one of the pair. Three funnels and two 500 ml erlenmyer flasks are required for one sample. A single blank is sufficient for up to 3 samples, provided they are analyzed simultaneously with the funnels cleaned, dried and brought into the box as a group.
4. Fill the funnels to the 50 ml graduation with mercury. Cut 2 sections of sample tubing 3-4 cm long and estimated to contain 3 g of Na, from near the center of the sample. Inspect the sections for voids or abnormal appearance and if none are observed drop each of them into a funnel.

5. When the vigorous reaction subsides cap the funnels and invert them repeatedly to dissolve any sodium or solid amalgam that may be in the tubing. Allow 5 minutes for the oxide to float to the surface before proceeding.
6. Drain all but about 0.3 ml of the amalgam from one funnel into a labeled flask. Similarly, drain the second funnel into the third or blank funnel. Cap the blank funnel and invert it repeatedly as if it contained a sample. Allow the amalgam to stand 5 minutes, then drain all but 0.3 ml of it into the second flask.
7. Put 25 ml of clean mercury in each of the three funnels. Replace the caps and invert the funnels ten times so that all the residual amalgam is dissolved. Drain the mercury into the flask as before. Mercury from the second funnel and the blank are drained into the same flask.
8. Repeat (7) three more times draining the mercury into a common container for disposal. Cap the funnels to protect the contents from atmospheric carbon dioxide and bring them and the flasks out of the glove box.
9. Add about 50 ml of water to each flask, then pipette in sufficient 4.35M hydrochloric acid to react with all the sodium and provide an excess of 2-10 ml of acid. After the evolution of hydrogen bubbles ceases, add several drops of thymol blue indicator. Titrate the red solution with a 4.35M sodium hydroxide to a pale blue color. Record the volume of acid and base used for each flask.
10. Standardize the pH meter with the titration probe immersed in pH 7.0 buffer solution. Adjust the argon flow to produce moderate stirring. Rinse the probe thoroughly with water then soak the probe in water for 5 minutes to remove the last traces of buffer. Quickly measure the pH of a fresh sample of water in a clean separatory funnel. Allow a few drops of standard acid to flow to remove any diluent that may have diffused into the delivery tube.

11. Uncap one of the sample funnels. Rinse down the walls of the funnel without wetting the ground throat which may contain minute droplets of amalgam. Titrate the solution to the pH of the water in (10) above with 0.0050M hydrochloric acid. Record the volume of acid required. Perform titration (11) for each funnel.

Calculations

The weight in grams of sodium in a section of tubing is 1/10 the difference between the volume in ml of 4.35M acid and base:

$$\frac{(\text{ml } 4.35\text{M acid}) - (\text{ml } 4.35\text{M base})}{10} = \text{grams sodium.}$$

The weight of oxide expressed in micrograms is 40 times the difference between the ml of 0.005M acid used in the titration of the sample and blank funnels:

$$(40) (\text{ml acid for sample} - \text{ml acid for blank}) = \text{micrograms oxide.}$$

Example:

Sample weight estimated at 3 g.

35.0 ml of 4.35M acid added to amalgam in the flask.

6.2 ml of 4.35M base required for titration.

$$\text{Sample weight} = \frac{35.0 - 6.2}{10} = 2.88 \text{ g.}$$

2.60 ml of 0.005M acid required to titrate sample funnel.

0.15 ml of 0.005M acid required to titrate blank funnel.

$$\text{Oxide weight} = 40(2.6 - 0.15) = 98 \text{ } \mu\text{g.}$$

$$\text{Oxide content of sample} = \frac{98}{2.88} = 34 \text{ } \mu\text{g/g.}$$

RESULTS AND DISCUSSION

The detection limit of the PNL procedure is determined by the magnitude and consistency of the blank. A low and constant "piggyback" blank, although desirable, does not take into account any blank that may be associated with the sample tubing. Tubing blanks of about 1 $\mu\text{g/cm}$ have been reported (3). We observe a blank of less than 0.1 $\mu\text{g/cm}$ from the exterior of our stainless steel tubing when using 120°C amalgam. Buffing the tubes with a stainless steel wire wheel does not reduce this blank. "Piggyback" blanks normally range from 4 to 8 μg of oxide but several blanks run simultaneously generally agree to within 1 μg . In performing a "piggyback" blank the amalgam has cooled about 20° before it is drained into the blank funnel but the size of

the blank is only slightly affected by amalgam temperature. In practice a detection limit of about 3 μg may be expected. Since this is independent of sample size, 1 ppm of oxide may be detected in a 3-4 g sample.

Precision of the method is difficult to assess with actual samples, apparently because of their non-homogeneity. The titration end point is easily seen to better than 1 ppm of oxide. The retention of oxide in the funnel is quantitative if low "piggyback" blanks from high oxide samples are reliable indicators. Analysis of the mercury from the final extraction shows that there is less than 0.03 μg of metallic sodium remaining as amalgam with the oxide at the time of the titration. Duplicate oxygen analyses on sodium taken from experimental loops usually agree within 1-2 ppm at the 10 ppm level and within 3 ppm at the 25 ppm level.

Oxygen is by convention assumed to be present as sodium monoxide although significant amounts of oxygen may be present as carbonate (6), hydroxide (7), or as oxygen compounds of other metals such as calcium which would be titrated or of iron which would not be titrated. To further complicate the problem any carbide, nitride, cyanide or hydride which may survive the heat of amalgamation would hydrolyze to give alkaline solutions that would be titrated although these materials contain no oxygen. Unfortunately, similar problems exist when vacuum distillation is used to isolate the sodium oxide or when the measurement of sodium is used to estimate the amount of oxygen present.

Good technique includes the prevention of contamination of the sample and apparatus with sodium oxide or other alkaline material, or with oxygen or water vapor. The interior of the glove box must be assumed to be grossly contaminated with sodium oxide regardless of the apparent cleanliness. Tubing cutters and other equipment that may come in contact with sodium should be washed after each use. Airborne sodium oxide has not been a problem.

The exposure of sodium to the box atmosphere for two hours does not increase the apparent oxygen content. The sodium surface does show some tarnishing in this time but it is probably due to mercury vapor which is present in large amounts. Unnecessary exposure of sodium to the box atmosphere should be avoided. Prolonged bubbling of box atmosphere through sodium amalgam indicated that the amalgam doesn't absorb more than 0.5 micrograms of oxygen during an analysis.

Voids are sometimes found when sample tubes are sectioned, presumably due to the presence of gas bubbles in the molten sodium or to the contraction of the sodium as it cools. Sodium adjacent to voids should be excluded from the analysis if possible. This sodium is often relatively high in oxygen and on occasion has been found to be brown or black at the void interface. This indicates that air has leaked to the void and at least the portion of sample from the void to one end of the sample tube is contaminated along the side where the cooling sodium has pulled away from the tubing wall. Results obtained on these samples should be reported as questionable.

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FIGURE 1-1

Glove Box and Purification Train

FIGURE 1-2
Amalgamation Funnel

FIGURE 1-3
Titration Probe

TOTAL CARBON DETERMINATION BY COMBUSTION

INTRODUCTION

Carbon in sodium used as a reactor coolant can have adverse effects on the coolant system. At elevated temperatures either carburization or decarburization of stainless steel can occur, depending on the carbon activity in the sodium. In either case, degradation of the steel's physical properties results. Because of these effects it is important to measure the low levels (0-10 ppm) of carbon present in high purity sodium.

Considerable work has been done on methods for the determination of total carbon in sodium. The Van Slyke wet oxidation method has been tried but found to give high and erratic blanks (1). Low temperature oxidation of the sodium in an argon-oxygen atmosphere followed by conversion of the resulting traces of carbonate to carbon dioxide with acid has been used (2). This method can accommodate a large sample which, in effect, reduces the blank. The major disadvantage of the process seems to be the intricate manipulations involved.

The procedure described here is based on the direct combustion of sodium starting at 400°C in a helium-oxygen atmosphere followed by the evolution of carbon dioxide as the temperature is increased to 1100°C in the presence of silica-alumina flux. The quantity of carbon dioxide released is measured with a gas chromatograph. The procedure is based on one described by Bradley and Meacham (3) and is probably the most widely used carbon procedure at the present time.

EXPERIMENTAL

Apparatus

A schematic diagram of the analytical system is shown in Figure 2-1. The various parts can be described as follows:

Gas Mixing and Purification Train

A mixture of oxygen and helium is used for the combustion of sodium. Flows of Grade A helium and ultra pure oxygen (99.99%) are controlled by needle valves and monitored by rotameters before mixing. Carboniferous impurities are removed by passage of the mixed gases over copper oxide and platinum on quartz wool beds at 700°C followed by 3 x 50 cm Ascarite column.

