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BEHAVIOR AND CALIBRATION OF DEVICES FOR MONITORING IMPURITIES IN SODIUM

J. Ross Humphreys, Jr., E. C. Filewicz,
S. Greenberg, S. B. Skladzien,
and P. Vilinskas

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BEHAVIOR AND CALIBRATION OF DEVICES FOR MONITORING IMPURITIES IN SODIUM*

by

J. Ross Humphreys, Jr.,** E. C. Filewicz,
S. Greenberg, S. B. Skladzien,†
and P. Vilinskas††

EBR-II Project

July 1971

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*Work performed while authors were members of the Reactor Engineering Division, which was dissolved Jan. 31, 1970.

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BEHAVIOR AND CALIBRATION OF DEVICES FOR MONITORING IMPURITIES IN SODIUM

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ABSTRACT

The sodium analytical loop (SAL) was used to study the behavior of two United Nuclear Corporation (UNC) oxygen meters and a dc resistivity meter. Oxygen was added to the loop in the form of sodium hydroxide and was removed by uranium getter tabs. Oxygen concentration in the sodium was periodically determined using in situ vacuum distillation.

The cells were calibrated by two methods:

(1) A material balance based on sodium hydroxide addition, uranium gettering, and distillation analysis. A least-squares fit of the data thus generated yielded the following calibration equations:

Meter TP 285: $\ln C\,(\text{ppm}) = 54.2 - 45.0\,V$;

Meter TP 286: $\ln C\,(\text{ppm}) = 56.4 - 46.9\,V$.

(2) The method of Minushkin and Goldmann, in which no sodium analyses are required. This method yielded the following equations:

Meter TP 285: $\ln C = 59.8 - 49.9\,V$;

Meter TP 286: $\ln C = 56.6 - 47.2\,V$.

The resistivity meter was not calibrated, but was confirmed to be sensitive to hydrogen concentration and relatively insensitive to oxygen concentration.

The average value for the uranium oxidation coefficient was found to be 16.9 $\mu\text{g cm}^{-2}\text{hr}^{-1}\text{ppm}^{-1}$ (range: 14.1-20.9).

During the experiment, zirconium wire (in excess of the amount required to form ZrH_2 based upon total hydrogen addition in the form of hydroxide) was used as a hydrogen getter. Thirty-eight percent of the hydrogen produced was absorbed.

I. INTRODUCTION

The sodium analytical loop (SAL) was designed to evaluate, compare, and calibrate a variety of existing in-line sodium analytical instruments, to test new instruments as they became available, to develop new instruments as needs became known, and to study the behavior of sodium-impurity systems in terms of LMFBR program objectives. The principal design criterion was a capability for close control of the levels of sodium impurities. The purpose of the program associated with the loop was the determination of accuracy, precision, speed of response, and reliability of the various instruments and techniques for large engineering systems.

Following completion of loop construction and shakedown runs, and a preliminary study of plugging meters,[1] this program was transferred from the Reactor Engineering Division to the Chemical Engineering Division as part of the consolidation of sodium-technology activities at Argonne. The transfer, which would involve physical movement of the SAL and associated support equipment, would necessarily result in a significant amount of downtime. One final experiment was planned, therefore, to calibrate two United Nuclear Corporation (UNC) oxygen meters for use on the secondary sodium system of EBR-II.

This report describes that final experiment and discusses the results from it. The SAL had to be modified considerably for the experiment, and some new operating techniques were required. Because the time available for this final experiment was limited, there was no time to optimize the new techniques; if the first attempt worked reasonably well, it was used throughout.

II. EXPERIMENTAL EQUIPMENT AND PROCEDURE

A. Equipment

Figures 1 and 2 show the SAL as originally designed and constructed. It was designed for operation at 600°F, and was of Type 304 stainless steel welded construction. Conoseal fittings are used for connections that must be frequently made and broken. Capacity is approximately 15 gal. Actual sodium inventory for this experiment was 47.7 kg* (13.6 gal).

The facility, as originally constructed, consisted of a main vessel and three small auxiliary loops through which sodium from the main vessel is pumped. Two of the auxiliary loops accommodated the in-line instrumentation, and one of these loops supplied sodium to the cold trap. Local gradients of temperatures and impurities are eliminated by recirculating sodium

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*This value is known to ±1%.

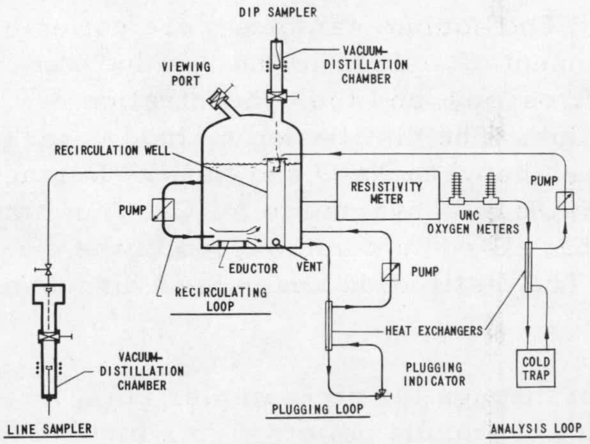

Fig. 1. Schematic Diagram of Sodium Analytical Loop (SAL)

from the upper region of the main vessel, through the third auxiliary loop, and back into the vessel at a lower elevation. The return line terminates at the inlet of an eductor at the bottom of the vessel. The eductor provides a vigorous mixing action.

The SAL also has a dip sampler and a line sampler with which samples are taken for distillation analysis for oxygen in the sodium. The line sampler was not used in this experiment. The dip sampler takes its samples from a recirculation well. Constant return of sodium from the analysis loop to the top of the well reduces errors caused by possible concentration of any surface impurities. In addition, the bottom vent in the well allows circulation and

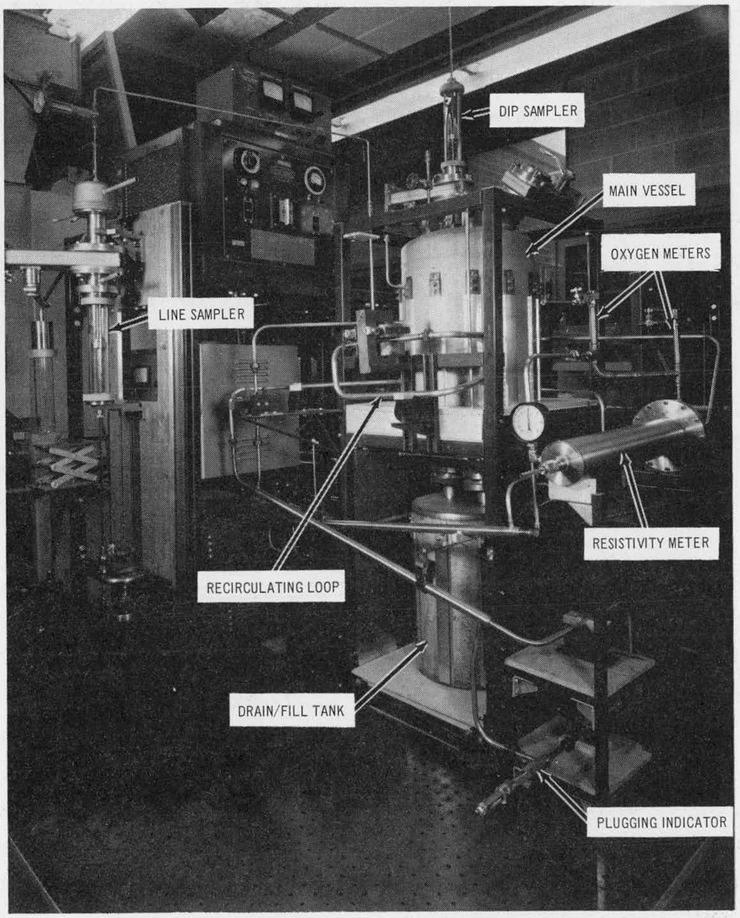

Fig. 2. Photograph of SAL. ANL Neg. No. 112-7387B.

thus ensures a representative sample. The sodium samples were collected in a polished molybdenum cup. The amount of sodium in the residue was determined by atomic-absorption spectroscopy, and the concentration of oxygen was calculated based on that value. The distillation method is insensitive to NaH and does not distinguish between Na_2O and NaOH. During distillation, NaH is decomposed, and NaOH is converted to Na_2O. Thus, the calculation, based on the assumption that all sodium and oxygen in the distillate was present as Na_2O, is valid. The distillation analysis is discussed in Appendix A.

Oxygen was added to the system through the dip-sampler port, in the form of weighed and assayed sodium hydroxide pellets. This method is described in Appendix B.

For this experiment, two major modifications were made in the SAL. The plugging indicator was removed and replaced by a tube designed to hold uranium tabs. During segments of the experiment when oxygen was being removed from the sodium, the tube contained depleted-uranium tabs* (0.018 in. thick) and was operated at 1020°F. During segments when oxygen was being added, an identical tube without uranium was operated at ambient loop temperature (600°F). The tab holder is shown in Fig. 3. The cold trap also was removed, and was replaced by a U-tube containing approximately 58 g of zirconium wire to serve as a hydrogen getter. The zirconium getter was operated at ambient loop temperature (600°F).

