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DETERMINATION OF OXYGEN IN LIQUID ALKALI METALS BY MERCURY AMALGAMATION METHOD

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INTRODUCTION:

C. R. F. Smith in his treatise "The Determination of Oxygen in Sodium - A Critical Review of Analytical Methods," is quoted saying, "There is much conflicting evidence as to the significance of Na_2O in liquid sodium corrosion, but until the problem is resolved the potential hazard should not be ignored." "Definitive studies of these problems have been hampered by the contradictory data provided from different laboratories." This lack of agreement continues today among laboratories.

Lewis researchers have been investigating a few of the known methods such as (1) Plugging Meter Method (Mechanical), (2) Pepkowitz - Judd Method, (3) Butyl Bromide Method, and (4) Gettering-Vacuum Fusion Method. The purpose of this report is not to add to the confusion but to discuss the analytical techniques developed by the author using the Pepkowitz-Judd Method under inert atmosphere within a vacuum dry-box.

At Lewis, the service chemist is responsible for the determination of the oxygen content of the alkali metal and its metal impurities, therefore, an existing technique developed by Pratt & Whitney Aircraft's Canel Materials Laboratory Analytical Section was used, although research chemists at Lewis are evaluating other procedures. The Pratt & Whitney technique was altered to meet Lewis technical problems. The problems involved include the handling of low eutectic NaK, cesium and rubidium.

The low eutectic NaK (78% K and 22% Na) cesium and rubidium are liquid or very near liquid at room temperature, therefore, special handling techniques were developed for this purpose. This will be discussed later.

EXPERIMENTAL

PRINCIPAL:

(1) When sodium, potassium or NaK are amalgamated with mercury under an inert gas atmosphere, their oxides being insoluble in the mercury, separate from the amalgam and rise to the surface. Repeated separations and additions of Hg serve to isolate the alkali metal oxides from the alkali metal. They are dissolved in water and acid and titrated.

SCOPE:

This procedure may be used for the determination of oxygen in alkali metals in the range of 5 ppm to 1%.

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APPARATUS:

Inert atmosphere dry box
250 ml Pyrex separatory funnels with Teflon Stopcocks
Glass stoppered bottles, beakers

REAGENTS:

Sulfuric acid, 0.5 N - prepare and standardize
Sulfuric acid, 0.002 N - prepare by diluting 8 ml of 0.5 NH_2SO_4 to two liters - standardize
Sodium hydroxide 0.5N - prepare and standardize
Mercury, triple distilled

PROCEDURE:

(1) Evacuate the glove box to a pressure of about 25 microns and fill the box with dry oxygen - free argon. Pressurize the box to about 1 psig and check the oxygen content in the box using a trace oxygen analyzer. The atmosphere should contain less than 1 ppm oxygen. Evacuate and purge the system until the proper oxygen content has been established.

(2) Add approximately 20 ml. of mercury to a 250 ml. pyrex separatory funnel. To this add 0.5 to 1 gram sample of the alkali metal sample. Shake for about 3 minutes, hold for 30 seconds and draw off all but 3 ml. of the amalgam into a marked bottle.

(3) Repeat additions and separations of the mercury 6 times.

(4) In the last extraction pour a small portion into a separate beaker to check the completeness of the extraction. (Add water and phenolphthalein to the beaker outside the box.)

(5) Remove all the material from the dry box.

(6) Dissolve the oxide from the mercury - oxide extract in about 50 ml. of distilled water and titrate with dilute acid to a pH of 7 using a titrimeter.

(7) React the alkali metal mercury amalgam with 80 ml. of 0.5N H_2SO_4. If bromcresol purple added to the solution turns blue, add additional acid.

(8) Titrate the acid extract, using the bromcresol purple as an indicator or a titrimeter to a pH of 7 with 0.5N NaOH.

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CALCULATIONS:

(1) Sample Weight:

$$W = (N_A V_A - N_B V_B) \text{ meq. wt.}$$

where

W = Sample weight, g

N_A = Normality of the 0.5N H_2SO_4 used to extract alkali metal from the amalgam

V_A = Volume of 0.5N H_2SO_4 used, ml.