Sample Combustion Train

The quartz combustion tube is 75 cm long and 2.5 cm I.D. The upstream end of the tube is attached to a port in the glove box wall with standard O-ring glass pipe flanges. Gases flow to and from the combustion tube in 1/8" O.D. stainless steel tubing. To prevent sodium oxide from attacking the combustion tube, the sample is oxidized in an expendable quartz liner 2 cm I.D. by 18 cm long with a quartz loop handle across one end (Figure 2-2). The sodium sample rests on a bed of about 2 grams of a 1 to 1 mixture of chromatographic grade silica gel and alumina contained in a quartz boat 5 cm long and 1.9 cm wide. The boat is placed in the liner between two plugs of quartz wool to prevent the escape of sodium oxide into the combustion tube. The combustion tube is heated by a hinged type tube furnace with a 30 cm heated zone.

Carbon Dioxide Collection and Measurement

The carbon dioxide in the combustion gases is trapped in a 3/16" O.D. by 20 cm Inconel tube packed with Molecular Sieve 5A, 60 mesh. This tube is an integral part of a Component Concentrator, Model 215 (SKC Inc., Pittsburgh). The Concentrator is connected to the combustion train through a Loenco L 208-8 multiport valve.

An F&M Model 700-2419E gas chromatograph with a 1 mv/10 inch recorder is used to measure carbon dioxide. The chromatographic columns are 1/4" O.D. by 6 feet long and packed with Porapak Q and maintained at 35°C. Helium carrier gas flows at 40 ml/min through each column. The thermal conductivity detectors operate at 135°C and use WX filaments at a current of 145 ma. The carbon dioxide peak appears about 2 minutes after direct injection onto the column.

Tools

Samples, liners and boats are handled with forceps and tongs that have been electrically heated for several hours in air at 600°C to oxidize surface carbon. Tools are taken into the glove box wrapped in aluminum foil for protection from contact with potential carbon sources.

Glove Box

All sample manipulation is carried out in an argon atmosphere glove box. The box is equipped with an evacuable antechamber for sample and equipment transfers. The argon atmosphere is maintained at less than 1 ppm carbon dioxide and moisture by constant recirculation through a Molecular Sieve bed. The atmosphere also typically contains 100 ppm of oxygen and 1000 ppm of helium.

Extruder

Samples are normally received in 1/2 inch stainless steel tubing with 0.035 inch wall thickness and ends closed with Swagelok caps. Sodium for the analysis is extruded from the tube with a Manco hydraulic crimper, the head of which (Figure 2-3) penetrates the glove box wall. By successively crimping adjacent sections sodium extrudes from an open end like toothpaste.

Procedures

1. Preparation of liners and boats

- 1.1 Form a loose cylinder of quartz wool about 5 cm long and 2 cm in diameter by gently rolling about 1 g of quartz wool between the hands.
- 1.2 Insert the plug into the quartz liner and push it to the end.
- 1.3 Place 2-3 g of silica-alumina flux in a quartz boat; insert the boat in the liner and push it in until it touches the quartz wool.
- 1.4 Prepare a second wool plug and place this plug in the liner. There should be no loose ends sticking out and the plug should not be too compact to impede the flow of gases.
- 1.5 Put the loaded liner in the preconditioning furnace tube and heat it overnight at 900°C while maintaining an oxygen flow of 1 ml/min.

2. Determination of carbon in sodium

- 2.1 Shut off the oxygen flow to the preconditioning and combustion tubes. Set the helium flow at 50 ml/min on both tubes. Allow the tubes to cool and flush for 20 minutes.

- 2.2 Open the glove box end of the preconditioning furnace tube; remove the liner with a wire hook and forceps. Place the liner on aluminum foil and close the preconditioning tube.
- 2.3 Remove the quartz wool plug from the open end. Tilt the liner so the boat will slide to the open end; pull it halfway out of the liner.
- 2.4 Extrude about 3 cm of sodium from the stainless steel sample tube, cut it off with a knife and discard it. Extrude another 0.5-0.7 cm of sodium and weigh it. Record the weight and place the sample in the boat.
- 2.5 Push the boat back in the liner and replace the quartz wool plug.
- 2.6 Open the combustion tube, which should be no hotter than 200°C, and insert the loaded liner. The liner should not touch anything but the inside of the quartz tube. Push the liner into the tube until it reaches the constriction. Close the combustion tube.
- 2.7 Quickly adjust the oxygen flow to 35 ml/min and turn off the helium. Set the combustion tube furnace controller at 1100°C.
- 2.8 Immediately operate the heater on the Concentrator for 1 minute to remove any carbon dioxide that may have been trapped before the analysis started.
- 2.9 Pass the combustion gases through the Molecular Sieve trap of the Component Concentrator for 2 hours. Approximately 1 hour is required for the sample to reach 1100°C.
- 2.10 Pull the 8-port valve to the "out" position to permit helium to flush oxygen from the Concentrator to the air. After 2 minutes move the Concentrator valve to "analyze" so carrier gas will be flowing through the Concentrator and then to the chromatograph.
- 2.11 When the recorder base line is steady, turn on the Concentrator's heater for 3 minutes. The carbon dioxide peak will appear about 2 minutes after the heater is turned on. Measure the peak height in millimeters and record this and the attenuation setting.

The following procedures are performed as necessary to calibrate the system and establish that it is operating properly. Operational blanks and yield determinations need to be run often enough to give statistically valid values for use in sample analysis. System blanks and operational blanks are used to

troubleshoot the system. A discussion of their use for this purpose is given in the "Discussion" section.

3. Determining operations blank

3.1 Perform Procedure 2, "Determination of carbon in sodium" omitting Step 2.4.

4. Determining process yield - standard.

4.1 Perform Steps 2.1 to 2.3 inclusive.

4.2 Remove a standard capsule* from its container with clean forceps. Place it in the boat.

4.3 Extrude 1 cm of low carbon sodium from a sample tube; cut it off and discard it. Extrude 1/2 gram of sodium and place it in the boat.

4.4 Perform Steps 2.5 to 2.11 inclusively.

5. Determining process yield - blank.

5.1 Perform Procedure 4 except that a blank capsule* is substituted for the standard capsule.

6. Preparing a calibration graph.

6.1 Inject 0.1 to 2.0 ml of 1% carbon dioxide in helium standard into the combustion train through the septum in the tee below the combustion tube.

6.2 Trap and analyze the standards just as the actual samples in Steps 2.9 through 2.11 except that only 10 minutes is required to trap the carbon dioxide.

6.3 Plot a graph of peak height versus μl of carbon dioxide similar to Figure 2-4.

*Tin encapsulated standards and blanks obtained from Laboratory Equipment Corporation (LECO).

Calculations

The volume of carbon dioxide trapped during the sample analysis can be read from the calibration curve after multiplying the observed peak height by the attenuation setting used and subtracting an amount equivalent to the Operations Blank. To convert the microliters of carbon dioxide to ppm of carbon in the sample, multiply by 0.48 and divide by the sample weight.

Example:

Sample weight	0.55 g
Sample peak height	85 mm
Sample attenuation	4
Operations blank peak height	90 mm
Operations blank attenuation	1

$(85 \text{ mm})(4) - (90 \text{ mm})(1) = 250 \text{ mm}$ peak height corrected for the blank; 250 mm corresponds to 5.0 μl of CO_2 (Figure 2-4 in this example).

$$\frac{(5.0 \mu\text{l})(0.48)}{0.55 \text{ g}} = 4.4 \text{ ppm of carbon}$$

DISCUSSION

As noted in the Experimental Section, a number of control procedures are used to assure the operator that the system is operating properly. These procedures can also be useful tools in troubleshooting. For example, high or erratic blanks are indicative of leaks or contamination in the system. High operation blanks and low system blanks indicate carbon contamination of the liners or a poor box atmosphere. If both blanks are high the purity of the oxygen and helium combustion mixture is suspect and leaks or inadequate purification may be the problem.

Low process yields may be due to improper operation of the chromatograph, too low a combustion temperature or incomplete collection of the carbon dioxide. The operation of the chromatograph can be checked by comparing the response to the injection of a known amount of carbon dioxide directly onto the column with the response obtained when the process yields were normal. Care must be taken to maintain the combustion tube at 1100°C for 50 minutes. There are three possible causes for the incomplete trapping of the carbon dioxide: ineffectiveness of the trap, gettering of some carbon dioxide by sodium oxide that has escaped from the hottest zone of the combustion tube, and failure to flush the combustion gas completely from the system. Escape of sodium oxide from the liner can be prevented by restricting the sample size to about 0.5 grams, by using the correct gas flow rates and by the proper use of the quartz wool. The amount of wool to be used must be determined largely by experience; enough is needed to retain all the sodium oxide but not enough to unduly restrict the gas exchange over the sodium. Gas appears to diffuse rather than flow through the liner.