The UNC meters have been described in the published literature.[2,3] In this experiment, meters TP 285 and TP 286 were used. The electronics circuitry and instrumentation used to obtain true output voltages are described in Appendix C.

The dc resistivity meter and associated circuitry are described in Appendix D. A Dymec data-acquisition system, which included a digital voltmeter and a punched-tape output, aided in reduction of the data.

B. Procedure

After removal of the plugging meter and the cold trap, the SAL was operated isothermally for several weeks to get baseline data and to "break in" the UNC meters. During this period, there was no uranium in the gettering section. The initial oxygen concentration at the start of the experiment described in this report was 30.8 ppm, as determined using the dip sampler. During this initial period, the temperature coefficients of the meters were obtained in the vicinity of 600°F. The values were 0.31 mV/°F for meter TP 285 and 0.28 mV/°F for meter TP 286. Previously reported[2] values were about 0.5 mV/°F.

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*Natural-uranium tabs would have served equally well.

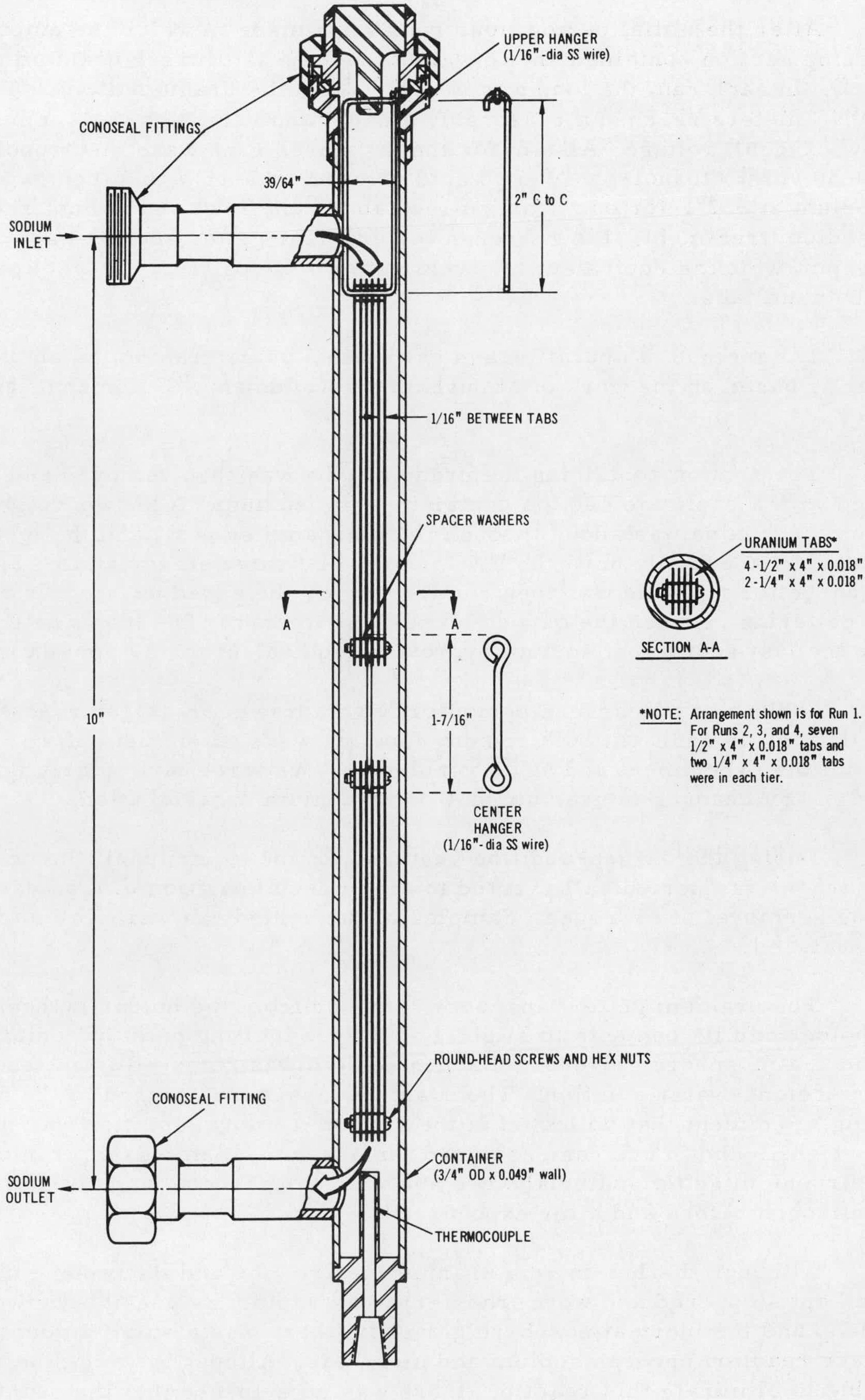

Fig. 3. Uranium-gettering Tube for SAL

After the initial period, four runs were made in which the empty gettering section contained known weights and areas of fresh uranium (see Fig. 3). In each run, the loop was operated with the uranium at 1020°F until the UNC meters reached a reasonably steady, and very high (i.e., indication of low oxygen), voltage. All tabs for the last three runs were electropolished in 50-50 vol % ethanol-phosphoric acid solution at 7-15 V and then exposed to sodium at 932°F for one hour. A few tabs in the first run did not receive the sodium treatment. Flow through the uranium-getter section was 0.38 gpm, which is equivalent to a velocity of 0.47 fps (14.2 cm/sec) past the uranium tabs.

The method of operation and calibration using uranium as an oxygen getter is based on the work of Minushkin and Goldmann,[4] Goldmann,[5] and Isaacs.[6]

The section containing the uranium tabs was then removed and replaced with a duplicate section containing only sodium. A known weight of sodium hydroxide was added through the dip-sampler port, and the loop was operated isothermally until the UNC meters indicated steady state. The oxygen-gettering mode was then run to recover the added oxygen. In each run, gettering reduced the oxygen level close to zero. The loop was frozen after the last addition of sodium hydroxide (equivalent to ~30 ppm oxygen).

Sodium samples were periodically withdrawn for oxygen analysis by distillation. In addition, bulk sodium samples were taken just before the start of the experiment and at its conclusion. We were particularly interested in any changes in uranium and/or zirconium concentration.

During the oxygen-addition segments of the experiment, the cover gas (argon) was periodically vented to aid in decomposition of the hydroxide through removal of hydrogen. Samples of the vented gas were collected and analyzed.

The uranium getter tabs were removed from the holder by heating the holder and its contents to slightly above the melting point of sodium in an inert-atmosphere glovebox. Excess sodium was removed from the tabs by an acetone-water solution. The uranium tabs were weighed to the nearest 0.1 mg. Sediment that collected in the sodium-removal solution was dried and weighed, and in one case analyzed for uranium. Samples of uranium and zirconium getter material were analyzed for carbon, oxygen, hydrogen, and nitrogen before and after exposure.

Although the 1/2-in.-dia uranium-getter tube and its replacement were kept stoppered and were transferred as rapidly as possible between the loop and the inert-atmosphere glovebox, there was a small amount of surface reaction between sodium and moist air. Although it would be desirable to eliminate this reaction, there was no evidence that the quantity of oxygen introduced in this manner affected meter calibration within the overall accuracy and precision of this experiment.

III. RESULTS

Results were obtained in a variety of forms during this experiment. Of direct use in the calibration of the UNC meters were: voltage output of the meters as a function of time (the response of the meters); oxygen concentration of sodium as a function of time; weight and assay of the sodium hydroxide added; weight gain of uranium gettering tabs. In addition, many other analyses and measurements were made to monitor the behavior of the system to confirm the basis of the calibration calculations and increase our understanding of the behavior of sodium systems in general. These included the resistance of the sodium, the temperature of the system, chemical and spectrochemical analysis of the sodium before and after the experiment, chemical analyses of the uranium and zirconium getters before and after exposure, analysis of the residue from evaporation of a solution that had been used to clean sodium from the uranium tabs, and analysis of the cover gas for hydrogen, methane, oxygen, and nitrogen.

A. Response of Oxygen Meters and DC Resistivity Meter

Figures 4-10 show the response of the oxygen meters and the resistivity meter during the experiment. They also show the times and results of the various experimental operations: distillation analyses, analyses of cover gas, uranium gettering, and hydroxide additions. Figure 11 shows, in greater detail, the response to uranium gettering of oxygen. Table I lists the maximum steady-state voltages developed by the oxygen meters after uranium gettering.

The curves in Figs. 4-11 were computer-plotted using a program based on the output of the Dymec data-acquisition system. Temperature of the sodium system and output of the UNC oxygen meters were plotted directly. For the dc resistivity meter, the plotted points were determined as follows. Resistance values measured every 10 min were converted, with the appropriate program, to specific resistivity of sodium at 600°F, the temperature of the sodium in the loop. Then, the average of seven successive converted values was determined, and this average was plotted at the midpoint of the time span over which the seven resistance values were measured. Thus, each plotted resistivity value is an average over a 100-min span. This method of presenting the data was used to reduce random variations arising in the highly sensitive measuring circuitry.

