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NRL REPORT 3865

FR-3865

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SOLUBILITY OF SODIUM MONOXIDE AND OF SODIUM HYDROXIDE IN METALLIC SODIUM

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Declassification authority: *NAVY DECLASS
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Site Authority *Black60*
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SOLUBILITY OF SODIUM MONOXIDE AND OF SODIUM HYDROXIDE IN METALLIC SODIUM

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September 26, 1951

Approved by:

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ABSTRACT

The combined solubility of oxygen in sodium, calculated as sodium monoxide and the separate solubilities of sodium monoxide and sodium hydroxide have been determined in sodium metal by two methods—first, using radioactive sodium²⁴ with a distillation process for separation of the oxide-hydroxide and metal; second, using a filtering process on liquid sodium for separation. The two methods gave comparable results in the overlapping temperature range. An equation for the percent oxide-hydroxide oxygen dissolved in sodium calculated as if present as monoxide only is: $\text{wt \% } O_2 = 2.27 \times 10^{-7} t^2 + 2.55 \times 10^{-5} t - 2.35 \times 10^{-3}$ for the range 100° to 500°C, where t is given in °C.

Individual solubilities were determined by chemical separation only. Sodium monoxide was produced in the apparatus by oxidizing pure sodium with dry oxygen. Chemically pure sodium hydroxide was used for the hydroxide tests. The equation for the solubility of sodium monoxide oxygen is: $\log (\text{wt \% } O_2 \times 10^3) = -0.0535 + 0.00351 t$ for the range 100° to 550°C, and for sodium hydroxide oxygen is: $\text{wt \% } O_2 = 3.71 \times 10^{-7} t^2 - 7.14 \times 10^{-6} t - 5.7 \times 10^{-4}$ for the range 100° to 350°C.

The method using sodium²⁴ is of particular advantage for heat-exchange metal used in a nuclear reactor. Determination of oxide content could be made on the raw metal at any time by remote control and with measuring instruments similar to those necessary for the safe operation of such a reactor. The second method is adaptable to soluble oxide in a liquid metal system where operations such as the filtering of a known volume at controlled temperatures along with the removal and analysis of filter residues can be accomplished.

PROBLEM STATUS

This is a final report on the solubility of oxygen in sodium; work on the solubility of other impurities is continuing.

AUTHORIZATION

NRL Problems C11-02R and C10-01R
NS 622-024

Manuscript submitted for publication July 12, 1951

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SOLUBILITY OF SODIUM MONOXIDE AND OF
SODIUM HYDROXIDE IN METALLIC SODIUM

INTRODUCTION

Statement of Problem

A project has been under way to determine the solubility of the oxides of sodium in metallic sodium and to assess the suitability of analytical procedures for the determination of oxide content of liquid sodium systems.

Background

The high potentialities and desirable characteristics of liquid sodium metal as a heat transfer medium has created a need for further information on a wider variety of the physical properties of the metal.

Oxides of sodium at elevated temperatures are among the most corrosive materials known. The amount of the oxides of sodium that can be carried in solution in liquid sodium used in heat-exchange work is, therefore, of paramount importance in the selection of the material as a heat exchanger and in the design of equipment to contain and transfer the liquid metal. It was for these reasons that determination of the solubility of oxides of sodium in sodium metal was begun. At the time this work was started there was no experimental data on the solubility of the oxides in sodium metal. Since it may be impractical to exclude all oxygen from a useful-size system, methods of determining soluble oxide in such systems were to be considered.

Oxygen in sodium is combined as two principal impurities, sodium oxide and sodium hydroxide. Its presence as both would result from the reaction of sodium metal with moist air, hence the combined solubility is desirable from a practical standpoint.

The combined solubilities were studied using commercial grade sodium monoxide which contained approximately 10% sodium hydroxide.

The results are reported as apparent percent oxygen, calculated as if it were present as sodium monoxide only. The individual solubilities were studied with oxide made by oxidization of sodium with pure oxygen and with pure hydroxide.

DETERMINATION OF THE COMBINED SOLUBILITY OF SODIUM MONOXIDE
AND HYDROXIDE IN METALLIC SODIUM USING 14.8-HOUR Na²⁴

Introduction

The solubility of sodium oxide and hydroxide in sodium metal can be determined using 14.8-hour Na²⁴ as a tracer (1). Inert sodium metal can be tagged with Na²⁴ by distilling the metal in the presence of a compound of sodium containing that isotope.

Samples used at NRL were prepared by bombardment in the Oak Ridge National Laboratory chain reacting pile (2). The traced sodium metal obtained as a result of atom exchange between reduced sodium (metal) and the oxidized sodium can be distilled away from the added compound and other impurities in the mixture. This metal containing Na^{24} was used for the determination of the solubility of sodium oxide and hydroxide in sodium metal.

Apparatus

The apparatus used is shown in Figure 1. Vessels (B), (D), and (F) are six inches high with an inside diameter of one inch. The wall thickness of the lower four inches of each vessel is 1/32 inch and of the upper two inches is 1/8 inch for welding purposes. The connecting arms are 1/4-inch-inside-diameter tubing with 1/16-inch walls. All parts are 304 stainless steel except filter (G) and the nickel tubing segment (E) which connects the stainless steel tubing between vessels (D) and (F). The connecting arms are approximately 14 inches in height from the tops of the vessels and the vessels are approximately 15 inches apart. Filter (G) consists of two layers of 200-mesh-nickel screen faced and backed by 100-mesh-nickel screen. The filter is clamped in place by a threaded collar which in turn is welded to the tube. All stainless steel parts are connected by heliarc welds. The nickel tubing is gas welded to the stainless steel tubing. Joints (A) and (C) are, respectively, stainless steel taper and ball joints for loading the apparatus and attaching it to a vacuum manifold.