Another problem associated with the escape of sodium oxide from the liner is the attack on the combustion tube. This results in the rapid destruction of the tube which would ordinarily last for several months. The addition of flux to the boat helps prevent the loss of sodium oxide by providing other sources of acidic oxides for high temperature formation of silicates and aluminates. Alumina is added so that the reaction product will be a solid at the combustion temperature rather than a liquid glass which could trap elemental carbon or carbon dioxide. Miles (5) has recently reported the use of potassium dichromate as an oxidizing flux. Potassium oxide might be expected to contribute to the problems associated with the sodium oxide and the addition of alumina or even the use of aluminum dichromate might result in a better flux than any presently in use.

The quality of the glove box atmosphere is important since the sodium, the liner and boat, and especially the quartz wool and flux with their large surface areas, absorb carbon dioxide rapidly. All the components of a loaded liner are exposed to the argon atmosphere for several minutes. Measurement of the carbon dioxide content is accomplished by gently sucking several liters of the atmosphere through the Concentrator via the open combustion tube port and the normal gas lines.

With the gas chromatograph operated under the described conditions, $1\ \mu\text{l}$ of carbon dioxide results in a peak height of about 25 mm. This makes it possible to detect $0.1\ \mu\text{g}$ of carbon; about the amount found in a system blank. Operation blanks are normally $1.5\text{--}2.5\ \mu\text{g}$ so the detection limit is 3 ppm when using a 0.5 gram sample. Recovery of carbon from the tin encapsulated standards run between 95 and 105 percent, however the validity of this standard is open to question. There have been conflicting reports regarding carbon segregation in sodium. This is a complex problem with a number of variables and it is under investigation. The extrusion technique used here compresses stainless tubing of 0.035 inch wall thickness to less than 0.06 inches but only removes about 97% of the sodium because of some back flowing. Compression of the tubing between rollers would eliminate this loss.

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FIGURE 2-1

Apparatus Arrangement

FIGURE 2-2. COMBUSTION BOAT AND LINER

FIGURE 2-3
Hydraulic Extruder

FIGURE 2-4. TYPICAL CALIBRATION CURVE

HYDROGEN DETERMINATION BY AMALGAM REFLUXING

INTRODUCTION

Hydrogen in sodium used as a reactor coolant causes hydriding or hydrogen imbrittlement of structural metals and may indicate system leakage. In addition, hydroxide causes a negative error and hydride can cause a positive error in the amalgamation method (1,2) of oxygen analysis. Of the methods available for hydrogen analysis, the amalgam reflux method of Meacham and Hill (3) is the only one that can determine hydride plus free hydrogen, then subsequently determine hydroxide hydrogen on the same sample.

The technique is an extension of the work of Naud and Sannier (4) and involves refluxing mercury, containing the sodium sample, under vacuum at 200° to liberate dissolved hydrogen and decompose sodium hydride and then at atmospheric pressure and 360° to decompose sodium hydroxide. The hydrogen evolved at each temperature is measured by gas chromatography.

EXPERIMENTAL

Apparatus

The system used to evolve the hydrogen is shown in Figure 3-1. The apparatus penetrates the glove box wall through a gas tight sleeve. The loading port cap is made from a greaseless, double O-ring grip joint obtained from Fusion, Inc., Rosemont, Illinois. A manifold with connections for vacuum, argon, a mercury manometer and a thermocouple-type vacuum gauge is attached to the reflux flask through a greaseless valve obtained from Fusion, Inc. The argon supply is dried by a Molecular Sieve column. The flask is a 100 ml Kjeldahl flask modified by extending the neck, attaching a 10 cm water jacket, and a 24/40 standard taper outer joint. Over-all length of the flask is 35 cm and the volume is 175 ± 3 ml. The glass section penetrating the glove box adds another 65 ml to the system. This section, in addition to providing the connection to the manifold, has a short side arm plugged with a 1.5 cm section of a gum rubber stopper which serves as a septum for insertion of the needle of a gas syringe. A third side arm contains a glass encapsulated iron rod which is used as a magnetic gate for controlling the admission of the sample. The 2-stage rotary vacuum pump is connected to the manifold through a trap cooled with dry ice.

A Beckman GC-2 gas chromatograph is used to measure hydrogen. Chromatographic columns are 0.45 x 200 cm and packed with 50-60 mesh molecular sieve 5A. The columns are operated at 30° with dry argon carrier gas at 20 psig inlet pressure. The argon flow rate is 30 ml/minute. Current through the thermal conductivity detector filaments is 160 ma and the detector signal is displayed on a 0.1 mv/10 inch Honeywell series 19 recorder. The hydrogen peak appears 65 seconds after injection.

The reflux system is attached to a Vacuum/Atmospheres Model HE-43-6 glove box containing an argon atmosphere maintained at less than 0.5 ppm of water by a recirculating purifier. An extruder (Figure 2-3) is used to remove sodium from the half-inch stainless steel sample tubes. Tubes formed from sections of iron foil 0.001 inch thick and 3.5 cm² are used for the transfer of extruded sodium to the reflux flask.

The hydrogen used for calibration contains less than 0.1% total impurities. Dilute sodium/calcium amalgam is prepared by dissolving 2 grams of sodium and 0.4 grams of calcium in 200 ml of mercury. By dispensing this amalgam from a separatory funnel equipped with a teflon stopcock, hydrogen-free amalgam is obtained. Mercury is purified prior to use by acid scrubbing and gold foil filtering (5).

Safety Precautions

Mercury vapor is toxic and is rapidly released by hot mercury or amalgam. Do not remove flasks from the apparatus while the amalgam is still hot. To prevent flasks from breaking while heating, handle them with care and do not subject them to thermal shocks by cooling with water or heating with a hot (oxidizing) flame. If a flask containing hot mercury breaks, evacuate the room immediately. Do not re-enter until the mercury concentration in the air is less than 0.1 mg/m³ as determined with a mercury vapor detector.

Procedure

1. To prepare flasks for reuse, remove grease from the ground joint with cotton moistened with toluene then rinse the flask successively with toluene, ethanol, water, hot chromic acid cleaning solution and water. Dry the flask at 150° for at least four hours. If the flask will not be used within 24 hours, cover the mouth with aluminum foil after a 4 hour drying period and leave it in the oven.

2. Take a dry flask from the oven and while it cools remove the flask used in the previous analysis from the apparatus. Argon should be flowing from the system to minimize the entry of air. Wipe the grease from the inner ground joint with a cloth moistened with toluene. Apply a small amount of Dow Corning High Vacuum grease to the upper part of the joint. Attach the clean flask and secure it with springs. The lower half of the assembled ground joint should be grease-free.
3. Evacuate the flask to 0.01 torr and heat the area below the water jacket to 300-400°C to remove adsorbed water. After the flask cools, add 30 ml of dilute amalgam through the funnel that extends from inside the glove box to a point below the condenser. Start water flowing through the water jacket. Isolate the system from the glove box.
4. Evacuate the system to 0.01 torr then pressurize it to 400 torr with argon. Isolate the flask and boil the amalgam at a rate that will cause mercury to reflux up to the condenser. Under these conditions the pressure will increase to about 800 torr in the flask. Continue refluxing for 30 minutes to remove the last traces of adsorbed moisture from the flask walls.
5. Cut a section of stainless steel sample tubing 15 cm long. Clamp it in the extruder and extrude about 3 g of sodium into a tared 12 mm cylinder formed from a 35 mm square of iron foil and dried in the glove box at 1000°C. Weigh the loaded foil to determine the sodium weight. Close the magnetic gate and load the sample into the system. The sodium must not contact any part of the apparatus.
6. Evacuate the system to 0.01 torr then pressurize it to 400 torr with argon. Isolate the flask and reflux the amalgam. After 15 minutes withdraw a 2 ml sample of gas with a syringe and inject it into the chromatograph. Cool the amalgam. If more than 0.05 μg of hydrogen was evolved the flask was not adequately blanked; repeat this step.
7. To determine hydride hydrogen, evacuate the blanked flask to 0.01 torr and isolate the flask from the manifold. Open the magnetic gate and allow the sample to slide into the amalgam. When the reaction subsides, gently reflux the amalgam for 15 minutes, cool the flask to room temperature and pressurize it to 800 torr. Allow 40 minutes for the gases to equilibrate then inject 2 ml of gas into the chromatograph. Record the hydrogen peak height in microvolts.

8. To determine hydroxide hydrogen evacuate the flask then pressurize it to 400 torr with argon. Isolate the flask from the manifold and reflux the amalgam for 15 minutes. Cool the flask, pressurize it to 800 torr and proceed as in Step 7.
9. Determine the blank by taking an empty foil tube through the procedure.
10. Calibrate the system by injecting 25 μl of hydrogen into the flask containing 30 ml of mercury or amalgam and argon at a pressure of 800 torr. Allow 40 minutes for the gases to mix then transfer a 2 ml aliquot to the chromatograph. Record the hydrogen peak height. Evacuate the system and repeat the process with 50, 100 and 200 μl of hydrogen to obtain data for a calibration curve.