B. Analyses of Sodium Hydroxide

Sodium hydroxide pellets taken from the same batch and treated in the same manner as those used for the oxygen additions were assayed

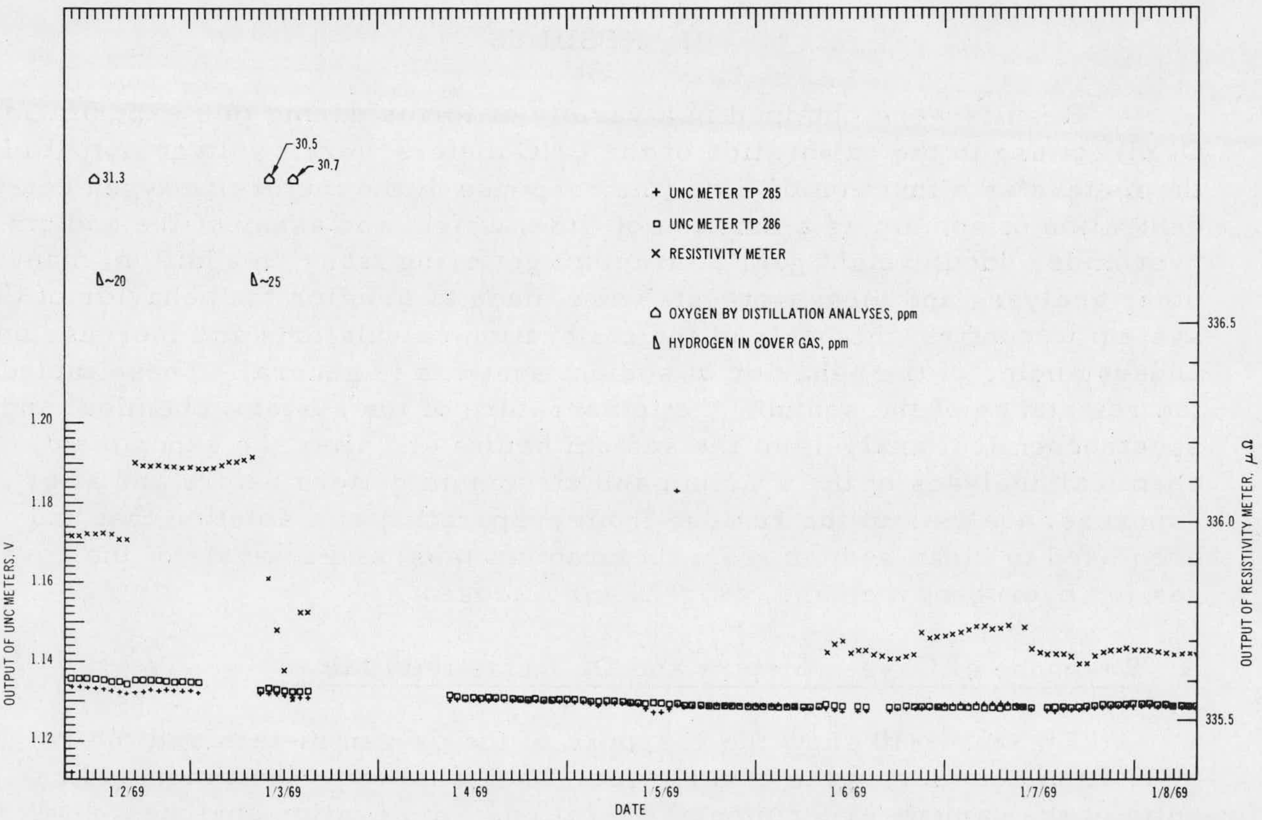

Fig. 4. Response of UNC Oxygen Meters and DC Resistivity Meter, 1/2/69–1/8/69

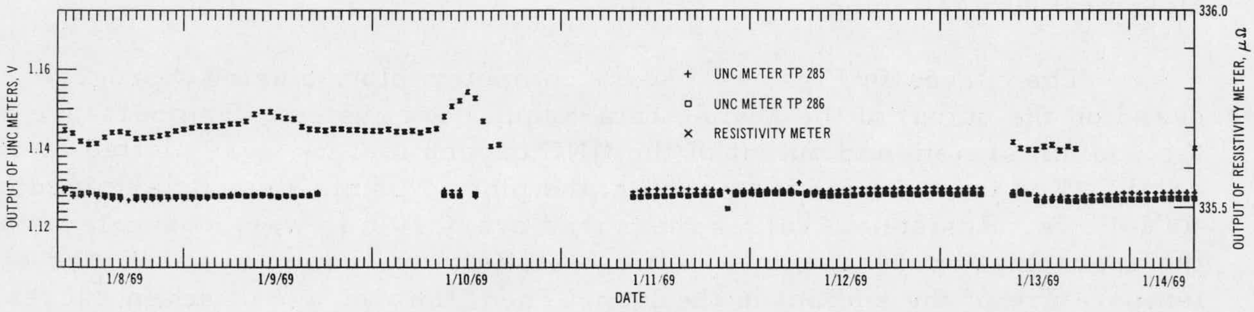

Fig. 5. Response of UNC Oxygen Meters and DC Resistivity Meter, 1/8/69–1/14/69

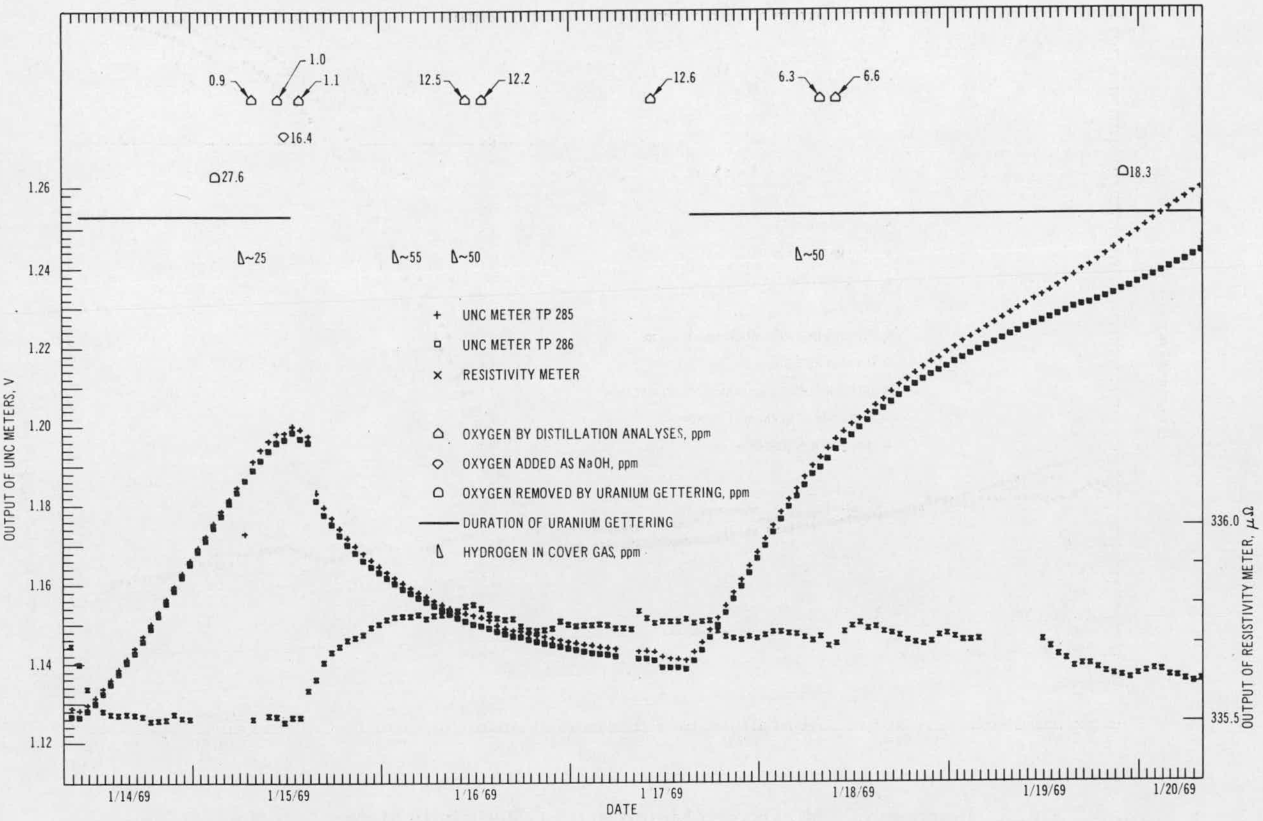

Fig. 6. Response of UNC Oxygen Meters and DC Resistivity Meter, 1/14/69–1/20/69

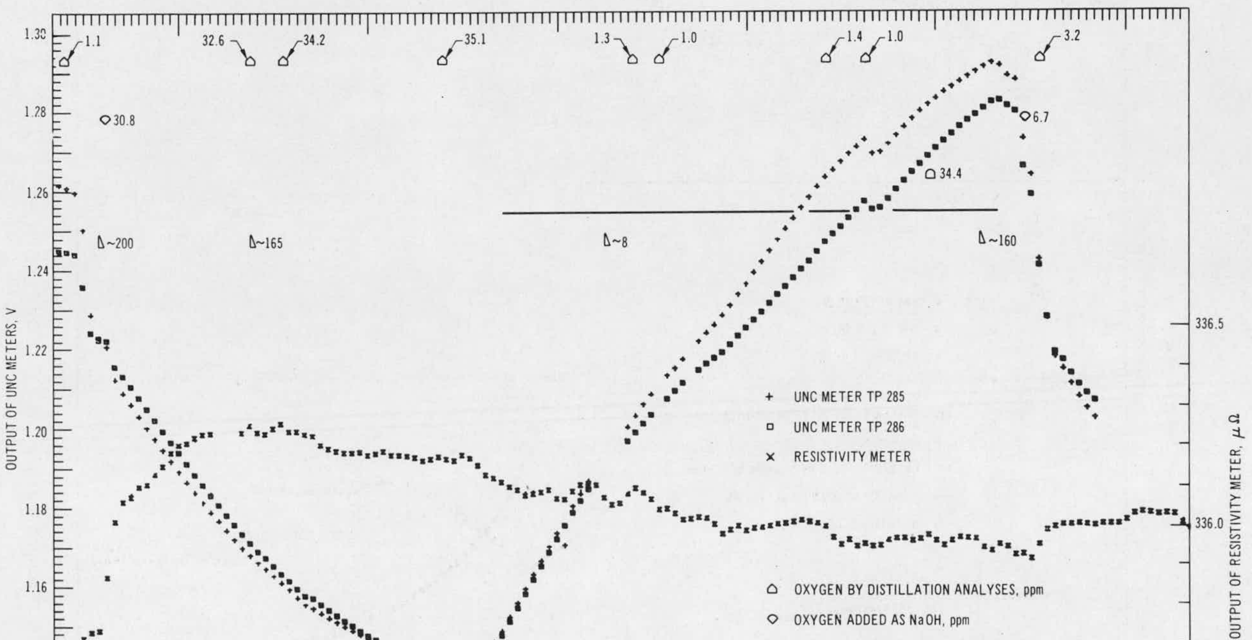

Fig. 7. Response of UNC Oxygen Meters and DC Resistivity Meter, 1/20/69–1/26/69

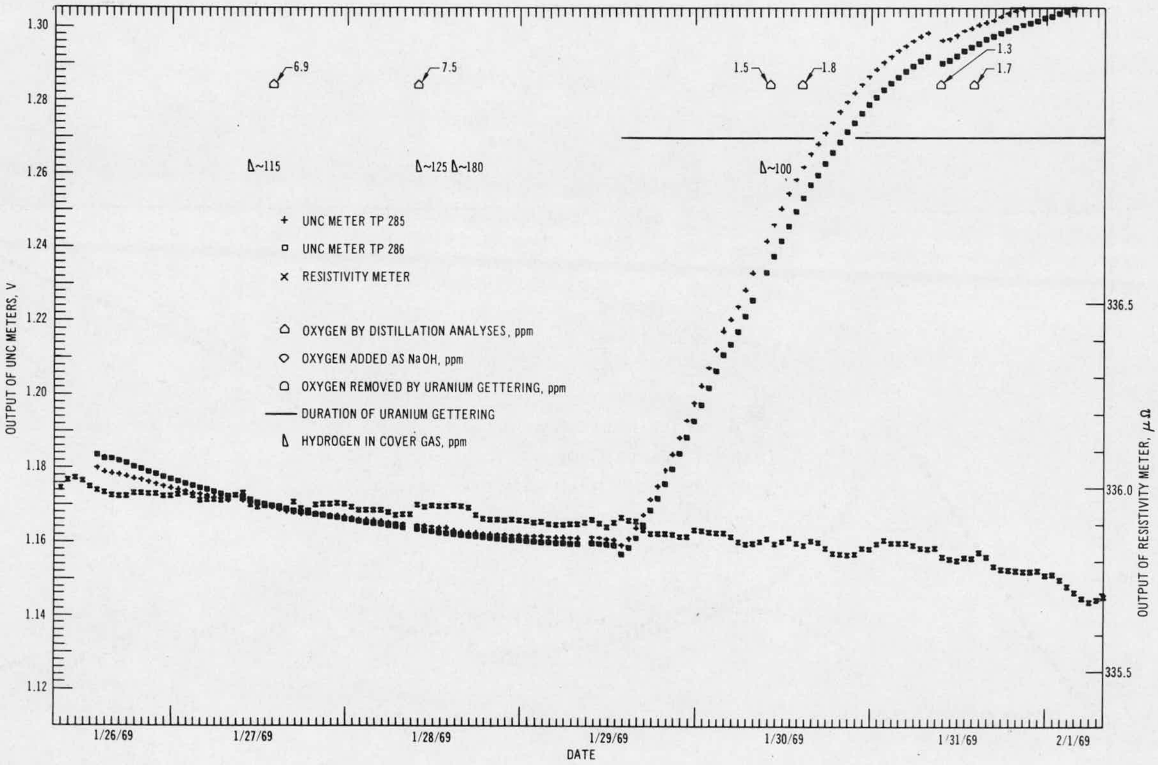

Fig. 8. Response of UNC Oxygen Meters and DC Resistivity Meter, 1/26/69–2/1/69

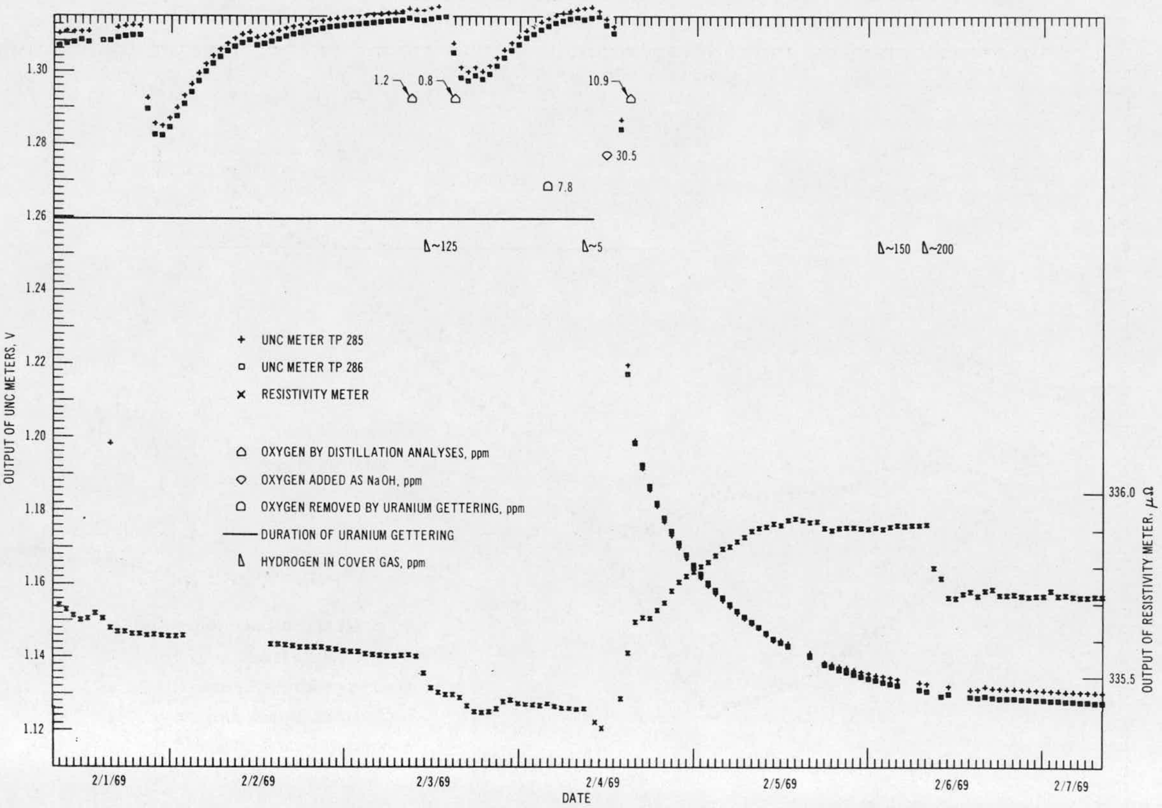

Fig. 9. Response of UNC Oxygen Meters and DC Resistivity Meter, 2/1/69–2/7/69

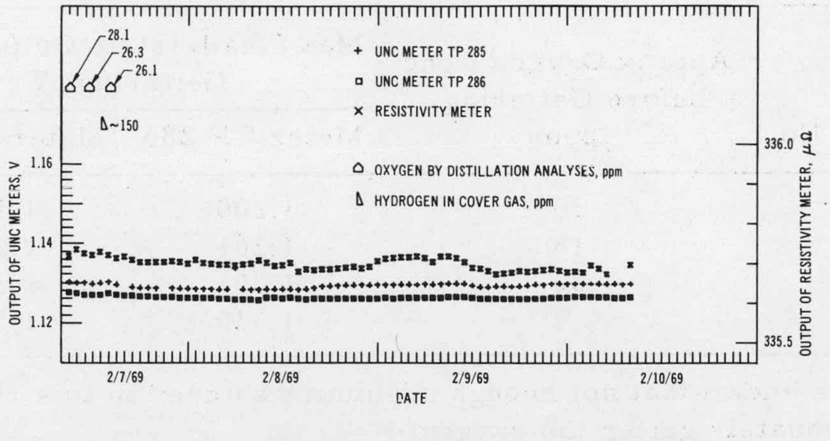

Fig. 10. Response of UNC Oxygen Meters and DC Resistivity Meter, 2/7/69–2/10/69

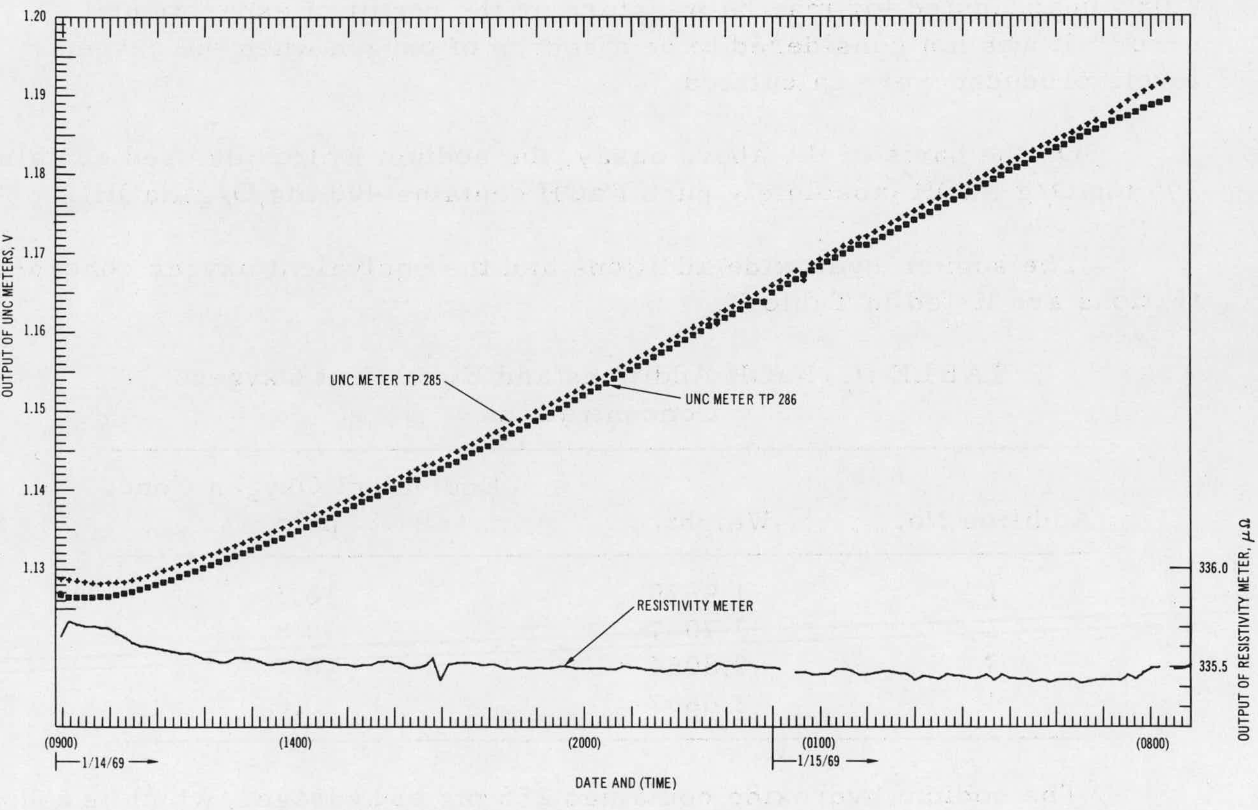

Fig. 11. Response of UNC Oxygen Meters and DC Resistivity Meter to Uranium Gettering of Oxygen

TABLE I. Maximum Outputs of UNC Oxygen Meters after Gettering

Run No.	Approx Oxygen Conc before Gettering, ppm	Max Steady-state Output after Gettering, V	
		Meter TP 285	Meter TP 286
1[a]	30	1.200	1.198
2	18	1.261	1.244
3	30	1.291	1.282
4	7	1.310	1.307

[a] It is known that not enough uranium was used in this run to adequately getter the oxygen.

(by titration) for sodium hydroxide and sodium carbonate content. The results were: sodium hydroxide--98.35%; sodium carbonate--0.57%. The 1.08% unaccounted for may be moisture or the result of experimental error. It was not considered to be a source of oxygen when the oxygen levels produced were calculated.