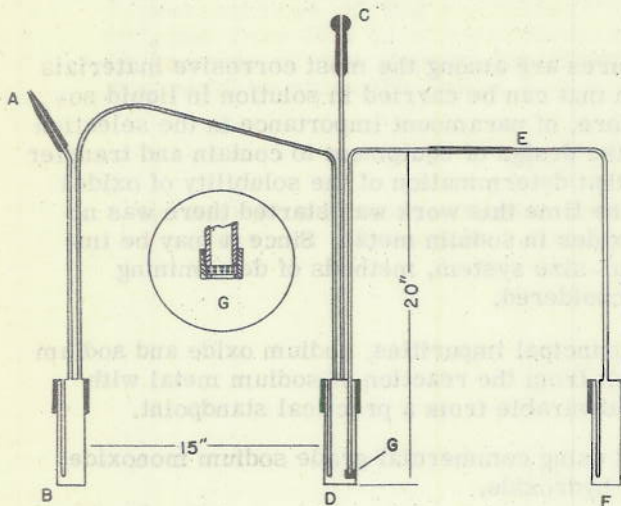


Figure 1 - Apparatus for the determination of the combined solubility of sodium monoxide-sodium hydroxide oxygen in metallic sodium by the Na^{24} tracer technique

Method

Sodium oxide-hydroxide was placed in vessel (D) through the stainless steel ball joint (C); the apparatus was connected to a vacuum manifold with a glass socket joint and evacuated. Then, the apparatus was filled with nitrogen, approximately 30 grams of metallic sodium and from 1 to 3 millicuries of Na^{24} activity in approximately 0.05 gram of Na_2CO_3 were introduced into (B) at the taper joint (A), and the opening was sealed with a glass cap. Radioactive sodium was then distilled under vacuum from the exchange vessel (B) into the sodium oxide-hydroxide in vessel (D). The radioactive sodium was brought to the temperature at which the solubility was to be determined by means of an electric furnace and held to $\pm 2^\circ\text{C}$ throughout the entire time the determinations were being made.

Temperatures were determined with chromel-alumel thermocouples inserted in the wells in the vessels and welded to the arms of the apparatus. By allowing nitrogen to enter the apparatus at (C), the metal and dissolved oxide-hydroxide above filter (G) were separated from the excess oxide and hydroxide by forcing the metal through the filter into vessel (F). The arm connecting vessels (D) and (F) was held at or above the temperature at which the solubility was being determined.

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TABLE 1
Na₂O-NaOH Determination on Sodium Metal at 400°C
(Base weight of metal, 15.00 Grams; Backgrounds, B_c 69 and B_t 140 counts/minute)

Sample No.	t _x min.	Metal Activity (Counts/Minute)			Grams of Metal	Count per Minute per Gram
		Gross	Corrected for Coincidence	Corrected to Oxide Times		
1	230	92,278	127,000	126,500	15	8433
2	297	89,194	120,000	119,600	15	7973
3	363	85,912	113,000	112,600	15	7507
4	427	76,592	98,300	98,000	13.8	7101

Sample No.	t _x min.	Oxide Activity (Counts/Minute)		Metal Equivalent (gm)	Δ Metal (gm)	Metal (%)	Oxygen (%)
		Gross	(B ₀ + B _v t _x)*				
1	278	1340	1214	0.1439	**		
2	343	1383	1260	0.1580	0.0141	0.094	0.033
3	410	1488	1367	0.1820	0.0240	0.160	0.056
4	527	1504	1386	0.1949	0.0129	0.094	0.033
					Average value 0.041		

* B_vt_x is the variable component of the total background remaining at time t_x
 ** The initial run of any series is used as a blank for subsequent determinations and as a degassing operation.

TABLE 2
Na₂O-NaOH Solubility Data (Na²⁴ Tracer Technique)

Temp (°C)	Oxygen (%)	Std. Dev.
200	0.010	0.004
250	0.020	0.005
300	0.023	0.011
350	0.036	0.007
400	0.041	0.011
440	0.052	0.013
490	0.066	0.014

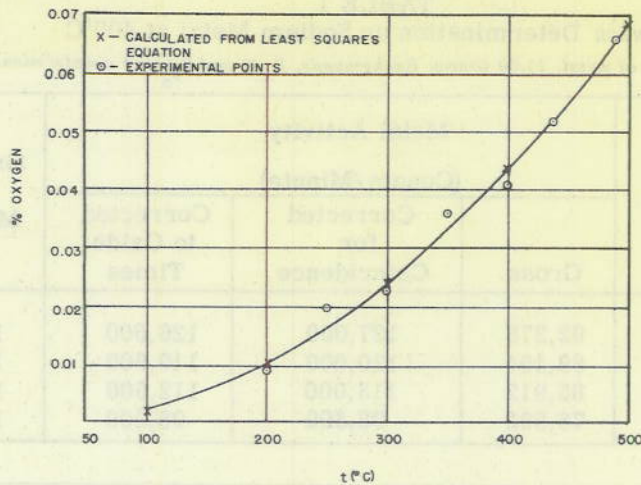


Figure 2 - Combined solubility of sodium monoxide-sodium hydroxide oxygen in metallic sodium— Na^{24} tracer technique—(calculated as if present as monoxide only)

The data show that at temperatures up to 500°C , the combined solubility of sodium oxide-hydroxide in sodium metal is low and the use of the metal as a coolant or heat exchanger should be possible without interference due to any appreciable change in physical or thermal properties. The effect of oxide or hydroxide on corrosion does not fall within the scope of this report.

DETERMINATION OF THE COMBINED SOLUBILITY OF SODIUM MONOXIDE AND HYDROXIDE IN METALLIC SODIUM BY CHEMICAL SEPARATION

Introduction

Concurrent with the Na^{24} tracer study, the problem of the solubility of oxygen in metallic sodium was being investigated from the standpoint of direct chemical separation. The purpose of this work was twofold—to establish the efficiency of filtration as a means of separating soluble and insoluble fractions of the sodium-oxygen system, and to provide an independent check on the solubility curve established by the tracer technique.

A prime requisite for this study was a means of quantitatively separating sodium metal from its oxide. The amalgamation process proposed by Pepkowitz and Judd (3) was modified at this Laboratory (4) to be of sufficient accuracy for this purpose. The modified apparatus was used in all analyses required by this problem.

Lee and Walters (5) reported a source of error in this method. This error comes from failure to preadjust the pH of the distilled water used to dissolve the oxide immediately prior to final titration. The magnitude of this error is dependent upon the sample size and the source of distilled water. At NRL, assuming a one gram sample, the maximum error resulting from failure to correct for pH is of the order of $0.004\% \text{ O}_2$.