Calculations

Prepare a graph of peak height in microvolts versus weight of hydrogen in micrograms. For normal laboratory conditions of 24-28°C and 740-760 torr a conversion factor of 12.4 $\mu\text{l}/\mu\text{g}$ may be used.

The amount of hydrogen, in parts per million, of either species is the amount of hydrogen found (corrected for the applicable blank) divided by the sample weight.

Example:	Carrier and sodium	3.8 g
	Empty carrier	<u>0.3 g</u>
	Sodium weight	3.5 g
	Sample hydroxide peak	86 μV
	Blank hydroxide peak	<u>3 μV</u>
	Corrected hydroxide peak	83 μV
	83 μV = 3.7 g of hydrogen (Figure 3-2 in this example)	
	$\frac{3.7 \mu\text{g}}{3.5 \text{ g}} = 1.06 \text{ ppm of hydroxide hydrogen}$	

RESULTS AND DISCUSSION

Sodium hydride readily decomposes when refluxed under vacuum with either mercury, sodium amalgam, or sodium/calcium amalgam. Sodium hydroxide does not decompose at the 200°C temperature obtained by vacuum refluxing. However, by refluxing at approximately atmospheric pressure, and 360°C with sodium/calcium amalgam the hydroxide is decomposed completely in 10 minutes. In the absence of calcium the recoveries are poor. Recovery of hydrogen from both hydride and hydroxide chemical standards average above 95%. Because of the physical

differences between hydroxide uniformly distributed through sodium and the chemical standards, longer reflux times were required with the standard sodium hydroxide. The spread between duplicates is typically 10% for hydrogen in the range of 0.5-5.0 ppm.

Hydride blanks are $0.05\mu\text{g}$ of hydrogen or less and hydroxide blanks are $0.1\mu\text{g}$ of hydrogen or less. With these blanks, as little as 0.1 ppm of hydrogen can be determined with a 3 gram sample. With the described apparatus and 2 ml aliquots of gas, the peak height is 20 μV (2 inches) per microgram of hydrogen. The sensitivity is twice this in Step 6 where the gas is sampled while the refluxing is in progress.

The glove box atmosphere does not contribute any detectable hydrogen to the sodium in 15 minutes but it is good practice to minimize the exposure of the sodium to this atmosphere. The sodium and the foil must not contact anything in the box that may be contaminated with sodium or sodium compounds. All tools should be taken from the glove box and rinsed with water after each use. Commercial argon contains enough water to prevent successful blanking. It is therefore dried by passing through a molecular sieve column. The column has an integral electric heater so that it can be conveniently regenerated at 400°C under a vacuum of 5×10^{-2} torr.

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FIGURE 3-1

Amalgam Reflux Apparatus

FIGURE 3-2
Typical Calibration Curve

NITROGEN DETERMINATION BY KJELDAHL DISTILLATIONINTRODUCTION

Nitrogen in sodium is found primarily in the form of nitrides or similar compounds which hydrolyze to ammonia when the metal is dissolved in water or alcohol. Nitrogen gas has a solubility of only 10^{-11} weight percent in sodium⁽¹⁾ and is of little importance. The usual nitrogen analysis is by a Kjeldahl-type method in which the sample is hydrolyzed and the ammonia is trapped in dilute acid and determined colorimetrically or by titration. Colorimetric methods are generally preferred for nitrogen in the zero to ten parts per million range. The Nessler and phenol-hypochlorite methods have both been used, with the use of the former most prevalent. Controlled hydrolysis of alkali metals has been accomplished with strong sodium hydroxide solution, moist gasses, alcohols, alcohol-water mixtures, and even water itself. The slow addition of methanol has been selected for use at PNL for the required hydrolysis. By this technique the reaction rate can be controlled to get the most rapid dissolution consistent with efficient trapping of the evolved ammonia. The phenol-hypochlorite⁽²⁾ method was chosen because it was found to be less sensitive to alcohol than the Nessler method⁽³⁾. A constant amount of methanol must be present, however, to obtain uniform color development.

The procedure involves dissolving the sodium in methanol, hydrolyzing the residue with water to form sodium hydroxide, ammonia, and methanol, and trapping the evolved ammonia for spectrophotometric analysis. The dissolution must be carried out in an argon atmosphere to prevent a possible hydrogen-oxygen explosion and a subsequent sodium and alcohol fire.

EXPERIMENTAL

Apparatus

The apparatus for dissolving the sample and trapping the liberated ammonia is shown in Figure 4-1. The flask is located behind a Plexiglas safety shield. The argon supply is passed through a column packed with Aquasorb, a granular, acidic product of the Malinckrodt Company intended for use as a desiccant but used here to remove traces of ammonia. A hydraulic type extruder⁽⁴⁾ is used to obtain sodium from the 0.5 inch stainless steel sample tubes. Photometric readings are made in a spectrophotometer using 4 cm matched cells.

Solutions

- A. Phenol - Dissolve 60 g of colorless phenol in sufficient water to make 1 liter of solution. Store in a dark bottle.
- B. Sodium Carbonate - Dissolve 106 g of anhydrous, reagent grade, sodium carbonate in sufficient water to make 1 liter of solution.
- C. Phenol-Sodium Carbonate - Mix 20 ml of Solution A with 100 ml of solution B and use within 4 hours.
- D. Manganese Chloride - Dissolve 0.06 g of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in sufficient water to make 1 liter of solution.
- E. Potassium Hypochlorite - Dilute 1M KOC1 in 0.1M KOH with 4 volumes of water. Make fresh every month. Store in a dark bottle.
- F. Ammonia Standard - Dissolve 0.382g of ammonium chloride in sufficient water to make 1 liter of solution. This solution contains 100 μg of nitrogen per ml. Dilute 10 ml to 100 ml with water for actual use. The dilute standard should be made fresh each day.
- G. Dilute Hydrochloric Acid - Dilute 0.9 ml of concentrated acid to 1 liter with water.

- H. Methanol - Reagent grade methanol, acetone free.
- I. Water - Pass tap deionized water through a high quality commercial mixed bed ion exchange column such as the Research Model of Illinois Water Treatment Company. Store under ammonia free air.

Safety Precautions

The dissolution of sodium involves the liberation of large amounts of heat and hydrogen. Serious explosions can occur if air-hydrogen mixtures ignite in a confined space. Observe these precautions:

1. Be sure 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 step.

Procedure

1. Set up the apparatus as shown in Figure 4-1. Remove traces of ammonia from the system by distilling water into the trap without cooling water circulating through the condenser. Discard the condensate. Start water flowing through the condenser jacket before proceeding to the blank determination.
2. Disconnect the flask, quickly rinse it with water then methanol. Vacuum dry it briefly and reconnect it to the system. This step should take less than 5 minutes.
3. Put 25 ml of dilute hydrochloric acid in the trap. Put 30 ml of methanol, 50 ml of water, and 1 drop of saturated sodium hydroxide in the reservoir. Drain the reservoir into the flask and distill a 50 ml blank into the trap.

4. Add 1 ml of hypochlorite solution to the trap, mix and let stand exactly 5 minutes. Add 1 ml of manganese solution, mix and add 12 ml of the phenol-carbonate solution. Quickly mix and dilute to 100 ml. Determine the absorbance in 4 cm cells at 650 m μ after 30 minutes using water as a reference.
5. Disconnect the flask and repeat step (2). The flask must be completely dry.
6. Extrude approximately a two gram sample of sodium in the argon atmosphere glove box. Remove the sample from the glove box in a tared and capped vial, weigh the vial and sample, then subtract the tare weight to determine the sample weight.
7. Flush the flask with argon, drop the sodium in and quickly replace the stopper. Adjust the argon flow to about 500 ml/minute. Put 30 ml of methanol in the reservoir and 25 ml of hydrochloric acid in the trap.
8. Allow 5 minutes for the argon to flush oxygen from the system then reduce the argon flow to 20 ml/minute.
9. Slowly drip methanol onto the sodium at a rate that will dissolve approximately 0.1 g of sodium per minute. All of the methanol must be added before going on to the next step.
10. After the sodium has completely dissolved, add 50 ml of water to the flask through the reservoir. Stop the argon flow.
11. Heat the flask to boiling and distill 50 ml into the trap. Remove the cylinder from the system before allowing the flask to cool so the distillate will not be sucked back. Save the residue in the flask for cyanide analysis if this is required.

12. Measure the ammonia content of the distillate as in (4) above.
13. Prepare a calibration curve by dissolving 30 ml of water in each of four 100 ml graduate cylinders. Add 0, 0.5, 1.0 and 2.0 ml of dilute ammonia standard, mix and develop the color as in (4) above.

