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Oxygen in Sodium and NaK by the
Distillation Method

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PROCEDURE FOR THE DETERMINATION OF OXYGEN IN SODIUM
AND NaK BY THE DISTILLATION METHOD

This report includes the working procedure for the determination of oxygen in sodium and NaK by the distillation method. The apparatus, which is based on that developed by The Argonne National Laboratory, can be connected to either dynamic or static systems and makes possible the direct sampling of alkali metals at operating temperatures. Sodium and NaK have been sampled with this device at temperatures as high as 1400° F.

The alkali metal is transferred, under pressure, to the sampler where a fixed volume of the metal is retained in a removable hemispherical cup. The metal is then distilled from the oxide at a temperature of 800° F and at a pressure of <5 microns of Hg. After the sampler has cooled, the cup is removed from the sampler and the oxide, which remains as a residue in the cup, is dissolved in water. The resulting solution of alkali metal hydroxide is then titrated to a methyl orange indicator end point with a standard solution of hydrochloric acid. The concentration of oxygen in the alkali metal is calculated on the basis of the equivalents of acid consumed in the titration, and the weight of the alkali metal, retained during sampling, in the cup.

Apparatus

The apparatus is shown schematically in Figure 1. A photograph is also presented, Figure 2. The apparatus is constructed of stainless steel and consists of two main sections, a sample cup insert, and a distillation chamber. The two sections are held together with "C" clamps. Five independent heating systems, controlled by variacs, are used to regulate the temperatures of the various sections of the sampler. The insert heater is simply a nichrome heating element wound around a suitable ceramic base. The thermocouples for measurement of the temperature of the sample cup are inserted through a hole in the center of the base. The heater is supported on a washer welded to the metal sheath which surrounds the thermocouple leads. Calrod heaters are used to heat the sample transfer line and the top of the sampler. The sampler discharge line to the overflow is heated by a wrap-around heater. A small pot furnace, which is fabricated from two, three-inch clam shell heaters, is fitted around the base of the transfer valve. The valve now in use is a 1/4-inch Hoke stainless steel bellows valve with an extension handle for ease of manipulation.

During distillation the lower half of the distillation chamber is cooled by passing air through the cooling coil to provide a condensing surface for the distillate. The lower half of the insert is cooled in the same manner to protect the "O" ring seal. The temperatures at the points indicated on Figure 1 are plotted continuously on a twelve-point recorder. Thermocouples are spot-welded at these points. The temperatures of the transfer line and valve are also recorded. The distillation temperature is regulated by a

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temperature controller which is connected in series with the insert heater circuit. The cut-off point on the controller is set ten degrees above the desired distillation temperature. The depression in the top of the insert is fitted with a removable liner which is fabricated from 5-mil nickel foil. The liner is fitted to the depression in the insert with a stamping die of close tolerance. These liners may be cleaned and reused.

The vacuum system should be capable of maintaining a pressure of < 5 microns. A vacuum pump with a free air displacement of at least 50 liters per minute is required.

Procedure

A. Preheating Period

1. Adjust the pressure of the helium supply to 1 to 2 psi.
2. Close the stopcock between the trap and the vacuum pump, and open the helium stopcock to admit helium to the sampler.
3. Place a clean nickel liner in the depression of the insert. Seat the liner firmly in place with the stamping die.
4. With the "O" ring, thermocouples, and heater in place, clamp the insert firmly into position in the distillation chamber, and connect the heater and thermocouple plugs at the base of the insert.
5. Start the vacuum pump; close the helium stopcock, and then open the stopcock between the trap and the vacuum system. (Check for leaks if the sampler does not pump down rapidly to the minimum pressure of the vacuum system.)
6. While the sampler is being evacuated, adjust the variac which control the calrod at the top of the sampler and the discharge line wrap-around heater so as to maintain a temperature of 400 to 500° F at the top of the sampler and 300° F along the discharge line.

7. Adjust the variac which controls the transfer valve pot furnace to heat the valve to the temperature of the alkali metal being sampled.

(Never heat the valve to a temperature higher than 1000° F.)

8. Adjust the variac to the transfer line calrod to heat the transfer line to the temperature of the metal being sampled. (Do not exceed a temperature of 1000° F.)

9. While the sampler is being heated to these operating temperatures, flush the system alternately with helium and evacuate it to <5 microns pressure at least three times.

The rate of heating should be such that the preheating period can be completed within one hour.

B. Transfer of Sample

1. Prior to transferring the sample, shut off the vacuum stopcock and open the helium stopcock to admit helium into the sampler. The pressure of the system from which the sample is to be taken should exceed 3 psi.

2. Open the pressure relief valve slowly. (If there is no helium flow through the relief valve, the discharge line is plugged and must be cleaned out before a sample is taken.)

3. Open the transfer valve and allow a sufficient volume (~200 ml) of the alkali metal to flow into the insert and into the overflow receiver to assure a complete flush of the transfer line and insert cup liner.

4. Close the transfer valve slowly and immediately close the pressure relief valve.

5. Shut off the variacs to the transfer line and transfer valve heaters.

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C. Distillation of Alkali Metal

1. Open the valve which connects the air line to the condensing coil. Open the valve to the "O" ring cooling coil. (The line pressure should be at least 60 psi.)

2. Close the helium line stopcock and slowly open the vacuum line stopcock.

3. Adjust the variac to the calrod on the top of the sampler to maintain a temperature of 1000° F during the distillation period.

4. Set the controller for the insert heater at 810° F, and adjust the variac which controls the insert heater so that the distillation temperature of 800° F is reached within 30 to 45 minutes. (It is desirable to maintain a temperature of 800° F by close adjustment of the variac. The controller should be used only to handle temperature surges resulting from power fluctuations.)