(In connection with this correction, the "standard" samples distributed by this Laboratory should analyze from 0.002-0.004% O_2 rather than the stated value of "less than 0.001%." Later analyses performed on sodium from the same source substantiated the arbitrary corrections assigned to the distributed samples.)

Apparatus

The apparatus used is shown in Figure 3. The saturation chamber (A) is equipped with a cap (I) containing a thermocouple well (J), a Corning sintered glass filter (E), and an outlet (K) for connection to a vacuum-inert gas manifold (not shown). Flask (A) is connected to (B) at (X) by a short length of glass tubing. The unit consisting of flasks (B), (C), and (M) with associated filter and stopcocks is a complete analysis assembly similar to that described in Appendix I. A thin-walled glass bulb (D) must be sealed off at (X_1) for insertion in the analysis assembly described in Appendix I. It is replaced by flask (M) by interchanging joints (L) and (L_1).

Method

The units were assembled (Figure 3) and connected to the vacuum-nitrogen manifold at (K). The entire apparatus was evacuated (stopcock (G) closed and (H) open) with gentle flaming to remove adsorbed gases and then filled with nitrogen. Cap (I) was then removed and approximately two grams of metallic sodium and 0.1 gram of sodium monoxide-hydroxide placed in (A). The cap was replaced, a chromel-alumel thermocouple was inserted in well (J), and a nichrome heater was wrapped around that portion of (A) containing the metal and oxide. The apparatus was re-evacuated and the temperature raised to the level at which the solubility was to be determined. The temperature was held within $\pm 2^\circ C$ of this point for five minutes. (Preliminary test runs established the fact that saturation equilibrium was achieved almost instantaneously. Identical oxide values were obtained for heating times ranging from one minute to one hour.)

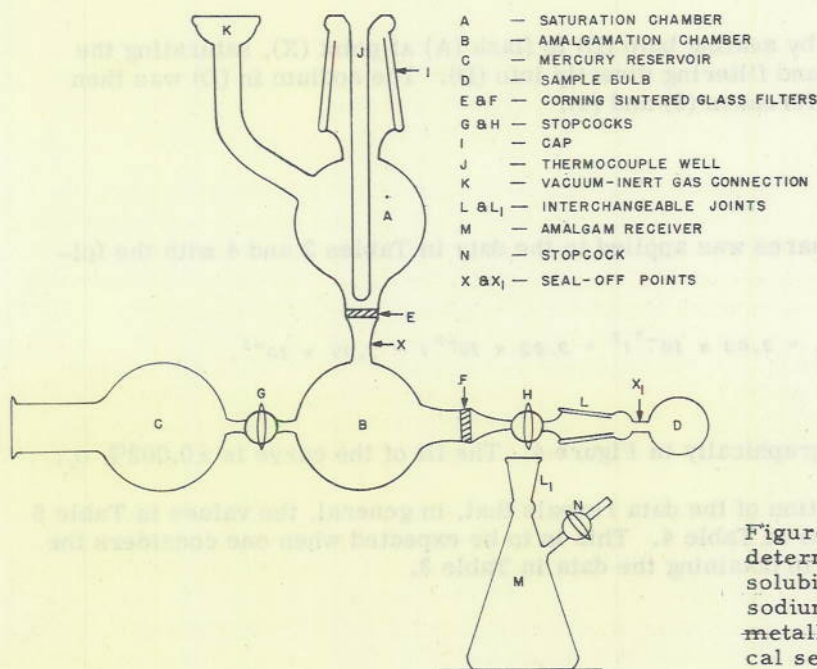


Figure 3 - Apparatus for the determination of the combined solubility of sodium monoxide-sodium hydroxide oxygen in metallic sodium by the chemical separation technique

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Stopcock (H) was then closed and nitrogen was admitted through (K) above the melt to a pressure of approximately 200 mm, thus forcing the saturated sodium metal through filter (E) into chamber (B). The apparatus was separated by flame sealing at point (X). The lower, or analysis, section of the apparatus was then turned so that flask (C) was uppermost. The melt was allowed to cool in a controlled bath to 105°C. Stopcock (H) was then opened and the sodium, now saturated only at 105°C, was forced through filter (F) into bulb (D) by the residual pressure in (B). Stopcock (H) was closed, and bulb (D) was sealed off at (X₁) and reserved for analysis in the regular apparatus (Appendix I). Flask (M) was placed on the apparatus by interchanging joints (L) and (L₁) and then was evacuated through stopcock (N).

There was, at this time, a pressure differential across the apparatus as follows: flask (C), atmospheric; flask (B), approximately 200 mm; flask (M), approximately zero. Proper manipulation of stopcocks (G) and (H) maintained this differential throughout the following amalgamation and washing steps.

Flask (B) now contained sodium monoxide-hydroxide equivalent to the difference in saturation values between 105°C and the temperature of the run, plus some residual sodium metal. The metal was removed by amalgamation with mercury added from flask (C) and by draining it into flask (M) where it was reserved for titration with the amalgam obtained from the analysis of the metal in bulb (D). The total alkalinity of these two gave the total sample size.

The oxide-hydroxide in flask (B) was dissolved and titrated in accordance with the procedure described in References (3) and (5). The sodium contained in bulb (D) was subjected to the analysis procedure described in References (3) and (4). The sum of the two oxygen figures thus obtained is equivalent to the equilibrium oxygen solubility at the temperature of the particular run. Since there was no method for differentiating between oxide and hydroxide oxygen, the results were all calculated as if the oxygen were present as sodium monoxide only.

Check runs were made by sealing bulb (D) to flask (A) at point (X), saturating the sodium as described above and filtering directly into (D). The sodium in (D) was then analyzed as described in References (3) and (4).

Results

The method of least squares was applied to the data in Tables 3 and 4 with the following equation resulting:

$$\text{wt \% } O_2 = 2.03 \times 10^{-7} t^2 + 3.82 \times 10^{-5} t - 3.09 \times 10^{-3}.$$

This equation is presented graphically in Figure 4. The fit of the curve is $\pm 0.002\%$ O_2 .

A comparative examination of the data reveals that, in general, the values in Table 3 are slightly higher than those in Table 4. This is to be expected when one considers the extra operations performed in obtaining the data in Table 3.