Calculations

Plot the micrograms of nitrogen used versus absorption observed from the data from (13) above to construct a calibration curve. Read the Kjeldahl nitrogen content of the sample directly from the curve. Divide the micrograms of nitrogen by the grams of sodium to get parts per million of Kjeldahl nitrogen. Example:

Vial with sample	14.68
Vial Alone	<u>12.56</u>
Sample weight	2.12 g

Absorbance of 0.34 = 15 μ g of nitrogen (from Figure 4-2 in this example)

$$\frac{15 \mu\text{g}}{2.12 \text{ g}} = 7.1 \text{ ppm Kjeldahl nitrogen}$$

RESULTS & DISCUSSION

The recovery of ammonia standards carried through the procedure with sodium average 95% and are consistently better than 90%. A typical calibration curve is given in Figure 4-2. The detection limit is 0.2 μ g of nitrogen and the sensitivity is 0.025 absorption units per microgram of nitrogen. There are no significant interferences. Methylamine if present would produce relatively little color for its nitrogen content (2). Cyanide does not interfere. Azide, amide, imide, and ammonium, if present would hydrolyze to give ammonia. The method is therefore not specific for nitride, nor does it include all nitrides since only the "ionic" nitrides, the nitrides of the more electropositive metals, are hydrolyzed to ammonia. Fusion of the sodium with lithium prior to hydrolysis increases the number of nitrogen species that can be determined but the blanks are excessively high (5).

For nitrogen at the levels encountered in sodium, particular care must be taken to avoid contamination of the sample and apparatus with atmospheric ammonia or organic nitrogen sources. Skin secretions are noteworthy in this respect. Distilling water through the system is the usual method for removing contamination and for determining the blank. The requirement that the distillation flask be dry when the sodium sample is added precludes the full use of this method. Since blanks distilled from the system have consistently contained less than 0.2 micrograms of nitrogen, the procedure used is deemed satisfactory.

Exposure of sodium to air does not appear to increase the amount of ammonia recovered although the impurities in the sodium could have some affect on this. It is unnecessary to expose the sample to air for more than a few seconds.

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FIGURE 4-1
Kjeldahl Apparatus

FIGURE 4-2
Typical Calibration Curve

CYANIDE DETERMINATION BY SPECTROPHOTOMETRYINTRODUCTION

A knowledge of the cyanide concentration of the sodium used in experimental reactor programs may be of considerable interest because of its potential nitriding and carburizing action on the containment systems. While no cyanide was found by Luner, et. al. (1) in sodium loops, cold traps (2) have been found to contain significant concentrations. Recent data (3) indicates that cyanide solubility in sodium has a very high temperature coefficient and cyanide should concentrate in a properly operating cold trap.

Cyanide has been formed under laboratory conditions in molten sodium by the reaction of carbon or carbonate with various nitrogen compounds or nitrogen gas (4). The reaction of organic nitrogen compounds with sodium to produce cyanide is a common technique in organic analysis and may provide another potential source of cyanide.

Traces of cyanide have been determined by a variety of titrametric, colorimetric, fluorimetric, and kinetic methods. The colorimetric procedure of Nusbaum and Skupeko (5) is the only one that has been applied to sodium (1). The Epstein (6) colorimetric method was selected for use at PNL because it has high sensitivity, can handle large volumes of dilute solution and the analysis can be performed directly on the alkaline residue from the Kjeldahl nitrogen analysis. The high sensitivity is attained by extraction of the colored product into butanol (7).

EXPERIMENTALApparatus

Colorimetric measurements are made with a spectrophotometer using matched 1 cm cells. No special equipment or glassware is required.

Solutions

- A. Sulfuric acid - Cautiously pour 220 ml of concentrated sulfuric acid into about 700 ml of water. Add sufficient water to make 1 liter.

- B. Sodium Hydroxide - 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.
- C. Chloramine T - Dissolve 0.20 g of chloramine T in 100 ml of water. Make fresh daily.
- D. Epsteins 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 daily.
- E. Tartaric Acid - Dissolve 10 g of tartaric acid in sufficient water to make 100 ml of solution.
- F. 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 1.0 ml to 1000 ml with water for actual use. The dilute standard must be made fresh each day.
- G. Water - Pass tap deionized water through a high quality commercial mixed bed ion exchange column such as the Research Model of the Illinois Water Treatment Company.

Safety Precautions

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. Flush cyanide waste down the sink with a lot of water. 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 non-flammable surface.

Procedure

1. Add 50 ml of water to the methanol-water-sodium hydroxide residue in the boiling flask after distilling off the ammonia in the Kjeldahl nitrogen analysis. Boil until the odor of methanol cannot be detected.
2. As an alternate to (1) above, accurately weigh a 2-3 gram sample of extruded sodium and dissolve it in 30 ml of anhydrous methanol in an open beaker. Add 50 ml of water to the solution and boil off the methanol.
3. Dilute the solution remaining from (1) or (2) to 100 ml in a graduate cylinder.
4. Pour an aliquot (Figure 5-1) containing 1.00 gram of sodium into a 100 ml beaker. Add a magnetic stir bar.
5. Dilute the sample to 60-70 ml and while stirring, add 2 ml of tartaric acid.
6. Insert the electrodes from a pH meter, continue to stir, and add sulfuric acid from a burette until the pH is 5.5 ± 1 . (Approximately 5 ml of acid will be required.)
7. Transfer the solution to a 100 ml volumetric flask and add 1.0 ml of chloramine T solution. Quickly cap, then shake for 1 minute.
8. Add 10 ml of Epsteins Reagent, mix and dilute to volume. After 1-1/2 hours transfer the solution to a separatory funnel, add 12 ml of n-butanol and shake for 1 minute. Drain off the aqueous layer and pipet a portion of the butanol into a 1 cm spectrophotometer cell. Read the absorbance at 630 m μ using water as a reference blank.
9. Prepare a calibration curve 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 (5) through (8) above.

10. Plot the micrograms of cyanide used versus the absorption observed from (9) above to obtain the calibration curve.

Calculations

Since a 1.0 g sample is used for the color development, the micrograms of cyanide in the sodium is equal to the parts per million of cyanide in the sodium.

Example: Original sample weight was 2.15 g.

Aliquot taken (from Figure 5-1) was 46 ml.

The observed absorbance was 0.45.

The calibration curve (Figure 5-2 in this example) shows this to correspond to 0.52 μg of cyanide or 0.52 ppm.

RESULTS AND DISCUSSION

The recovery of cyanide standards carried through the procedure with sodium average 95% and are consistently above 85%. The detection limit is 0.03 μg of cyanide and the sensitivity is 0.7 absorption units per microgram of cyanide. A typical calibration curve is given in Figure 5-2. 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.

In addition to increasing the sensitivity several fold, extraction into butanol provides a separation from the small amount of insoluble material that is sometimes observed in the aqueous phase. This material probably results from the attack of the glass by hot alkali. Care must be taken to prevent any of the aqueous solution from getting into the spectrophotometer cell. If water is observed in the pipet during the transfer from the separatory funnel to the cell, the pipet should be drained into a small dry beaker. The water will adhere to the walls and the butanol can then be poured into a cell.

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.

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FIGURE 5-1
Graph for Determining Aliquot size from Sodium Weight

FIGURE 5-2
Typical Calibration Curve

HALOGEN (CHLORIDE) DETERMINATION

INTRODUCTION

The halogens, chlorine, bromine and iodine, occur as impurities in sodium primarily as a result of the commercial production of sodium metal by the electrolytic reduction of a molten sodium-calcium chloride mixture. Because of this chlorine is the predominant halogen impurity. A satisfactory method of halogen analysis, which is a prerequisite to meaningful in-loop studies, has not been available and therefore very little is known about the chemical behavior of these elements in sodium systems. Based on thermodynamic considerations, the halogens are believed to exist in sodium as halides exclusively, although the existence of complex halides has been postulated (1). Chloride, bromide and iodide have many chemical characteristics in common and it is convenient to determine them as a group. Fluorine, another halogen, has dissimilar properties and is excluded from this discussion. Traces of halides are generally determined either by titration with silver or mercury(II) salts or spectrophotometrically by oxidation of colored organic compounds by liberated free halogen. A particularly sensitive method for iodide utilizes its catalytic effect on the redox reaction between cerium(IV) and arsenic(III). An attempt to measure chloride from metallic sodium with a chloride specific electrode (2) encountered problems.

The method described here (3) takes advantage of the formation of undissociated mercuric halide from mercuric thiocyanate and the reaction of the freed thiocyanate with iron(III) to form a series of red complexes. The intensity of the red color provides an indirect measure of the amount of halide involved and is read on a spectrophotometer.

EXPERIMENTAL

Apparatus

Color measurements are made with a spectrophotometer accepting 4 cm or longer cells. Extrusion is done with a Manco hydraulic crimper (Figure 2-3).