N_B = Normality of 0.5N NaOH

V_B = Volume of 0.5N NaOH used to titrate excess 0.5N H_2SO_4

meq. wt. = milliequivalent weight of the alkali metal

(2) Results:

$$\text{ppmO} = \frac{N_a V_a \times \text{meq. wt. O} \times 10^6}{W}$$

where, Na = Normality of 0.002 N H_2SO_4 used to titrate the oxides

V_a = volume of dilute H_2SO_4 used

meq. wt. O = 0.008

RESULTS:

Table #I shows a comparison between plugging meter temperatures, using the MSA solubility curves for oxygen in sodium, and the amalgamation procedure. The analytical results compared favorably with the plugging runs with a few noted exceptions. Sample PS-1 with 8 ppm O did not compare to the plugging run of 40 ppm indicated by the MSA curve. Contaminated argon was pressurizing the loop, but the diffusion of oxygen was not noted in the sample. PS-2 contained a loose connection and air leaked into the sample. As the sodium circulated the loop, uniformity between samples and plugging data correlated closely. With PS-5, the loop had a power failure, therefore, a plugging run was not determined.

TABLE II.

SAMPLE	OXYGEN PPM BY VACUUM AMALGAMATION	OXYGEN, PPM ARGON ATMOS. AMALGAMATION	OXYGEN, PPM IN ARGON	DATE
POTASSIUM	90 ppm	176 ppm	0.5 ppm	5-29-63
	-	180	0.5 ppm	6-7-63

Table II shows a comparison between the dry box amalgamation method and a vacuum amalgamation method on a potassium sample. The disagreement between these samples may be argued from both sides. The vacuum amalgamation method involves the extrusion of the sample from the container into an evacuated chamber. The amalgamation then takes place under a pressure of 10^{-5}mm Hg vacuum. It can be argued that by extrusion the precipitated oxide remains on the container walls and, therefore, the extrusion sample may not be representative.

Also, the question arises "how good a vacuum is good enough?" In mass spectrometry a pressure of 10^{-6}mm Hg may indicate a background concentration of 100 ppm oxygen from outgassing of component materials. It could be possible that an O_2 content in excess of 100 ppm be present in the vacuum amalgamation chamber. Therefore, the true O_2 content of the evacuated chamber should be checked by a quantitative mass spectrometer.

With an O_2 content of less than 1 ppm in the argon cover gas, potassium samples were determined a week apart and good oxide precision was noted.

DISCUSSION:

It is the author's opinion that the amalgamation method using an inert gas atmosphere is the most reliable of the known methods of oxygen analysis in liquid metals. Its versatility is displayed when samples of varying lengths, sizes, shapes and materials can be handled easily. Other methods require specific sample containers of uniform length, size, shape and material. The method lends itself applicable to the fluid samples such as NaK, cesium and rubidium without much adjustment of the existing equipment.

RECOMMENDATIONS:

The original Pepkowitz-Judd amalgamation method employed the use of an indicator whose pH color change occurred at a pH of 8 (phenolphthalein). Titrating to a pH of 7 with a titrimeter overcomes the uncertainty associated with a color change. The outside walls of the stainless steel sample tubes were carefully vapor degreased with a suitable solvent, wiped with acid, rinsed with distilled water and dried with acetone. This removed all the surface oxides which may contaminate the sample.

Tubing cutters and all glassware should also be cleaned thoroughly before use. Glassware is cleaned with chromic acid, rinsed with distilled water and dried in an oven at 110°C. The warm hardware is outgassed in the air-lock of the dry box at 15 microns for 15 minutes before use. Polyvinyl chloride dry box gloves were installed to replace the neoprene rubber gloves. Since under vacuum conditions the rubber gloves outgassed sulfur which reacted with any mercury in the dry box forming a black mercury sulfide. This change of gloves facilitated faster pump-down times as well. Teflon stopcocks were used on the pyrex separatory funnels to eliminate contamination from stopcock greases as precision was non-existant when greased stopcocks were used.