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TABLE 3*
Na₂O-OH Solubility Data
(Double Filtration Method)

<i>t</i> (Temp of Saturation in °C)	<i>o₂</i> in Flask (B) (wt %)	<i>o₂</i> in Bulb (D) (105°C) (wt %)	Total <i>o₂</i> (wt %)
155	0.007	0.001	0.008
235	0.017	0.003	0.020
340	0.032	0.002	0.034
405	0.042	0.002	0.044
410	0.046	0.001	0.047

* Data is reported as weight percent O₂ in keeping with prior reports on this subject.

TABLE 4*
Na₂O-OH Solubility Data
(Single Filtration Method)

<i>t</i> (Temp of Saturation in °C)	<i>o₂</i> (wt %)
105	0.002
250	0.015
250	0.017
265	0.019
400	0.042

* See footnote for Table 3

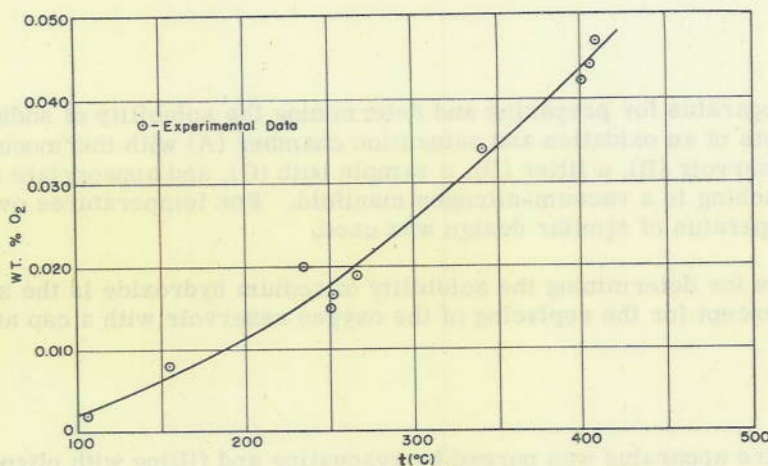


Figure 4 - Combined solubility of sodium monoxide-sodium hydroxide oxygen in metallic sodium—chemical separation technique—(calculated as if present as monoxide only)

The comparatively constant value for the oxygen content of bulb (D) (Table 3, third column), the reproducibility of oxygen content at any particular temperature, and the fact that filtration into bulb (D) was made immediately upon reaching 105°C demonstrate that sodium does not supersaturate, and that filtration will separate soluble and insoluble fractions of the sodium-oxygen system.

Further proof of the efficiency of the filtration mechanism is that reproducible results were obtained regardless of which grade of filter was used for filter (E). Corning grades fine, medium, and coarse were used with equal efficiency. The coarse grade was always used for filter (F) since it alone would permit the passage of mercury under the stated pressure conditions.

DETERMINATION OF THE INDIVIDUAL SOLUBILITY OF SODIUM MONOXIDE AND OF SODIUM HYDROXIDE IN METALLIC SODIUM

Introduction

Aside from purely academic considerations, the individual solubility of sodium monoxide and of sodium hydroxide is of interest because of the separate effects on the corrosion of various materials. Also it was desirable to determine the existence or extent of mutual interdependence of one solute upon the other.

Preparation of Sodium Monoxide

The sodium monoxide used in these experiments was freshly prepared for each "run" by oxidizing pure sodium metal with dry oxygen in the saturation chamber of the apparatus. The oxide thus formed was recovered for analysis by amalgamating and filtering the excess sodium metal. The oxide remaining on the filter was weighed, converted to sodium hydroxide, and titrated with standard acid. The oxide analyzed by this method was 99.9+% pure Na_2O . No evidence of peroxide was noted, which is logical since oxidation occurred at relatively low temperatures and in the presence of an excess of metallic sodium. The most stable oxide of sodium is sodium monoxide.

Apparatus

The pyrex apparatus for preparing and determining the solubility of sodium monoxide (Figure 5) consists of an oxidation and saturation chamber (A) with thermocouple well (F), an oxygen reservoir (B), a filter (D), a sample bulb (C), and appropriate stopcocks and joints for attaching to a vacuum-nitrogen manifold. For temperatures over 400°C a stainless steel apparatus of similar design was used.

The apparatus for determining the solubility of sodium hydroxide is the same as described above except for the replacing of the oxygen reservoir with a cap at joint (E).

Method

After the entire apparatus was purged by evacuating and filling with nitrogen, approximately 2 grams of sodium metal were pipetted into the oxidation chamber (A) and the oxygen reservoir (B) was filled with dry oxygen. The chamber was re-evacuated and

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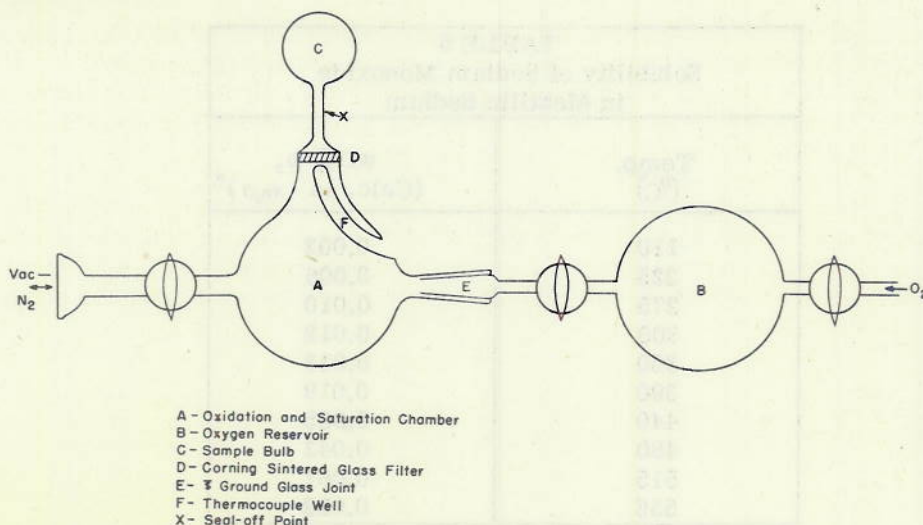


Figure 5 - Apparatus for the determination of the individual solubility of sodium monoxide and of sodium hydroxide oxygen in metallic sodium

oxygen was allowed to pass slowly over and react with the metallic sodium. The apparatus then was turned so as to bring the metal and oxide onto filter (D), the temperature was raised to the desired saturation level ($\pm 5^\circ\text{C}$), and a slight nitrogen pressure was applied above the melt forcing the saturated metal into the sample bulb (C). The bulb was removed by flame sealing at point (X) and reserved for oxide analysis by the method described in References (4) and (5).