On the basis of the above assay, the sodium hydroxide used contained 396 mg O/g NaOH (absolutely pure NaOH contains 400 mg O/g NaOH).

The sodium hydroxide additions and the equivalent oxygen concentrations are listed in Table II.

TABLE II. NaOH Additions and Equivalent Oxygen Concentrations

Addition No.	Weight, g	Equivalent Oxygen Conc, ppm
1	1.9679	16.3
2	3.7067	30.8
3	0.8054	6.7
4	3.6807	30.6

The sodium hydroxide contained 256 mg of hydrogen, which is equivalent to a concentration of 5.3 ppm if all the hydroxide dissolved in the sodium.

C. Distillation Analyses

Table III lists the results of all distillation analyses in chronological order. It also includes information concerning sodium hydroxide additions and uranium gettering.

TABLE III. Results of Distillation Analyses

Sample No.[a]	Date	Time	Oxygen Conc, ppm	Comments
1	1/2/69	1345	31.3	Average oxygen content for samples 1-3 is 30.8 ppm. This is considered the initial base state for the experiment.
2	1/3/69	0950	30.5	
3	1/3/69	1308	30.7	
4	1/15/69	0749	0.9	Samples 4-6 represent conditions after gettering with 265 cm^2 of uranium. (It is now known that this was insufficient.)
5	1/15/69	1008	1.0	
6	1/15/69	1317	1.1	
7	1/16/69	1054	12.5	Samples 7-9 represent conditions after addition of NaOH equivalent to ~15 ppm of oxygen.
8	1/16/69	1323	12.2	
9	1/17/69	0950	12.6	
10	1/18/69	0752	6.3	Samples 10-12 show change in oxygen concentration during gettering with 421 cm^2 of uranium.
11	1/18/69	1041	6.6	
12	1/20/69	0930	1.1	
13	1/21/69	0921	32.6	Samples 13-15 represent conditions after addition of NaOH equivalent to ~30 ppm of oxygen.
14	1/21/69	1320	34.2	
15	1/22/69	0937	35.1	