5. Adjust the flow of air to the "O" ring cooling coil to limit its temperature to 150° F.

6. Adjust the condensing coil air pressure to maintain a temperature of $\sim 300^{\circ}$ F. (If the temperature of the condensing region of the sampler is too high, an increase in the pressure will be registered by the vacuum gauge.)

7. Continue heating the insert at 800° for 2.5 hours.

8. Following the distillation period, shut off the variacs to the insert heater and to the calrod at the top of the sampler.

9. When the temperature of the insert has dropped to $< 200^{\circ}$ F, close the vacuum line stopcock and slowly open the helium stopcock.

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10. Shut off the variac controlling the discharge line heater.
11. Shut off the air pressure to the cooling coils.
12. Place 25 ml of distilled water into each of two 150-ml beakers and add 2 drops of a solution of methyl orange indicator to each of the two beakers.
13. Remove the insert from the sampler by removing the C-clamps.
14. Transfer the nickel cup from the insert depression into one of the beakers.
15. Replace the insert into the distillation chamber after fitting a new liner into the depression.
16. From a buret add 0.010 N HCl to the beaker which contains the sample cup until the color of the solution becomes a permanent red.
17. Record the volume of HCl added as (T_1).
18. Repeat Step 16 with the second beaker containing only the water.
19. Record the volume of HCl added as (T_2).
20. Place both beakers on a hot plate and bring the solutions to a boil.
21. Allow the solutions to cool, and add additional HCl to both solutions until the color of the solution becomes red again.
22. Record the volume of HCl added to the solution containing the sample as (T_3) and the volume of HCl added to the solution of water as (T_4).

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D. Cup Sample

1. Follow the procedure through Section B, Step 5.
2. Shut off the variac controlling the calrod at the top of the sampler.
3. Completely open the valve connecting the air line to the condensing coil.
4. Close the helium stopcock, and slowly open the vacuum line stopcock.
5. After the temperature of the insert has dropped to $< 200^{\circ} \text{F}$ close the vacuum line stopcock and slowly open the helium stopcock.
6. Allow the insert to cool to room temperature.
7. Shut off the variac to the discharge line heater.
8. Shut off the air pressure to the cooling coil.
- 9a. When sampling sodium, remove the insert from the sampler and place the cup liner into a beaker containing 250 ml of absolute ethanol. Replace the insert in the distillation chamber.
- 9b. When sampling NaK, remove the thermocouples and heater from the insert. Freeze the NaK in the cup liner with a CO_2 fire extinguisher which is equipped with a modified nozzle made from 3/4-inch stainless steel tubing. (Insert the nozzle into the space normally occupied by the insert heater and turn on for 30 seconds.) Place 250 ml of absolute ethanol in a beaker and cool the beaker in a bath of crushed ice. Carefully remove the insert from the sampler and place the cup liner in the beaker. Control the reaction of the NaK and alcohol by removing the beaker from the ice bath

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and returning it if the reaction becomes too vigorous. Replace the insert in the distillation chamber.

10. Allow the alkali metal to react completely with the alcohol in a well-ventilated area to reduce the danger from the hydrogen gas evolved.

11. When the alkali metal is completely dissolved transfer the solution to a 500-ml volumetric flask and dilute the solution to the mark with distilled water.

12. Stopper the flask and shake it to thoroughly mix the solution.

13. Record the volume as (V_1).

14. By means of a pipet transfer exactly 10 ml of the solution to a 250-ml beaker which contains 25 ml of distilled water.

15. Record the volume as (A_1).

16. Add 2 drops of a solution of phenolphthalein indicator to the solution in the beaker.

17. From a buret add 0.10 N HCl to the solution in the beaker until the pink color of the indicator has faded completely.

18. Record the volume as (T_5).

Calculations

1. Oxygen, Per Cent

$T_1 + T_3$ = volume of titrant (HCl) consumed by sample, ml

$T_2 + T_4$ = volume of titrant (HCl) consumed by reference solution, ml

N_1 = normality of hydrochloric acid

8.00 = equivalent weight of oxygen

$$\text{Oxygen, per cent} = \frac{[(T_1 + T_3) - (T_2 + T_4)] N_1 \times 8.00 \times 100}{(\text{weight of cup sample, mg})}$$

2. Weight of Cup Sample of Sodium, mg V_1 = volume of sample solution, ml A_1 = test portion of sample solution, ml T_5 = volume of titrant (HCl), ml N_2 = normality of hydrochloric acid

22.99 = molecular weight of sodium

$$\text{Weight of sodium, milligrams} = \frac{T_5 \times N_2 \times V_1 \times 22.99}{A_1}$$

3. Weight of Cup Sample of NaK, mg V_1 = volume of sample solution, ml A_1 = test portion of sample solution, ml T_5 = volume of titrant (HCl), ml N_2 = normality of hydrochloric acid

22.99 = molecular weight of sodium

39.1 = molecular weight of potassium

30 = Mean Mol. Wt. NaK Comp. 56-44

Mean Molecular Weight, NaK =

$$\frac{(\% \text{ Na}_{\text{Eutectic}} \times 22.99) + (\% \text{ K}_{\text{Eutectic}} \times 39.1)}{100}$$

$$\text{Weight of NaK, milligrams} = \frac{T_5 \times N_2 \times V_1 \times \text{Mean Mol. Wt.}}{A_1}$$

G. Goldberg
G. Goldberg

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Group Leader

J. White
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Figure 1
Sodium and NaK Distillation Apparatus

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Fig. II
Sodium -NaK Distillation Apparatus

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