The operation of the apparatus for sodium hydroxide solubility was essentially the same as described above except that CP sodium hydroxide was placed in the saturation chamber along with the metallic sodium and the oxygen reservoir was replaced by a cap on joint (E). Heating, filtering, sealing, and hydroxide content analysis was the same as for the monoxide.

Results

The experimental data for sodium monoxide (Table 5) did not lend itself to plotting as an exponential equation, but was found to be adequately expressed as a logarithmic function, the equation for which is

$$\log (\text{wt \% monoxide } O_2 \times 10^3) = -0.0535 + 0.00351 t,$$

where t is $^\circ\text{C}$ and the oxygen is present as sodium monoxide only. (This data is presented graphically in Figure 6.)

Applying the method of least squares to the data in Table 6 results in the following equation:

$$\text{wt \% hydroxide } O_2 = 3.71 \times 10^{-7} t^2 - 7.14 \times 10^{-8} t - 5.7 \times 10^{-4}.$$

This equation is presented graphically in Figure 7.

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TABLE 5 Solubility of Sodium Monoxide in Metallic Sodium	
Temp. (°C)	wt % O ₂ (Calc. as Na ₂ O)*
110	0.002
225	0.006
275	0.010
300	0.012
350	0.013
390	0.019
440	0.025
490	0.043
515	0.061
555	0.092

* Since the method of oxygen analysis is based on the formation of sodium hydroxide and its subsequent titration, it must be kept in mind that the equivalent weight of oxygen in the case of sodium monoxide (Na₂O) is 8, and in the case of sodium hydroxide (NaOH) is 16

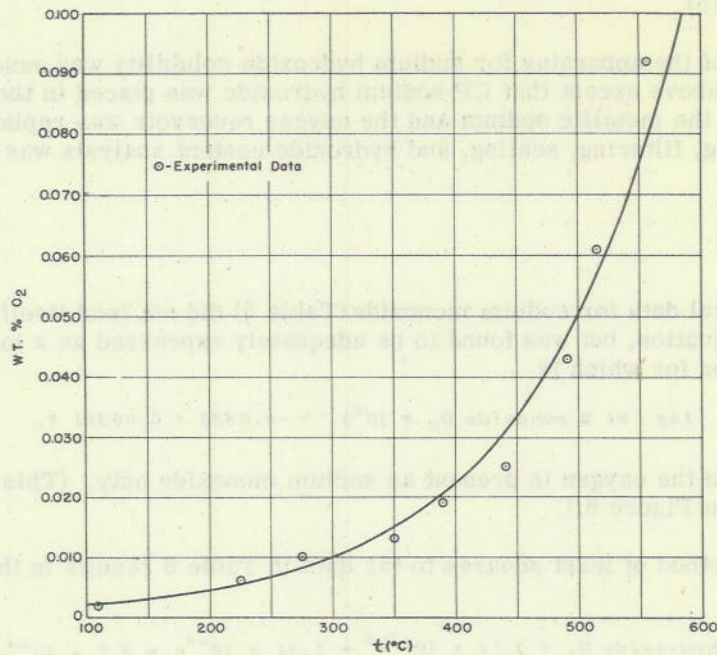


Figure 6 - Solubility of sodium monoxide oxygen in sodium

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Temp. (°C)	wt % OH (Calc. as NaOH)*
110	0.004
150	0.006
200	0.012
250	0.022
300	0.031
350	0.042

*See footnote for Table 5

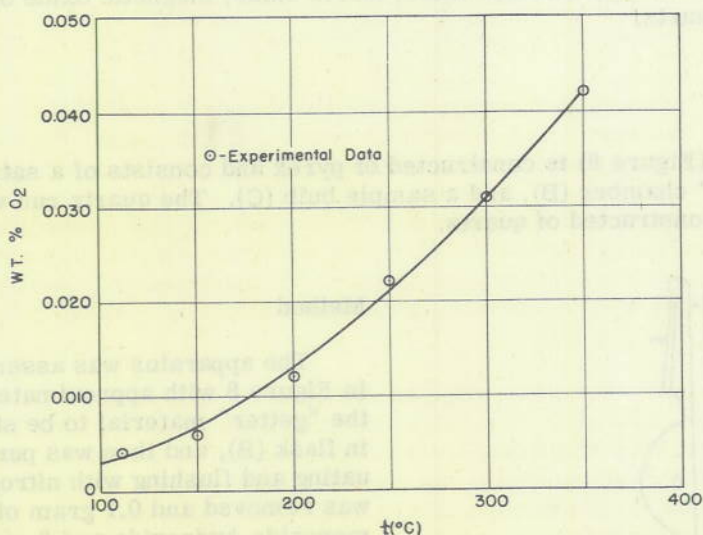


Figure 7 - Solubility of sodium hydroxide oxygen in sodium

Because of the reduction of sodium hydroxide by metallic sodium at about 400°C (4), higher temperature values could not be obtained. The point at 350°C (Table 6) is well over the melting point of sodium hydroxide and could include hydroxide not necessarily in solution. As shown in Figure 7, however, the point agrees with the smooth curve extended from the other data. It is probable that any fused hydroxide was held on the filter by reaction with the glass and that only dissolved hydroxide passed into the sample bulb.