16	1/23/69	0927	1.3	Samples 16-19 show change in oxygen concentration during gettering with 421 cm^2 of uranium.
17	1/23/69	1318	1.0	
18	1/24/69	0945	1.4	
19	1/24/69	1504	1.0	
20	1/25/69	1315	3.2	Samples 20-25 represent conditions after addition of NaOH equivalent to ~7 ppm of oxygen.
21	1/27/69	0940	11.3	
22	1/27/69	1342	6.9	
23	1/28/69	1018	7.5	
24	1/28/69	1317	9.7	
25	1/29/69	0957	8.5	
26	1/30/69	0938	1.5	Samples 26-31 represent conditions after gettering with 421 cm^2 of uranium.
27	1/30/69	1446	1.8	
28	1/31/69	0920	1.3	
29	1/31/69	1320	1.7	
30	2/3/69	0918	1.2	
31	2/3/69	1451	0.8	
32	2/4/69	1448	10.9	Samples 32-35 represent conditions after addition of NaOH equivalent to ~30 ppm of oxygen. Experiment was terminated, and system was frozen in this condition.
33	2/7/69	0915	28.1	
34	2/7/69	1134	26.3	
35	2/7/69	1344	26.1	

[a] Sample weights were between 4.1 and 4.7 g.

D. Results of Uranium Gettering

Table IV summarizes the results of the four gettering runs with uranium tabs. If the weight gain of the uranium is assumed to be due solely to pickup of oxygen, 4.21 g of oxygen were removed by the uranium. The oxygen available (i.e., that initially present, as determined by distillation analysis, plus that added in the first three hydroxide additions) was 4.04 g.

On the basis of the work of Isaacs,[7] it is desirable to limit the pickup of oxygen by the uranium to ~4 mg/cm^2. (For pickups greater than this value, oxide is lost, thus depriving the procedure of its value as an analytical tool.) As shown in Table IV, the value of 4 mg/cm^2 was exceeded for the first uranium loading. Consequently, the quantity of uranium was increased for the subsequent loadings, and the weight gain was held below 4 mg/cm^2.