Careful monitoring of the oxygen content in the argon cover gas will facilitate the oxide analysis to a great extent. When the atmosphere is not controlled to a high degree of purity, analyses are worthless.

APPENDIX I:

The freezing technique for the determination of oxygen in NaK, cesium and rubidium.

PRINCIPAL:

The various methods for determining oxygen in sodium and potassium have been well investigated although with little agreement between methods. Special handling techniques had to be developed to analyze NaK, cesium and rubidium for their oxygen contents. There are but a few scattered reports of work done on these metals all without much success.

It has been hoped that the basic mercury amalgamation procedure could be used for these metals as well. Some analysts state that the suboxides of cesium and rubidium appear to be soluble in the mercury as indicated by unusually low oxide results. No data supporting this theory has been published. Preliminary studies at this laboratory using the freezing point method for the low eutectic NaK have given some very promising results.

The chemical activity of NaK is reduced by freezing the NaK into a solid and proceeding with the mercury amalgamation. A special refrigeration plate of stainless steel was placed in the dry box with a plexiglass box surrounding the refrigerator for insulation. Acetone, cooled externally with a dry ice-acetone mixture, is used as the circulating refrigerant. The temperatures in the refrigerator unit were easily maintained at -50°C with the effluent at -85°C. These temperatures are sufficiently cold enough to freeze NaK, CS and Rb.

PROCEDURE:

(1) Evacuate the dry box to 25 microns Hg and backfill the box with high purity dry argon. Pressurize the box to about 1 psig and check the oxygen content in the box. The atmosphere should contain less than 1 ppm O_2. Evacuate and purge the system until this oxygen content has been established.

(2) Start the refrigerator pump and cool the unit to less than -30°C.

(3) Place the NaK (or CS or Rb) sample into the refrigerator unit to freeze the sample. (This should take less than 15 minutes.)

(4) Carefully cut a section of the frozen sample tube and place plastic caps over the exposed ends of the tubes. Then cut another section about 1 inch away from the first cut and transfer the sample to the amalgamation chamber retaining the plastic cap. Cap the remaining exposed sample tube.

(5) Proceed with the amalgamation and analysis as outlined for sodium.

RESULTS:

Sample	Oxygen, ppm O	Ave, ppm O
NaK in pyrex glass	38 25 21	28

The frozen sample of NaK is safely and conveniently handled in this manner with little or no loss of sample.

A fair order of precision was noted which indicates the reliability of this freezing technique. The NaK was sampled in evacuated pyrex glass tubing and taken pipette fashion.

RECOMMENDATIONS:

Tubing cutters were mounted on the plexiglass inside the refrigerator to cut samples contained in stainless steel. The sample therefore, can be kept cold while cutting the sample.

A splash tray should be included in the hardware to catch any alkali metal spillage. Polyethylene, rather than aluminum foil, is safer to dispose of and handle as NaK will react with aluminum.