STUDY OF THE EFFECT OF "GETTERING" ON THE SATURATION OF METALLIC SODIUM BY SODIUM MONOXIDE-HYDROXIDE

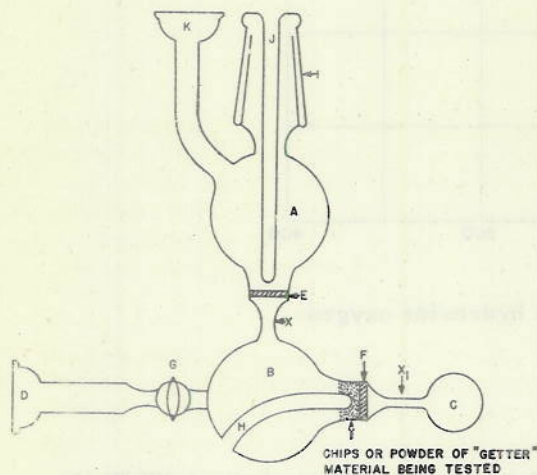
Introduction

In order to obviate any errors arising from the use of stainless steel and pyrex in the preceding portions of the report, a study of the "gettering" action of various construction materials was undertaken. The materials were to be held in intimate contact with sodium saturated with its oxide and hydroxide at some arbitrary temperature. Saturation temperatures were approximately 25°C higher than the "soaking" temperatures to insure that the test material was exposed to saturated sodium. Keeping the ratios of sodium to "getter" material to solute more or less constant, the time element was to be varied, following which the sodium metal would be removed by filtration and analyzed for apparent oxide content. Any reduction of the oxide content with time would indicate "gettering" by the material under study.

The materials selected for study were stainless steel (type 304), armco iron nickel, chromium, titanium, chromic oxide, ferric oxide, magnetic oxide of iron, nickelic oxide, pyrex, and quartz.

Apparatus

The apparatus (Figure 8) is constructed of pyrex and consists of a saturation chamber (A), a "soaking" chamber (B), and a sample bulb (C). The quartz run was made in a similar apparatus constructed of quartz.



- A - SATURATION CHAMBER
- B - REACTION CHAMBER
- C - SAMPLE BULB
- D, K - CONNECTORS FOR VACUUM - N₂ MANIFOLD
- E, F - CORNING SINTERED GLASS FILTERS
- G - STOPCOCK
- H, J - THERMOCOUPLE WELLS
- I - CAP
- X, Q, X₁ - SEAL-OFF POINTS

Figure 8 - Apparatus for the study of the "gettering" effect of various materials

Method

The apparatus was assembled, as shown in Figure 8 with approximately 0.1 gram of the "getter" material to be studied contained in flask (B), and then was purged by evacuating and flushing with nitrogen. Cap (I) was removed and 0.1 gram of sodium monoxide-hydroxide and 2 grams of sodium metal were inserted in flask (A). The cap was replaced, a chromel-alumel thermocouple was inserted in well (J), and the apparatus was re-evacuated. The melt was heated by means of a wrapped nichrome heater. When the temperature reached a level indicative of the desired saturation, the sodium was forced through filter (E) by means of a slight nitrogen pressure. The apparatus was then separated by flame sealing at point (X), connected at (D) to the vacuum-nitrogen manifold, and re-evacuated. A heater was then wrapped around filter (F) and that portion of flask (B) containing the sodium and the "getter" metal. A thermocouple was inserted into well (H), and the temperature was brought to the "soaking"

temperature and held there for various time intervals. Nitrogen was introduced to force the sodium into bulb (C), which was then sealed off at (X₁) and inserted into the regular analysis apparatus (Appendix I) where its apparent oxide content was determined.

Some runs, in which an excess of sodium oxide-hydroxide was present, were made by sealing bulb (C) to flask (A) at (X). Approximately 0.001 gram of the "getter" material being studied was then placed in (A) along with 2 grams of sodium and various excesses of sodium monoxide-hydroxide. This mass was then heated at 250°C for varying time intervals, filtered into (C), and analyzed as before. The purpose of such runs was to determine whether an equilibrium could be reached at which point the sodium oxide-hydroxide would cease reacting with the material under test and again saturate the sodium metal.

An attempt was made to isolate chromium, nickel and/or iron in various fractions of the runs. Because of the micro quantities involved, however, no conclusive results were obtained. A trace of iron was found in one instance, but the presence of chromium and nickel was never established beyond reasonable doubt.

Results

It should be noted (Tables 7 and 8) that since maximum "gettering" was being sought, the "soaking" times are somewhat arbitrary. In the cases of titanium and the various oxides, the reaction may well have occurred much more rapidly than indicated.

It can be readily seen that for times up to two hours and for temperatures of less than 300°C, glass has little effect upon the saturation of sodium by sodium oxide-hydroxide. For times in excess of two hours, the glass apparatus has at least a contributory effect, and in the presence of nickel, could have been the sole reactant in the apparent "gettering" indicated.

The data on stainless steel in Table 8 indicates the existence of an equilibrium such that when an excess of sodium oxide-hydroxide is present, saturation may still be attained. This could indicate a reaction of sodium monoxide or hydroxide with surface oxides resulting in a protective layer being established on the stainless steel. Likewise, the data with iron indicates that, under the conditions of this experiment, no such equilibrium exists. The possibility of reactions such as those above is borne out by existing corrosion data wherein the oxide content was uncontrolled.

The data indicates that, for the most part, the reduction in "apparent" oxide content was due to the removal of hydroxide oxygen only, possibly by the formation of sparingly soluble alkali ferrates, chromates, etc. (Figure 9). This fact could have considerable bearing on alkali metal corrosion data wherein the oxidation of the metal is uncontrolled.