TABLE IV. Results of Gettering with Uranium Tabs

Run No.	Wt of Tabs, g	Surface Area of Tabs,[a] cm²	Gettering Time, hr	Weight Gain of Tabs g	Weight Gain of Tabs mg/cm²	Wt of Residue,[b] mg	Equivalent Reduction of Oxygen Conc,[c] ppm
1	100.6328	265	28	1.3181	5.0	58.1	27.6
2	171.4123	421	67	0.8762	2.1	23.9	18.3
3	173.0169	421	66	1.6402	3.9	39.1	34.4
4	172.6257	421	78	0.3720	0.9	8.5	7.8

[a] Includes edges.

[b] The sodium-removal treatment (dissolution in acetone) left a residue, which was dried. The dried weights of these residues are listed here. The residue from Run 4 was analyzed for uranium. It contained 7.1 mg of uranium, which is equivalent to <1 mg oxygen if the uranium is assumed to be UO_2. The oxygen content of the residue was ignored in all calculations.

[c] Assuming that the weight gain of the tabs was completely due to pickup of oxygen.

Table V lists the weight gains per unit area for each uranium tab from Run 2 in the same order as the tabs were in the holder. Gettering action appears to be unrelated to tab position.

TABLE V. Individual Weight Gains of Uranium Tabs from Run 2

Upper Tier Tab No.	Upper Tier Wt Gain, mg/cm²	Lower Tier Tab No.	Lower Tier Wt Gain, mg/cm²
77[a]	2.7	59[a]	2.2
110	2.2	26	1.8
67	1.9	104	1.7
47	1.8	148	2.2
166 (center)	2.0	117 (center)	2.1
45	2.2	160	1.6
50	2.2	178	1.6
183	2.3	131	1.8
15[a]	2.9	92[a]	1.5

[a] 1/4-in.-wide tab; all others 1/2-in.-wide.

Representative samples of the tabs were analyzed for carbon, hydrogen, nitrogen, and oxygen after exposure as well as in various stages and conditions of pretreatment. Table VI summarizes the results.

All samples (except No. 3, listed in Table VI) were examined metallographically in the as-polished condition. At 400X, there was no difference between the as-received sample (A) and the samples that had received the various pretreatments. After functioning as getters, the tabs were, as expected, covered with an oxide coating. The thickness of the coating and the degree of cracking increased with increased oxygen concentration, as would be expected.

TABLE VI. Effect of Pretreatment and Exposure on Concentration of Some Impurities in Uranium Getter Tabs

Tab No.	Condition	Carbon,[a] ppm	Hydrogen,[b] ppm	Nitrogen,[b] ppm	Oxygen,[b] %
A	As received	129	4.1	27	0.062
B	Pretreated in 932°F Sodium for 1 hr	95	2.3	29	0.032
C	Pretreated in 932°F Sodium for 1 hr; electropolished[c]	71	1.5	27	0.011
D	Electropolished	81	3.3	8	0.005
2	First loading--top (electropolished + sodium)	161	9.0	8	2.08
3[d]	First loading--top (electropolished)	172	-	-	-
59	Second loading--bottom (electropolished + sodium)	93	3.9	57	0.390
68	Third loading--top (electropolished + sodium)	85	1.3	<4	0.580
54	Fourth loading--bottom (electropolished + sodium)	100	1.8	31	0.190

[a] Determined by combustion.
[b] Determined by fusion in inert gas.
[c] In 50-50 ethanol-phosphoric acid at 7-15 V.
[d] Included only as a check on the carbon value determined for Tab 2.

E. Analyses of Sodium

One sample of sodium was analyzed spectrochemically before and after the experiment. In addition, one sample was chemically analyzed for uranium and zirconium. Table VII gives results of the latter analyses.

TABLE VII. Change in Uranium and Zirconium Concentration of SAL Sodium during Experiment

Element	Concentration, ppm Before Experiment	Concentration, ppm After Experiment
U	<0.05	0.18
Zr	<1	1.3

The spectrochemical analyses showed that other elements were below the limits of detection before and after the experiment

F. Analyses of Zirconium Getter

The zirconium wire used as a hydrogen getter was analyzed for carbon, hydrogen, nitrogen, and oxygen before and after the experiment. Table VIII summarizes the results. Based upon the formation of ZrH_2, 11.64 g of zirconium were required to react with the hydrogen added as sodium hydroxide; 57.88 g of zirconium were actually used.

G. Analyses of Cover Gas

The cover-gas space of the SAL was vented 22 times during the experiment, and samples collected while the cover gas was being vented were analyzed by gas chromatography. Hydrogen concentration varied between about 5 and 200 ppm. Nitrogen concentration varied from about 20 to over 700 ppm. Methane was detected in all but one sample, and oxygen was detected in 16 samples.

TABLE VIII. Effect of Exposure on Some Impurity Concentrations in Zirconium Getter

	Concentration, Wt %	
Element	Before Experiment	After Experiment
C	0.0131	>0.0012[a]
H	0.0027	0.17[b]
N	0.0016	0.0036
O	0.086	0.109[c]

[a] Carbon recovery probably incomplete--value low.
[b] This is equivalent to 98 mg or 38% of the hydrogen added as hydroxide.
[c] 0.01 g of oxygen was removed by the zirconium.

IV. DISCUSSION

Table IX shows the relationship of the output of the UNC meters to the measured and/or calculated oxygen concentrations taken from Tables II-IV.

TABLE IX. Correlation of Outputs of UNC Meters with Oxygen Concentration of Sodium

	Output, V	
Oxygen Conc, ppm	Meter TP 285	Meter TP 286
34.4[a]	1.127[b]	1.127[b]
33.9[c]	1.127[b]	1.127[b]
30.8[d]	1.127[b]	1.127[b]
30.8[c,e]	1.129	1.127
30.5[d]	1.130	1.127
26.8[c]	1.130	1.127
19.6[d,f]	1.141	1.139
18.3[a]	1.141	1.139
12.4[c,g]	1.141	1.139
7.8[a]	1.161	1.159
7.2[c]	1.161	1.159
6.7[d]	1.161	1.159

[a] From uranium gettering.
[b] Not enough time was allowed for conversion of hydroxide to oxide (see Fig. 5). A visually extrapolated value of 1.127 V is used for both meters.
[c] From distillation analysis.
[d] From hydroxide addition.
[e] Initial system condition.
[f] Based on material balance using results of first (incomplete) uranium gettering and initial distillation analysis.
[g] This point is discarded in subsequent calculations. Apparently the analytical result is in error, but the reason is not known.

Based on a least-squares fit of the data (but ignoring the one very low distillation-analysis result as indicated in footnote g of Table IX), the relationship of oxygen concentration (C) in ppm to meter voltage is:

Meter TP 285: $\ln C = 54.2 - 45.0\ V$;

Meter TP 286: $\ln C = 56.4 - 46.9\ V$.

The theoretical slope at 600°F is $-39.4\ V^{-1}$. The reason for the greater-than-theoretical slope (as well as the difference in slopes) is not understood. However, the phenomenon of nontheoretical slope is common, if not universal, and demonstrates the necessity of calibrating each meter individually. (It may be noted that the data for these meters fall much closer to the theoretical calibration than the data for most of the meters reported on in the original development report.[2])

It would be advantageous if the meter could be reliably calibrated using a method not requiring sampling and analysis of sodium. Such a method has been developed by Minushkin and Goldmann.[4] It consists of adding known amounts of oxygen to a gettered system, observing the voltage change, and performing the appropriate algebraic manipulations on a series of simultaneous equations relating oxygen concentration and voltage.

The method of Minushkin and Goldmann has been applied to the results of this experiment, using the values for sodium hydroxide additions 2 and 3 (30.8 and 6.7 ppm, respectively; see Table II). With these values, the following equations relating oxygen concentration and voltage were obtained:

Meter TP 285: $\ln C = 59.8 - 49.9\ V$;

Meter TP 286: $\ln C = 56.6 - 47.2\ V$.

As with the previous method of calibration, the slopes are much greater than the theoretical value. Besides, the two methods of calibration yield markedly different results for Meter TP 285. The reason for the difference in these results is not understood. Making a choice between the two equations would require comparing them for systems of known oxygen concentrations (as determined, for example, by chemical analysis, vanadium-wire equilibration, uranium oxidation rate, or cold-trap control).

It is of interest and importance to know the "oxidation constant" for the uranium used as gettering material in these experiments. If a constant value is indeed obtained, the oxidation rate of uranium can be used as a measure of oxygen concentration in sodium, as suggested by Isaacs.[6]

The change in concentration of oxygen in sodium and the weight gain of the uranium can be related by the equation[6]

$$dC = -\frac{kAC\,dt}{W_{Na}}$$

where

C is concentration of oxygen in sodium in ppm,

W_{Na} is mass of sodium in system in g,

A is area of uranium in cm^2,

t is time in hours,

and

k is slope of the curve relating the rate of weight gain of uranium to oxygen concentration in sodium.