Solutions

- A. Ferric nitrate - dissolve 1.0 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 100 ml of 8M HNO_3 .
- B. Mercuric thiocyanate - stir 0.1 gm of $\text{Hg}(\text{CNS})_2$ with 25 ml of ethanol for 30-60 minutes; filter through a glass frit and dilute to 50 ml with additional ethanol.
- C. Chloride standard - dissolve 0.415 g of dried sodium chloride in 500 ml of water to get a 500 ppm standard. Prepare a working standard of 10 $\mu\text{g}/\text{ml}$ daily by diluting 5 ml to 250 ml with water.
- D. Methanol - redistill from quartz in the presence of a few milligrams of sodium carbonate.
- E. Nitric acid - distill concentrated HNO_3 from a quartz still retaining only the middle fraction. Dilute 100 ml to 400 ml for use.
- F. Sodium carbonate - recrystallize sodium carbonate twice from water then dry at 250°C . Dissolve 1 gram of the product in 100 ml of water.

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 a beaker, never a flask or bottle which could permit an explosive atmosphere to build up. The beaker 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 second beaker rather than directly from the bottle to eliminate the chance of igniting a large amount of methanol. In the event that the beaker's contents do ignite, smother the fire with a cover glass or piece of aluminum foil.

Procedure

1. Dissolve a sodium sample weighing 0.9 to 1.1 grams in 15 ml of methanol in a 50 ml beaker.
2. Add 4M nitric acid until carbon dioxide bubbles are evolved. Slowly continue the addition of acid dropwise just until the evolution of gas ceases; a total of 10-12 ml of acid will be needed.
3. Add 10 ml of water and evaporate the solution to 10-15 ml to remove the methanol.

4. Add 1 ml of mercuric thiocyanate, mix and add 1 ml of ferric nitrate. Dilute to 25 ml and determine the absorption in 4 cm cells at 480 m μ using water as a reference solution.
5. Prepare a calibration curve by carrying 0.5, 1.0, and 2.0 ml standards through the procedure substituting 1 ml of sodium carbonate solution for the sodium in Step 1.

Calculations

Plot the micrograms of chloride used versus the absorption observed from the standards in (5) above to construct a calibration curve. Read the chloride content of the sample directly from the curve. Divide the micrograms of chloride by the grams of sodium taken to get parts per million of halogen expressed as chloride.

Example:

Sample weight 1.05 g
 Sample absorbance 0.15
 An absorbance of 0.15 = 5 μ g of chloride (from
 Figure 6-1 in this example)

$$\frac{5 \mu\text{g}}{1.05\text{g}} = 4.75 \text{ ppm halide expressed as chloride}$$

DISCUSSION

The recovery of chloride carried through this procedure is 95% or better. Similar recoveries could be expected with bromide but a significant amount of iodide would be oxidized and volatilized during Steps 2 and 3. Fluoride is not detected by this procedure. Reagent blanks can be kept to less than 0.5 μ g by using care in the preparation and storage of reagents. Particular care must be taken to avoid contamination of glassware with airborne chloride. Skin secretions are noteworthy in this respect also. It would be desirable to use an equivalent amount of sodium hydroxide or carbonate in the blanks and standards, but the reagent grade compounds contain relatively gross amounts of halide which are difficult or impossible to reduce to an acceptable level. Experiments in this laboratory have shown that the salt concentrations involved have a negligible effect on the color development.

The detection limit of 0.5 ppm and the sensitivity is about 0.02 absorption units per microgram of chloride. At the 5 ppm level, duplicates should be within 10-15% of each other.

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FIGURE 6-1
Typical Calibration Curve

TRACE METAL DETERMINATION BY COPRECIPITATION AND EMISSION SPECTROGRAPHY

INTRODUCTION

Measurement of trace metal impurities is necessary as one step in monitoring the quality of the coolant sodium in nuclear reactors and in interpreting the results of some associated research and development programs.

Coprecipitation/emission spectrographic analysis is used at the Pacific Northwest Laboratory as a supplementary technique to both vacuum distillation/flame spectroscopy and vacuum distillation/mass spectrography. The two advantages of this technique are that a number of metals are determined that are lost by vacuum distillation and that it provides a reasonably rapid survey analysis for most of the metals of interest in sodium technology.

Direct spectrographic analysis is not feasible for impurity levels below 1 ppm so a preconcentration step is required. Lanthanum hydroxide coprecipitation has been used⁽¹⁾ for atomic absorption analysis of sodium and its use has been extended to emission spectrography⁽²⁾. In this procedure the sodium is dissolved in alcohol, neutralized, and the trace metals are co-precipitated with lanthanum hydroxide. The precipitate is dissolved and an aliquot analyzed by d-c arc emission spectrography.

EXPERIMENTAL

Apparatus

A Bausch & Lomb large Littrow Spectrograph is operated under the following conditions:

Wavelength region	- 2350 to 4300 Å
Mask	- medium
Slit width	- 10 microns
Slit height	- 1 mm
Current	- 11 amp d-c (short circuit)
Exposure	- 30 seconds

Samples are burned in National Carbon Company SP9036 cupped electrodes against SP9006 counter electrodes. The cupped electrodes are water proofed with a 1% solution of Apiezon L grease in petroleum ether. Spectra are recorded on Kodak Spectrum Analysis No. 1 plates and the processed plates are read on a Jarrell Ash 23-100 microphotometer.

Reagents

Hydrochloric Acid: Distill concentrated reagent grade hydrochloric acid in a fused silica still. Standardize against sodium hydroxide solution of known concentration. Store in a plastic bottle.

Water: Redistill water in a fused silica still. Store in a plastic bottle.

Methanol: Distill reagent grade methanol in an all Pyrex still. Store in a plastic bottle.

Sodium Hydroxide: Dissolve 20 g of sodium hydroxide in sufficient water to make 100 ml of solution. Store in a plastic bottle.

Lanthanum-Indium: Dissolve 11.7 g of La_2O_3 and 2.4 mg of In_2O_3 in redistilled HCl and dilute to 100 ml with water.

Thymolphthalein: Dissolve 0.1 gm of thymolphthalein in 100 ml of ethanol.

Safety Precautions

The dissolution of sodium in methanol generates heat and hydrogen gas. A sodium-alcohol-hydrogen fire can occur spontaneously. Carry out the dissolution behind a suitable protective shield and in an area where a small fire would cause no hazard. Do not dissolve sodium in containers with narrow necks such as flasks or bottles.

Procedure

1. Add approximately 1 gram of sodium to 10 ml of methanol in a 50 ml polypropylene test tube. After the initial reaction subsides, add methanol in 2-3 ml increments to dissolve the remaining sodium. Use a minimum of methanol.
2. Add 2 drops of thymolphthalein to the methanol solution and cautiously titrate with hydrochloric acid to a colorless end point. Record the volume of acid used.
3. Evaporate the methanol under a heat lamp. The final volume should be about 10 ml and all of the salt should be in solution.
4. Add 1 drop of thymolphthalein and 100 μl of La-In solution. Mix, then add sodium hydroxide solution dropwise while stirring until the solution turns blue. Add 1 drop more to insure the complete precipitation of lanthanum hydroxide.

5. Centrifuge the mixture for 3 minutes then decant the supernate.
6. Dissolve the precipitate in 3 drops of hydrochloric acid. Dilute with 10 ml of water and repeat the precipitation (Steps 4, 5).
7. Dissolve the precipitate in 1 ml of hydrochloric acid and transfer duplicate, 100 μ l aliquots to graphite cupped electrodes treated with Apiezon grease.
8. Evaporate the solvent under a heat lamp, arc the samples on the spectrograph and process the plates.
9. Make semi-quantitative estimates of impurity concentrations by visual comparison with standard plate prepared by taking known amounts of impurities in pure sodium chloride solutions through the procedure.
10. Determine the corrosion products of stainless steel by densitometering the following lines:

Mn	2605.69 Å
Cr	3843.25
Fe	3020.64
In	3039.36 (Internal Standard)
Co	3044.00
Ni	3050.82
11. Run a blank through the entire procedure with each set of samples.

Calculations

Determine the sample weight from the equation:

$$\frac{(\text{normality of HCl})(\text{ml of HCl})(23)}{1000} = \text{g of Na.}$$

Convert the micrograms of impurity to parts per million using the following equation:

$$\frac{(\mu\text{g impurity in sample}) - (\mu\text{g impurity in blank})}{(\text{g of Na in Sample})(0.1)} = \text{ppm of impurity.}$$

Example:

Acid Normality = 9.6N
 Acid Volume = 4.5 ml
 Fe in Sample = 0.65 μ g
 Fe in Blank = 0.05 μ g

The sample weight is:

$$\frac{(9.6)(4.5)(23)}{1000} = 1.2 \text{ grams.}$$

The iron concentration in sample is:

$$\frac{.65 - .05}{(1.2)(0.1)} = 5 \text{ ppm}$$

RESULTS AND DISCUSSION

The elements determined densitometrically show a precision of $\pm 13\%$ (relative standard deviation). Accuracy, as determined by comparison of spiked samples with standards added directly to the electrode cups, was within the precision of the measurement. The visual comparison analysis is good within a factor of two. The detection limits (Table 6-1) vary from .01 ppm for manganese to 100 ppm for barium. More than half of the impurities measured have detection limits of 1 ppm or less.