SUMMARY

Smoothed curves for the individual and combined solubilities of sodium monoxide and sodium hydroxide in sodium metal are shown in Figure 9. The curve for combined solubility is calculated as if all oxygen were present as sodium monoxide. For comparison, the dotted line shows the solubility of sodium hydroxide calculated as if it were sodium monoxide. It is readily apparent that the sum of the oxygen values for the monoxide and the hydroxide calculated as the monoxide show excellent agreement with the combined

TABLE 7
Gettering Data Using $\text{Na}_2\text{O-OH}$ Saturated Sodium

Material	"Soaking" Temp ($^{\circ}\text{C}$)	O_2 Available* (wt %)	Time (min)	O_2 Recovered (wt %)
SS	300	0.026	30	0.019
SS	300	0.026	60	0.017
SS	325	0.030	90	0.014
SS	285	0.024	120	0.008
SS	250	0.018	120	0.004
Fe	260	0.019	60	0.006
Fe	250	0.018	120	0.005
Fe	265	0.020	240	0.007
Ni	265	0.020	120	0.019
Ni	260	0.019	120	0.016
Ni	250	0.018	240	0.005
Cr	250	0.018	120	0.005
Ti	230	0.016	180**	0.003
Cr_2O_3	225	0.015	120**	0.004
Fe_2O_3	250	0.018	60**	0.005
Fe_3O_4	225	0.015	60	0.003
Ni_2O_3	225	0.015	120	0.002
Pyrex	250	0.018	60	0.017
Pyrex	250	0.018	90	0.015
Pyrex	240	0.017	120	0.013
Pyrex	230	0.016	360	0.004

* Calculated as sodium monoxide and based on "soaking" temperature and solubility curve in Figure 4

** Visual observation of the sodium surface indicated a more rapid "gettering" action than these times demonstrate

TABLE 8
Gettering Data Using $\text{Na}_2\text{O-OH}$ in Excess

Material	"Soaking" Temp ($^{\circ}\text{C}$)	O_2 * Added (wt %)	O_2 Should Recover** (wt %)	Time (min)	O_2 Recovered (wt %)
SS	270	3	0.021	120	0.021
SS	250	3	0.018	120	0.017
Fe	250	2	0.018	120	0.005
Fe	225	5	0.015	180	0.010
Fe	230	3	0.016	360	0.006
Pyrex	260	1	0.020	1	0.020
Pyrex	270	1	0.021	15	0.020
Pyrex	230	1	0.016	240	0.005
Quartz	250	1	0.018	240	0.003

* Calculated as sodium monoxide and based on amount of O_2 required to saturate 2 grams Na at "soaking" temperature

** Based on "soaking" temperature and solubility curve in Figure 4

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ADDRESS REPLY TO
DIRECTOR, NAVAL RESEARCH LABORATORY
WASHINGTON 20, D. C.

AND REFER TO:

APPENDIX I
NAVY DEPARTMENT
NAVAL RESEARCH LABORATORY
WASHINGTON 20, D. C.

3230-5A50 eb

16 January 1950

Subj: A Modified Apparatus for the Determination of Sodium Monoxide in Metallic Sodium, NRL Problem No. 32011-02R (BuShips Project 990/46), Interim Report on.

Ref: (a) KAPL #127 - The Determination of Sodium Monoxide in Sodium by L. P. Pepkowitz and W. C. Judd, March 9, 1949 (Declassified July 14, 1949).

1. The amalgamation method for the separation of sodium monoxide as proposed by reference (a) appears to be an ingenious and accurate solution to a very difficult analytical operation. It is, in fact, more accurate than the authors have stated.

2. The principal deterrents to high order precision lie in the proposed apparatus and its manipulation rather than in the theory of the method. The most consistent error results from the use of alternate evacuation and flushing with inert gas as a means of purging the apparatus. Various errors are introduced here, all of a positive nature. The original oxygen is never completely removed -- more is added with the inert gas (no simple purification train will remove all the oxygen from bottled gases) -- and even with the positive pressure employed during a "run", back diffusion of air through the Gooch rubber fittings is considerable. (At this Laboratory, no high purity alkali metal system has ever operated successfully with rubber tubing -- unless the tubing was in short immobile lengths completely sealed with Glyptal.) A second type error lies in the short reaction chamber. The amalgamation reaction is sufficiently vigorous to cause particles of amalgam to be thrown into the upper portion of the chamber. It is impossible to remove these particles during the scrubbing operation which follows. Should one become dislodged during the final oxide solution step, it would result in a spoiled analysis if detected, or a high oxide value to be reported, if not detected.

3. With the intent of avoiding some of these errors, and obtaining, thereby, more accurate results, the apparatus shown in Figure 1 was constructed. The all-glass construction eliminates gas diffusion and purging problems; the longer reaction chamber eliminates errors from chance amalgam splashes; and, operation in a vacuum eliminates most of the error resulting from impure cover gas.

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ALL DIMENSIONS APPROXIMATE

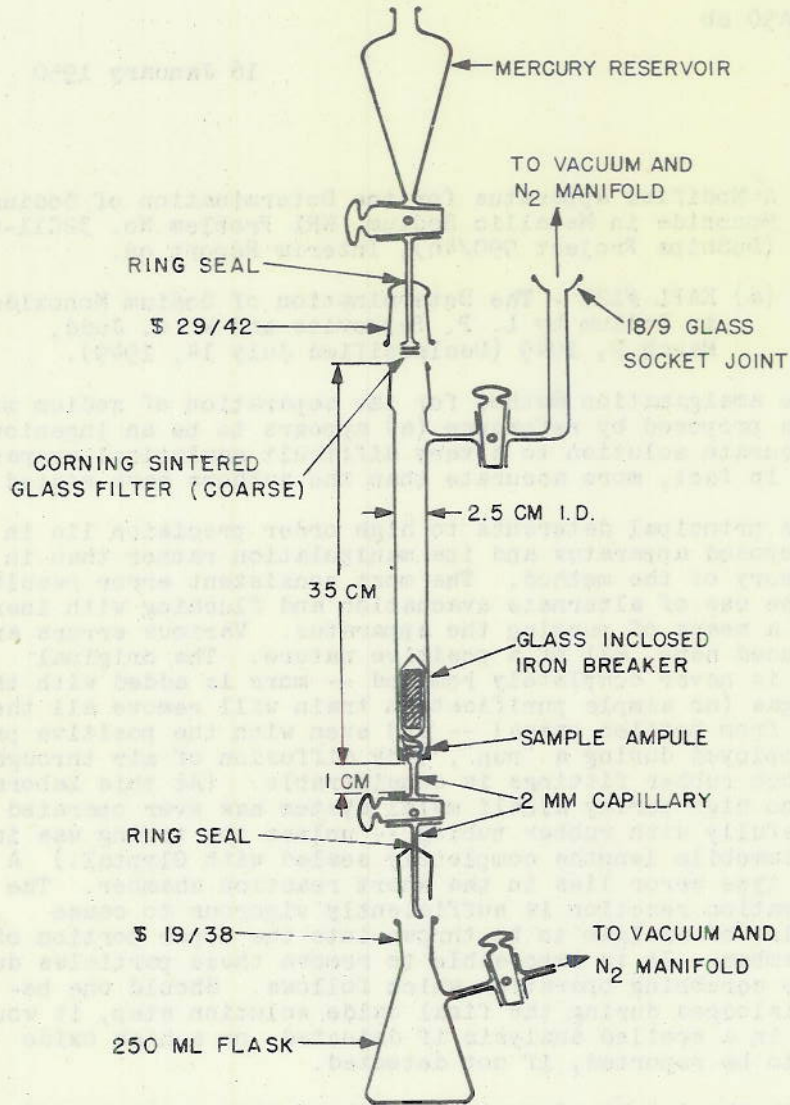


Figure 1 - Apparatus for the determination of oxygen in sodium

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4. A somewhat different technique of operation is dictated by the modified apparatus. The method of operation is as follows:

Assemble the apparatus as shown in Figure 1 and connect to a high vacuum-inert gas manifold. Evacuate, with appropriate flaming to remove adsorbed gases, cool, and flush with inert gas, purging all stopcock bores. Reevacuate, close the lower stopcock, and break the sample bulb by allowing the magnetic breaker to fall upon it from a height of several centimeters. (The breaker is also used as a stirrer and is manipulated externally by the use of hand magnets.) Add approximately 20 milliliters of mercury from the upper reservoir, stirring vigorously with the magnetic breaker. Atmospheric pressure on the mercury reservoir provides head for the addition of the mercury to the evacuated reaction chamber. The filter placed at the end of the mercury reservoir delivery tube provides an efficient "shower" system which effectively washes the sides of the reaction chamber. After the amalgam has cooled to room temperature, open the bottom stopcock and drain all but one or two milliliters of the amalgam into the receiving flask. In the ideal "run", the amalgam will drain under its own head. Usually, however, a slight pressure of inert gas must be introduced above the amalgam. When this is necessary, the stopcock to the manifold should remain closed following the addition of the inert gas. In this manner, head is provided for the drainings which follow and oxygen pickup from the small amount of gas added is negligible. More mercury is added, stirred and drained until a test of the effluent mercury indicates complete separation of sodium metal and sodium monoxide. The test of the effluent mercury is accomplished by appropriate manipulation of the connection from the receiving flask to the vacuum-inert gas manifold. (Fill the receiving flask with inert gas and replace it with a similar flask containing a small quantity of water and a few drops of phenolphthalein. Reevacuate and drain some mercury from the reaction chamber into the flask. If the water layer remains colorless, separation is complete -- if a red color develops, further washing is indicated.) Final solution and titration of the sample is identical to the procedure prescribed by reference (a). If the presence of carbonate is known or suspected, the titration should be continued beyond the phenolphthalein end point to that of a suitable carbonate-sensitive indicator (Congo Red, Brom - Phenol Blue, Methyl

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Orange, etc.) In the event of such a titration, suitable provision for end-point selection and indicator blank must be made. (Indicator blank may be as high as one or two milliliters when using .01 normal acids. Great care must be exercised in the duplication of the selected end point.) In any event, the phenolphthalein end point should be taken as indicative of the oxide content and suitable corrections applied if carbonate is found to be present.

5. Once operating technique has been established, routine analysis proceeds smoothly. Excluding sampling time, a complete "run" can be made in less than thirty minutes.

6. Results at this Laboratory indicate that the purity of sodium with respect to oxide is of a much higher order than has heretofore been stated (reference a). Seventeen samples, representative of the so-called "standard" sodium samples shipped from NRL to six cooperating laboratories, analyzed by the use of the herein described modified apparatus gave the results shown in Table I.

TABLE I

Chronological Sample Number From a Total of 87 Samples Taken	Oxide Content (Wt. % O ₂)
4000
5000
6000
13000
14001
18000
20001
22000
27000
33001
36000
48000
50000
56001
63001
69001
76000

Note: All values reported as .000% are those which gave no alkaline reaction to phenolphthalein when the oxide was prepared for titration. A more reasonable claim for those samples would possibly be that their oxide content was "less than .001%".

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7. The metal used in these analyses was duPont, air cast, brick sodium. Chunks were cut from the bricks, melted in a flask and sampled by passing the metal through a capillary into weighed glass ampules, after appropriate evacuations and flushing to insure a dry, oxygen-free atmosphere in the capillary and ampule. The ampule is then sealed off and re-weighed.

8. Samples of the same sodium, plus weighed quantities of mercuric oxide, were broken in the reaction chamber, and the mercuric oxide reduced by heat and sodium amalgam. Known oxygen contents were thus provided, and when analyzed, gave the results shown in Table II. The data speaks for itself as proof of the accuracy of the modified apparatus and the method.

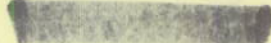
TABLE II

Wt. % O ₂ Added	Wt. % O ₂ Found	Deviation
.037	.037	.000
.074	.075	+.001
.126	.123	-.003
.151	.152	+.001
.275	.280	+.005
	Mean deviation	±.002

9. In conclusion, let it be pointed out that this report by no means casts any doubt on the validity of the method as proposed by reference (a). It is, rather, an attempt to enhance the method and provide means for obtaining more accurate data on a difficult, and, until now, much maligned analytical problem. The value of the method, though limited somewhat by sampling problems, should not be underestimated.

Dale D. Williams

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Physical & Inorganic Branch
Chemistry Division



The model used in these studies was defined, and used in a similar manner. The model was defined in a similar manner to that used in the previous studies. The model was defined in a similar manner to that used in the previous studies. The model was defined in a similar manner to that used in the previous studies.

The results of the model are given in Table 1. The results of the model are given in Table 1. The results of the model are given in Table 1. The results of the model are given in Table 1. The results of the model are given in Table 1.

Wavelength	Wavelength	Wavelength
100	100	100
101	101	101
102	102	102
103	103	103
104	104	104
105	105	105
106	106	106
107	107	107
108	108	108
109	109	109
110	110	110

The results of the model are given in Table 1. The results of the model are given in Table 1. The results of the model are given in Table 1. The results of the model are given in Table 1. The results of the model are given in Table 1.

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