Integrating and solving for k gives

$$k = \frac{W_{Na} \ln \frac{C_1}{C_2}}{At}.$$

The values of k were determined for Runs 2, 3, and 4. (Run 1 was not included, because insufficient uranium was used and oxygen pickup exceeded the limits for which this approach is believed to be applicable.) Table X summarizes the results of the calculations.*

TABLE X. Calculations of k for Uranium Gettering[a]

Run No.	C_1,[b] ppm	C_2,[b] ppm	Gettering Time, hr	k
2	20.0	1.0	24.0	14.1
3	22.6	1.0	22.4	15.8
4	8.8	1.0	11.8	20.9

[a] The constants used for the three runs were $W_{Na} = 47.7 \times 10^3$ g and $A = 421$ cm^2.

[b] C_1 and C_2 were taken from a plot of oxygen concentration vs time for Meter TP 286, using the least-squares correlation. C_2 was arbitrarily chosen as 1.0, and the time in column 4 is the time to reach this value. The value for k would not change significantly if either the calibration curve for Meter TP 285 or the Goldmann-Minushkin correlation were used.

The high value of k for Run 4 is disappointing. Various manipulations were performed on the data of that run in attempts to bring the value

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*By coincidence, the average of the three values, 16.9, is very close to the value of 16.3 reported by Isaacs.[6] Isaacs' results were obtained at 932°F in static sodium; ours were obtained at 1020°F.

for k into closer agreement with the values of k for Runs 2 and 3. An increase in gettering time to 16.5 hr would have resulted in a k of 15. However, after 16.5 hr of gettering, the indicated oxygen concentration was 0.48 ppm. If k is calculated for the concentration range of 8.8-0.48 ppm of oxygen, the value obtained is 20.0; i.e., the value of k is essentially constant for this particular run.

As observed by Subbotin et al.,[8] the dc resistivity meter is sensitive to hydrogen and relatively insensitive to oxygen. No attempt was made to calibrate that meter.

APPENDIX A

Analysis of Sodium Samples by Vacuum Distillation

Figures 12 and 13 show the arrangement for dip sampling and vacuum distillation in the SAL. The distillation tube is made from Pyrex tubing that is 12 in. long, 2.344 in. in OD, and has a wall thickness of 0.172 in.

1. Sampling and Vacuum Distillation with the Dip Sampler

a. Prepare the molybdenum sample cup as follows:

(1) Polish all over using 0.3-μ metallographic polishing alumina and water as the lubricant.

(2) Rinse with water, then ethyl alcohol; air dry.

b. Install the distillation unit, which includes a Pyrex glass tube, two gland seals, a thermocouple/dip rod, and a sample cup. (Note: Prebake the glass tube in an oven at 115°C for 2 hr or more.)

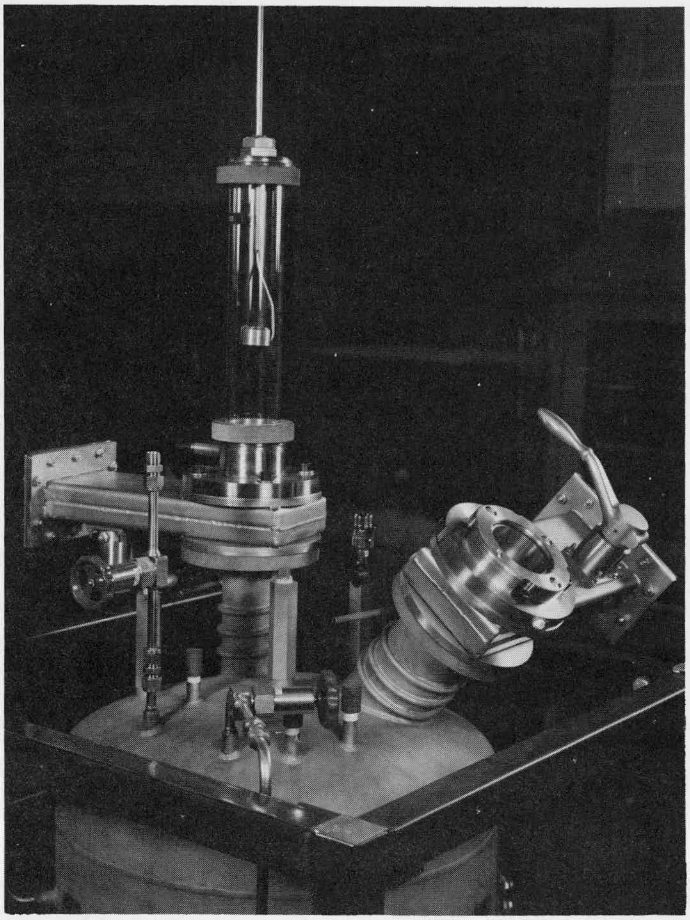

Fig. 12. Photograph of Top of Main Vessel of SAL, Showing Dip Sampler and Vessel Viewing Port. ANL Neg. No. 112-7388.

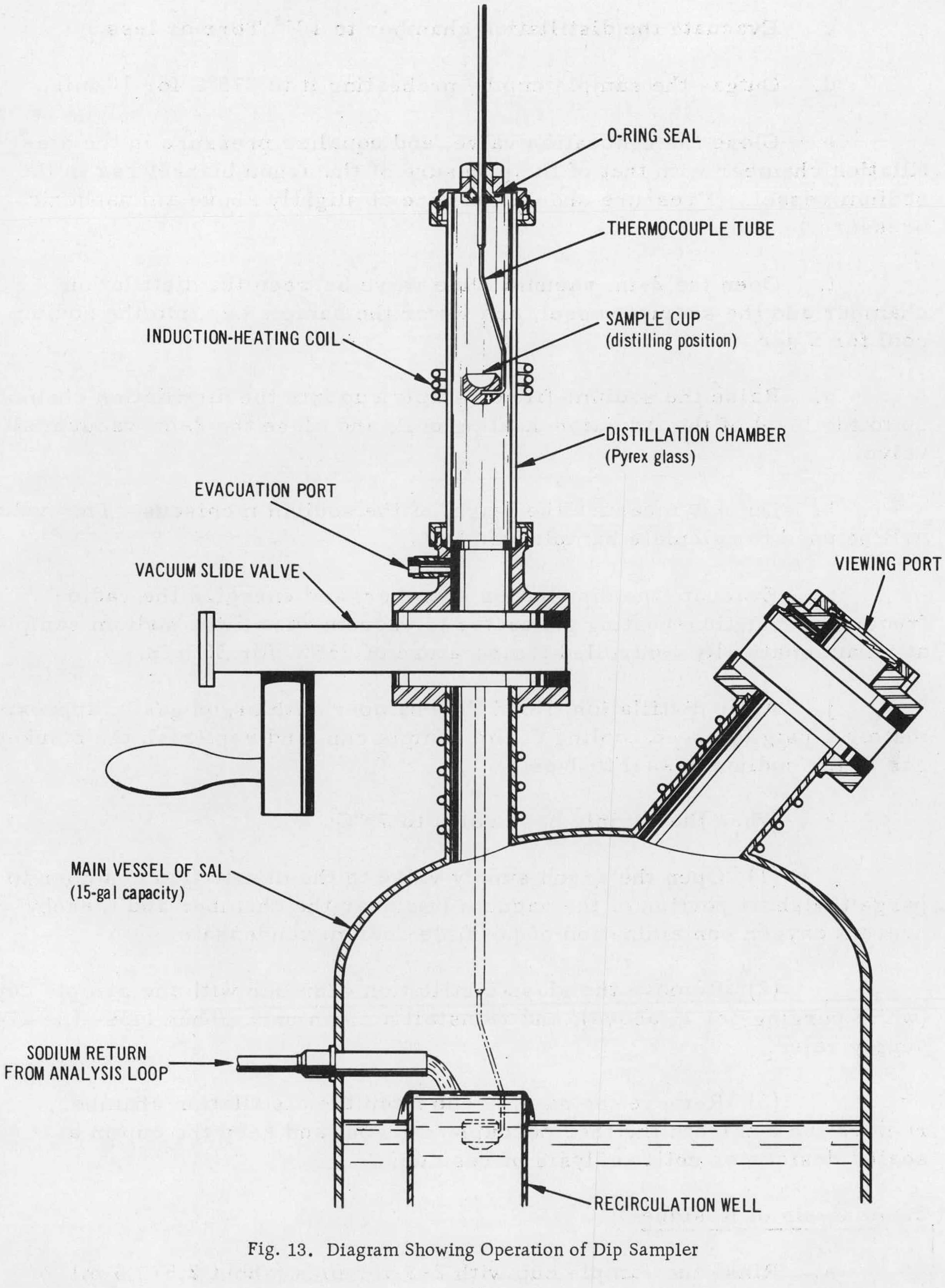

Fig. 13. Diagram Showing Operation of Dip Sampler

c. Evacuate the distillation chamber to 10^{-3} Torr or less.

d. Outgas the sample cup by preheating it to 375°C for 10 min.

e. Close the evacuation valve, and equalize pressure in the distillation chamber with that of the pressure of the argon blanket gas in the sodium vessel. (Pressure should equalize at slightly above atmospheric pressure.)

f. Open the 2-in. vacuum slide valve between the distillation chamber and the sodium vessel, and lower the sample cup into the sodium pool for 5 sec.

g. Raise the sodium-filled sample cup into the distillation chamber up to the level of the induction-heating coil, and close the 2-in. vacuum slide valve.

h. Quickly measure the height of the sodium meniscus. This value will be used to calculate sample weight.*

i. Evacuate the distillation chamber, and energize the radio-frequency induction-heating generator to vacuum-distill the sodium sample at an automatically controlled temperature of 355°C for 30 min.

j. After distillation, flood the chamber with argon gas to approximately 1 psig to speed cooling of the sample cup, and replenish the blanket gas in the sodium vessel to 1 psig.

k. When the sample has cooled to 75°C:

(1) Open the argon supply valve to the distillation chamber to purge the short portion of the vacuum line near the chamber and thereby prevent oxygen contamination of possible sodium condensate.