References

1. J. M. Scarborough, C. D. Bingham and P. F. DeVries, Anal. Chem., **39**, 1394 (1967).
2. R. Ko and P. Anderson, Anal. Chem., **41**, 117 (1969).

<u>Element</u>	<u>Detection Limit, ppm</u>	<u>Element</u>	<u>Detection Limit, ppm</u>
Mn	0.01	Y	0.5
In	0.1	Pb	1
Mg	0.1	Ru	1
Ag	0.2	Sc	1
Al	0.2	Si	1
Au	0.2	Ca	2
Be	0.2	Sb	2
Co	0.2	Tl	2
Cu	0.2	Cd	5
Ga	0.2	Bi	5
Ni	0.2	Nb	5
Ti	0.2	Zn	5
Cr	0.3	As	10
Fe	0.5	Zr	10
Mo	0.5	P	20
Rh	0.5	W	20
Sn	0.5	Ta	50
V	0.5	Ba	100

TABLE 7-1

Detection Limits for Impurities in Sodium

DETERMINATION OF POTASSIUM BY FLAME SPECTROPHOTOMETRYINTRODUCTION

Potassium is the major impurity in reactor grade sodium, generally occurring in the 100 ppm range. The properties of potassium are very similar to those of sodium and no adverse effects on reactor operation have been associated with the presence of traces of this metal. Nevertheless, a knowledge of the potassium content is needed for the complete characterization of sodium.

Flame emission spectrophotometry is generally considered to be the best method for determining trace levels of the alkali metals, although atomic absorption is occasionally used. The procedure used at PNL employs scanning flame emission spectrophotometry to measure the potassium in the presence of the sodium.

EXPERIMENTALApparatus

A Perkin-Elmer Model 403 scanning double beam flame spectrophotometer with a 3 slot air-acetylene burner is used for all spectral measurements. Spectra are recorded on a 1-10 mV strip chart recorder.

Solutions

- A. Methanol - Redistill methanol from a quartz still and store in polyethylene bottles.
- B. Nitric Acid - Redistill nitric acid from a quartz still and store in polyethylene bottles after diluting to approximately 5M.
- C. Water - Pass tap deionized water through a high quality mixed bed ion exchange column and store in a polyethylene tank.
- D. Bromcresol Green - Dissolve 0.04 g of indicator in 100 ml of ethanol.
- E. Potassium Standard - Dissolve 0.24 gm of KNO_3 , dried at 110°C , in 1000 ml of water to make a 100 $\mu\text{g/ml}$ standard.

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 methanol.

Procedure

1. Dissolve a weighed sample of 1.8-2.2 grams of sodium in a minimum of methanol in a 100 ml polypropylene graduate cylinder.
2. Add several drops of bromcresol green followed by sufficient dilute nitric acid to weakly acidify the solution and turn the indicator from blue to yellow.
3. Dilute the acidic sample to 100 ml with water, mix and scan the flame spectrum over the range of 7620 to 7680Å. For the Perkin-Elmer 403 Spectrophotometer, the critical instrument settings are:
Grating - visible
Filter - in
Wavelength drive speed - 3
Flame - oxidizing
Burner - 3 slot
4. Prepare working standards by repeating the procedure substituting 4.5 g of sodium carbonate and 0, 1.0, 2.0 and 4.0 ml of the potassium standard for the sodium. Add 20 ml of methanol to each standard. Samples and standards must be flamed consecutively.

Calculations

Prepare a calibration curve similar to Figure 8-1 from the standards. From this curve read the micrograms of potassium in the sample. Then to determine the parts per million of potassium in the sodium, divide the micrograms of potassium by the weight of sodium taken.

Example:

Relative emission intensity of sample = 15 units

Sample weight = 2.1 g

15 units corresponds to 280 μg of potassium (using Figure 8-1 in this example)

$$\frac{280 \mu\text{g}}{2.1 \text{ g}} = 133 \text{ ppm potassium in the sodium}$$

DISCUSSION

This is a simple analysis at the levels of potassium commonly found in sodium. If the potassium were less than 5 ppm either an ultra pure sodium carbonate or a standard additions technique would be required. Selected batches of reagent grade sodium carbonate are suitably low enough in potassium to be used in preparing standards for most sodium.

The detection limit for this procedure is largely dependent on the instrumentation available but for the Perkin-Elmer 403 Spectrophotometer the resolution is excellent (Figure 8-2) and 2-3 ppm can be detected; duplicates at the 50 ppm level agree within 10%.

FIGURE 8-1
Typical Calibration Curve

FIGURE 8-2

Potassium Spectrum; 20 ppm Potassium in Sodium

TRACE METAL DETERMINATION BY DISTILLATION AND FLAME SPECTROMETRY

INTRODUCTION

Trace metal impurities occur in reactor sodium primarily as initial impurities in the sodium supply and as the result of corrosion, nuclear reactions, and fuel element ruptures. Although the presence of modest amounts of some metals appears to be inconsequential, other metals can be potential sources of trouble. For example, calcium and lithium may be involved as a vehicle for nitrogen transport and subsequent nitriding of steels. The content of the stainless steel metals in the sodium is an indication of the corrosion and mass transport that is occurring.

Most of the metals of interest never occur at levels above one part per million. A preliminary concentration is therefore required for their determination. The separation of trace metals from aqueous solutions of sodium ions is, in principle, relatively easily accomplished by solvent extraction, coprecipitation or ion exchange. In practice, blanks associated with the dissolution of the sodium and neutralization of the resulting alkaline solution seriously effect the detection limit. Vacuum distillation of sodium and subsequent analysis of the residue has been investigated by a number of laboratories (1,2,3). The procedure described here is largely from the work of Ramachandran and Hareland (3).

A few relatively volatile metals are largely lost in the distillation process. They include zinc, cadmium, mercury, and most of the alkali metals. In the presence of a few milligrams of sodium oxide, those relatively volatile metals that form oxides more stable than Na_2O will be converted to the non-volatile oxide. Thus, in practice, lithium and the alkaline earth metals are recovered in the distillation residue.

The apparatus for vacuum distillation can be relatively simple. A metal cup (commonly tantalum) containing sodium is heated by an induction heater to about 300°C under a vacuum of 10^{-3} torr. Sodium evaporates from the cup and condenses on the glass or quartz walls of the vacuum containment system. After disassembly, the cup residue is dissolved in a few milliliters of acid and analyzed.

The actual analysis of the residue solution is done by either flame emission or atomic absorption analysis. These techniques provide the best combination of sensitivity, speed, accuracy, and selectivity for most metals of interest. Some of the more refractory metals could be determined with greater sensitivity by colorimetric methods and for some purposes a survey method using one of the emission (4) or mass spectrographic (5) techniques would be more suitable.

EXPERIMENTAL

Apparatus

A 100 ml high purity tantalum cup, fabricated by Norton Company, rests on a pedestal inside the quartz and pyrex vacuum system (Figure 9-1). A Lepel 2.5 kW rf generator provides heat through a copper induction coil. A mercury diffusion pump and mechanical back up pump provide a vacuum of 10^{-3} torr which is monitored by a cold cathode vacuum ionization gauge. The rf generator is set to melt a 50-60 gram sodium charge in about 5 minutes. When the distillation is complete the outer surface of the apparatus rapidly cools from about 80°C to about 60°C. This change is sensed by a Cole-Parmer Versatherm Controller which then turns off the generator.

Flame spectrophotometry is done with a Perkin-Elmer Model 403 spectrophotometer equipped with both 3 slot and nitrous oxide burners. Acetylene is used as fuel. High intensity, Perkin-Elmer hollow cathode lamps are used for atomic absorption.

Solutions

- A. Hydrochloric acid - Redistill concentrated hydrochloric acid from a quartz still and store in a polyethylene bottle.
- B. Nitric acid - Redistill concentrated nitric acid from a quartz still and store in a teflon bottle.
- C. Ethanol - Redistill absolute ethanol from a quartz still and store in a polyethylene bottle.
- D. Water - Pass tap deionized water through a high quality mixed bed ion exchange column such as the research model of the Illinois Water Treatment Company. Store in a polyethylene tank.

- E. Stock metal standards - Prepare 1000 ppm standards in 1M hydrochloric acid according to the Perkin-Elmer manual (5). Store in polyethylene bottles.
- F. Sodium chloride - Dissolve 2 gm of sodium chloride in 100 ml of water. Store in a polyethylene bottle.
- G. Working metal standards - Dilute 25 μ l aliquots of the stock standards (E) with 2.0 ml of hydrochloric acid, 0.5 ml of sodium chloride, and sufficient ethanol to make 2.5 ml.
- H. Aqua regia - Mix 25 ml of concentrated nitric acid with 75 ml of concentrated hydrochloric acid and use immediately.

Safety Precautions

Power leads (copper tubing) from rf generators can produce serious burns. These leads should be insulated with Tygon tubing where possible. Do not attempt to position the heater coil while the power is on.