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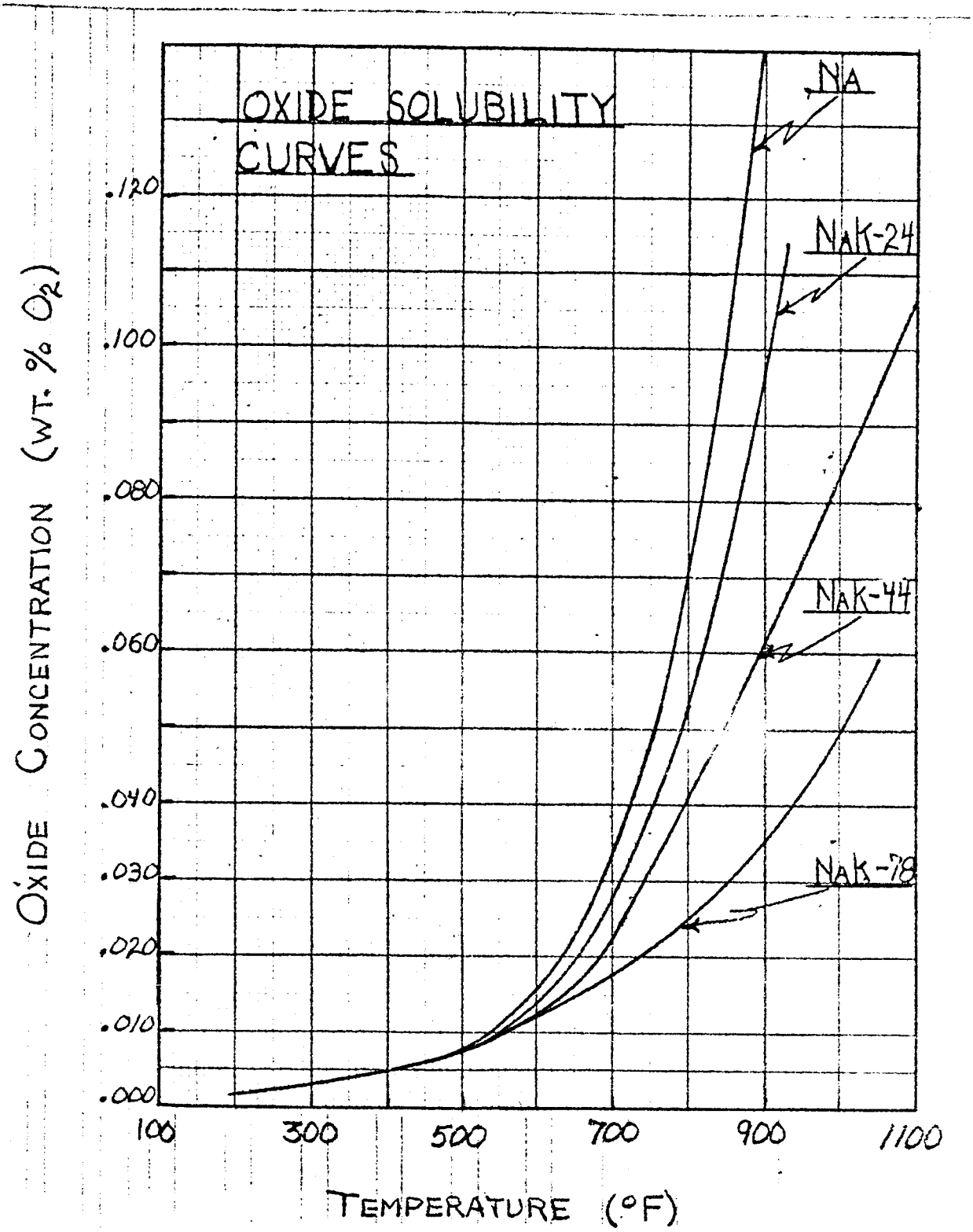
(2) Canel Materials Laboratory Manual Analytical Section

"Determination of Oxygen in Sodium, NaK and Potassium", Pratt & Whitney Aircraft, Chem-O-Vol-1, July, 1961

TABLE I

DETERMINATION OF OXYGEN LIQUID ALKALI METALS
BY MERCURY AMALGAMATION METHOD

SAMPLE NUMBER	SAMPLE TEMP. °F	OXIDE PPM O	COLD TRAP TEMP. °F	M.S.A. CURVE, SOLUBILITY-O	PLUGGING TEMP. °F	OXIDE, PPM O (MSA CURVE)	COMMENT
PS-1	1020	8	375	40	360	—	
PS-2	1200	102	—	—	<240	23	VOIDS IN SAMPLE
PS-3	1450	5	260	25	<220	20	AIR IN ARGON
PS-4	1580	39	290	30	280	30	
PS-5	680	33	250	25	—	—	
SS-1	630	26	—	—	<240	23	
SS-2	1200	1	260	25	<220	20	AIR IN ARGON
SS-3	1250	35	290	30	<280	30	


OXIDE SOLUBILITY CURVES
Na
NaK-24
NaK-44
NaK-78
.120
.100
.080
.060
.040
.030
.020
.010
.000
100
300
500
700
900
1100
OXIDE CONCENTRATION (WT. % O2)
TEMPERATURE (°F)