Although a sodium fire is improbable, it could occur if the vacuum system should implode during the distillation. The distillation should be carried out in a metal fume hood. Water, aqueous solutions, and organic solvents should not be present in the hood.

The bulk of the distilled sodium should be disposed of by melting and pouring it into a disposable metal container. The balance can be reacted with either moist air or alcohol.

Procedure

1. Prepare the tantalum cup by filling it with aqua regia, heating to about 80°C, emptying, rinsing with hydrochloric acid and deionized water. Store the cleaned cup in a plastic jar until used.
2. In an inert atmosphere glove box transfer a measured 40-70 grams of sodium to the cup. Assemble the distillation apparatus with the cup in place using Dow Corning high vacuum grease on the ground surfaces. Place a cap on the standard taper outlet and take the apparatus out of the glove box.
3. Insert the apparatus in the coil of the heater. Then remove the standard taper cap and connect the vacuum system to the distillation apparatus. Start the mechanical and diffusion pumps immediately to minimize air contamination of the sodium.

4. When the pressure in the system has been reduced to 5×10^{-3} torr start the heater. The pressure may rise briefly but should drop to approximately 10^{-3} torr after distillation begins. Heater controls should be set at 100 ma grid current and 0.2 amp plate current.
5. After 30-60 minutes, when the system has reached a steady state, set the Versatrol controller to turn the heater off when the surface temperature drops 5°C .
6. When the distillation is complete and the apparatus has cooled, stop the vacuum pumps, allow air to enter the still by slowly opening the standard taper joint, and disassemble the apparatus.
7. Add 2 ml of aqua regia to the cup, wetting all of the wall, then loosely cover the cup with a Teflon watch glass and evaporate to dryness at a low heat. Add 2.5 ml of 6M hydrochloric acid to the cup and dilute to 25 ml with ethanol.
8. Determine the metals of interest by the methods shown in Table 9-1. Refer to the Perkin Elmer manual (5) for detailed instructions on instrument settings and operation. Both working standards and samples should be used soon after diluting with ethanol.

Calculations

At the low metal concentrations encountered in this procedure, the calibration curves can be assumed to be linear. The concentration of any metal in the sample solution can be found by its relative absorption or emission intensity with a blank and a single working standard for that element. Determine the concentration of the metal in sodium by dividing the sample weight (in grams) by the solution volume (25 ml) and multiplying by the measured concentration in ppm in the sample solution.

Example:

61 grams of sodium is distilled

1 ppm iron standard = 80 recorder units of absorbance

Sample = 20 recorder units of absorbance

Blank = 3 recorder units of absorbance

The solution contains $\left(\frac{20-3}{80-3}\right) = 0.23$ ppm of iron

The sodium contains $\left(\frac{61}{25}\right) 0.23 = 0.56$ ppm of iron

DISCUSSION

The most realistic blank is obtained by carrying the empty tantalum cup through the various manipulations, particularly treatment with acids. None of the metals sought have been detected in these blanks so for routine use, blanks prepared in the same manner as the standards are used. The sensitivity of flame spectrometric measurements for various metals varies widely and a number of metals that would be recovered in the distillation residue cannot be detected by these methods at the levels of interest. Colorimetric or spectrographic survey methods can be used for these metals. The detection limits and the precisions obtainable at the 0.1 ppm level for the methods used in this procedure are listed in Table 9-2. The precision improves significantly at higher concentrations for metals with the poorer detection limits.

The major problems encountered in this analyses are first, obtaining a representative sample and second, preventing contamination of the sample or apparatus. The prevention of contamination is largely a matter of technique. Acid washed plastic ware should be substituted for glassware wherever possible. Samples and associated equipment should be protected from dust and metal particles and corroded metal.

The best method of obtaining a sample is to fill the distillation cup directly from a valved "T" in a pipe or tube of flowing sodium. The first sodium drawn from such an arrangement should be received in a waste container so that what amounts to a "dead leg" in the "T" will be flushed before the analytical sample is taken. Frequently the only sample available will be in a secondary container such as a bypass loop sample in nickel or stainless steel tubing. Sodium from these containers may be transferred to the distillation cup by melting or extruding. Particular care must then be taken to prevent metal cuttings from contaminating the sample. Because the problem of radial segregation has not been clearly defined for most metals, the use of sampling techniques involved the use of secondary containers should be discouraged.

References

1. V. J. Rutkauskas, "Vacuum Distillation System for Sodium" in ANL-7520, Part I, Argonne National Laboratory, Argonne, Illinois, November 1968.
2. H. T. Carmichael, S. A. Meacham and J. O. Kermoshchuk, "Determination of Iron, Nickel and Chromium in Sodium by Atomic Absorption", APDA-207, Atomic Power Development Associates, Detroit, Michigan, July 1968.
3. T. P. Ramachandran and W. A. Hareland, "Determination of Metallic Impurities at the PPB-PPM Level in Sodium", ANL-7668, Argonne National Laboratory, Idaho Falls, Idaho, March 1970.
4. "Trace Metal Determination by Emission Spectrography", this manual, Section 7.
5. E. Berkey, G. G. Sweeney and W. M. Hickam, "Sodium Analysis by Spark Source Mass Spectrography", Nuc. App., 5, 344, (1968).
6. Perkin-Elmer Corporation, "Analytical Methods for Atomic Absorption Spectrophotometry", Part 303-0152.

<u>Metal</u>	<u>Method</u>	<u>Wavelength, A</u>	<u>Flame</u>	<u>Oxidant</u>
Barium	FE	5536	Reducing	N ₂ O
Calcium	AA	4227	Reducing	N ₂ O
Chromium	AA	3579	Reducing	Air
Cobalt	AA	2407	Oxidizing	Air
Copper	AA	3247	Oxidizing	Air
Iron	AA	2483	Oxidizing	Air
Lithium	FE	6708	Oxidizing	Air
Magnesium	AA	2852	Oxidizing	Air
Manganese	AA	2800	Oxidizing	Air
Molybdenum	AA	3133	Reducing	N ₂ O
Nickel	AA	2320	Oxidizing	Air
Strontium	AA	4607	Reducing	N ₂ O

TABLE 9-1

Conditions for Determining Trace Metals by Atomic Absorption (AA)
Or Flame Emission (FE) Spectroscopy

* * * * *

<u>Metal</u>	<u>Detection Limit (PPB)</u>	<u>Std. Dev. (%)</u>
Barium	50	30
Calcium	2	5
Chromium	5	10
Copper	5	10
Iron	10	15
Lithium	1	5
Magnesium	1	5
Manganese	5	10
Molybdenum	20	30
Nickel	5	10
Strontium	2	5

TABLE 9-2

Detection Limits and Precision at the 0.1 ppm Level
For Metals in Sodium

FIGURE 9-1

Vacuum Distillation Apparatus

APPENDIX

MERCURY CLEANING PROCEDURE

Mercury used in the determination of oxygen in sodium by the amalgamation method must have no acidic or basic impurities nor can it contain impurities that react with sodium. This cleaning procedure is specifically intended for mercury contaminated with sodium although other alkali or alkaline earth metals may be present.

Apparatus

Impure mercury is forced by air pressure from a stainless steel storage tank onto a glass column 4 cm by 120 cm packed with 0.6 cm glass beads (Figure A-1). A polypropylene water aspirator draws 2M nitric acid from a plastic carboy through the column countercurrent to the mercury flow. The scrubbed mercury collects at the bottom of the column and is withdrawn through a teflon stopcock from a tube that opens 10-15 cm below the surface of the mercury pool. The mercury is then passed through a gold adhesion filter (Bethlehem Apparatus Company) and stored in a 15 liter stainless steel reservoir (Figure A-2) at 25 psig of argon. Mercury is delivered to a valve in the inert atmosphere glove box through stainless steel tubing.

Safety Precautions

Because of the poisonous nature of mercury and mercury compounds and vapor, this procedure should be performed in a fume hood. Rubber gloves should be worn and spilled mercury cleaned up promptly. The quality of the atmosphere should be monitored frequently with a mercury vapor detector.

Procedure

1. Remove gross amounts of sodium from the mercury by allowing the amalgam to stand under 3M hydrochloric acid until hydrogen evolution ceases.
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/minute.

4. Tighten the fill plug and pressurize the mercury storage tank to 25 psig with air. Adjust the flow of mercury onto 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 the funnel at about 50 ml/minute 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.

DISCUSSION

Mercury cleaned by this procedure does not contribute any detectable blank to the oxygen determination. It has no surface film after exposure to air for one month and it contains less than one part per billion of metallic sodium. Other meaningful impurities are insoluble in mercury and appear to be completely separated when the mercury is drained from the scrub column. Subsequent filtering and dispensing from the tank provide backup purification.

FIGURE A-1

Mercury Scrubbing Apparatus

FIGURE A-2
Mercury Reservoir

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