(2) Remove the glass distillation chamber with the sample cup (while purging per a, above), and reinstall a clean unit. Then close the argon supply valve.

(3) Remove the sample cup from the distillation chamber, remove the cup from the thermocouple/dip rod, and keep the cup in a sealed desiccator until analysis of residue.

2. Analysis of Residue

a. Rinse the sample cup with 2-3 volumes (about 2.5-3.5 ml) of ~0.01N HCl. Note the exact concentration and volume of acid used.

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*See Sec. 3 of this appendix for discussion of how sample weight was calculated.

b. Transfer the acid wash to a clean 25- or 50-ml volumetric flask (depending on the sample size). Rinse the cup with about four small portions of water, and transfer each washing to the flask.

c. Fill the flask exactly to the mark with water. Stopper the flask, and shake well.

d. Determine the concentration of sodium by atomic absorption using three standards, two of which bracket the concentration range of the unknowns being analyzed. For example, the μg of sodium in a residue from a 5-g sodium sample having an oxygen concentration of ~10 ppm would be approximately

$$(5)(10)/0.3478 = 143\ \mu g.$$

This concentration of sodium in 50 ml would amount to ~2.8 μg/ml.

Note: For best precision, samples should have sufficient concentration to give an absorption reading of about 60%. The standards should cover the absorption range of 40-80%. For sodium, where sensitivity is about 0.05 ppm per 1% absorption, 2.8 μg/ml would give an absorption reading of ~56%. At concentrations greater than 4 μg Na/ml, the working curve of ppm Na versus absorbance deviates from linearity.

e. Calculate the total oxygen based on the assumption that all the sodium in the residue exists as Na_2O:

$$(\text{ppm Na})\ (\text{vol of soln})\ (0.3478) = \text{total}\ \mu g\ \text{oxygen}.$$

Parts per million of oxygen are

$$\mu g\ \text{oxygen}/\text{sample weight in}\ \mu g.$$

3. Determination of Sample Size

Sample size was determined by using a method relating sample volume to the height of the sample as measured to the top of its meniscus above the lip of the cup.* The volume of water the cup contained was determined as a function of liquid level. Then, from this information and the density of sodium at 600°F, a table was constructed relating liquid level to sample weight.

Immediately upon withdrawal of a sample for distillation, the height of the meniscus was measured to the nearest 1/16 in., and the cup and sample were photographed to provide a record of each sampling.

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*In general, the liquid surface was not level with the lip of the cup. Its meniscus was convex.

Before the experiment discussed in this report, this method of determining sample weight was checked by recovering all distilled sodium from the inside of the distillation apparatus (by washing) and determining, by titration, the sodium in the washings. The result of many determinations showed that the method was accurate to better than 2%.

APPENDIX B

Addition of Sodium Hydroxide

The sodium hydroxide pellets used for adding oxygen to the SAL system were taken from a freshly opened bottle of AR (Analytical Reagent) grade sodium hydroxide. The pellets were transferred to weighing bottles in quantities to provide approximately 30, 15, and 7.5 ppm oxygen. The bottles were then stored in a larger vessel, which was continuously evacuated. The bottles were removed from the vacuum system as needed, accurately reweighed, and then placed in an inert-atmosphere glovebox. In the glovebox, the pellets were transferred to the special glass loading device (see Fig. 14).

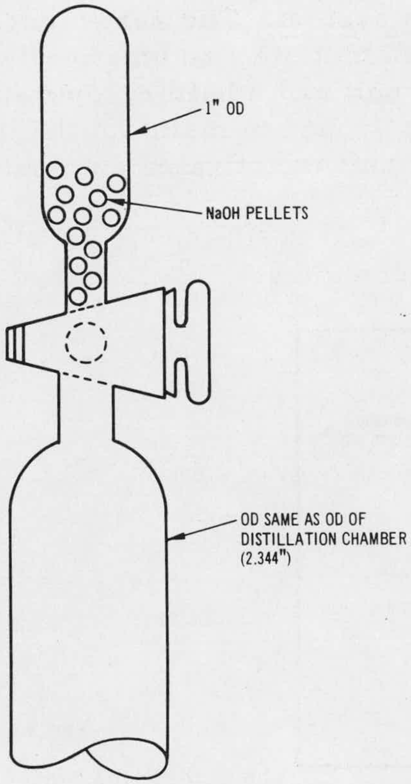

Fig. 14

Device Used for Loading Sodium Hydroxide Pellets into SAL

This device, after being loaded with the pellets, was attached to the SAL in place of the dip sampler, and made vacuum-tight with the O-ring and collar that provided the seal for the dip-sampler chamber. The lower region of the device was then evacuated and refilled several times with high-purity argon from the SAL blanket-gas supply.

Finally, the large slide valve at the top of SAL and the glass stopcock in the loading device were opened, allowing the pellets to drop into the vessel.

APPENDIX C

Readout of UNC Meters in the SAL

The output voltage of the UNC meters was read out automatically with a Hewlett-Packard data-acquisition system (No. DY-2010D). With this system, three readings are taken and mathematically totaled to determine the actual output voltage of the sensor. These readings are: (1) reference voltage, (2) panel-meter voltage (indicates difference between reference voltage and sensor voltage), and (3) zero-drift voltage of the electrometer.

The reference and panel-meter voltages are fed directly to the switching unit of the data-acquisition system. The zero-drift voltage of the electrometer is indicated on the panel meter by automatically closing the zero-check circuit via the switching unit and a battery-operated relay. The relay and battery were isolated from ground to maintain the integrity of the electrometer circuit. The switching unit is activated automatically by selective preset timing.

Figure 15 shows the readout circuitry.

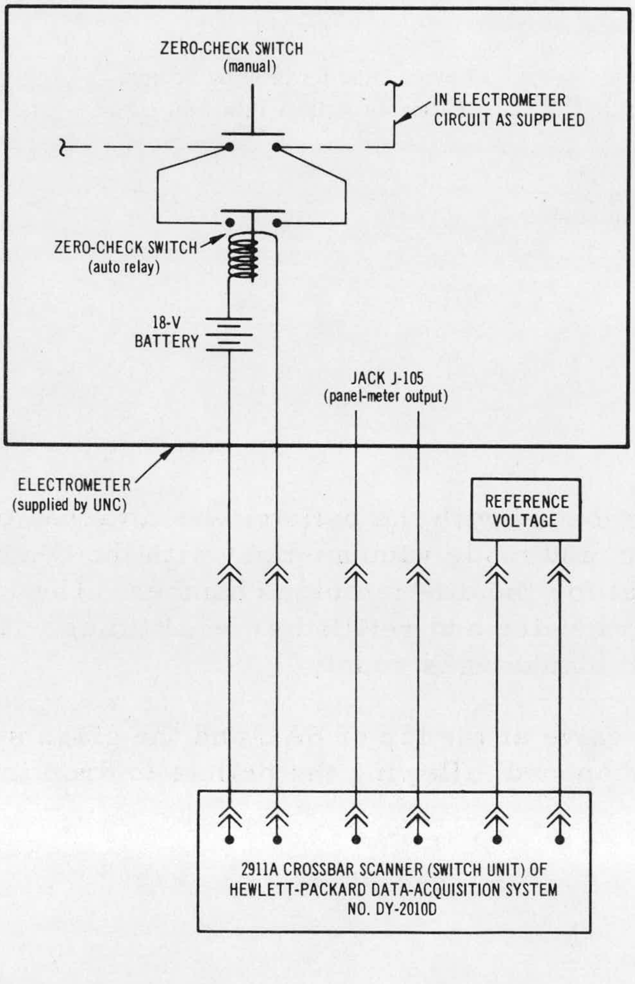

Fig. 15

Schematic Diagram of Circuit Connections for Readout of Output of UNC Oxygen Meters in SAL

APPENDIX D

DC Resistivity Meter

The dc resistivity meter used in this experiment is based on unpublished work of Eric Caldwell and J. Ross Humphreys, Jr. (then of Los Alamos). Figure 16 is a sectional drawing of this meter.

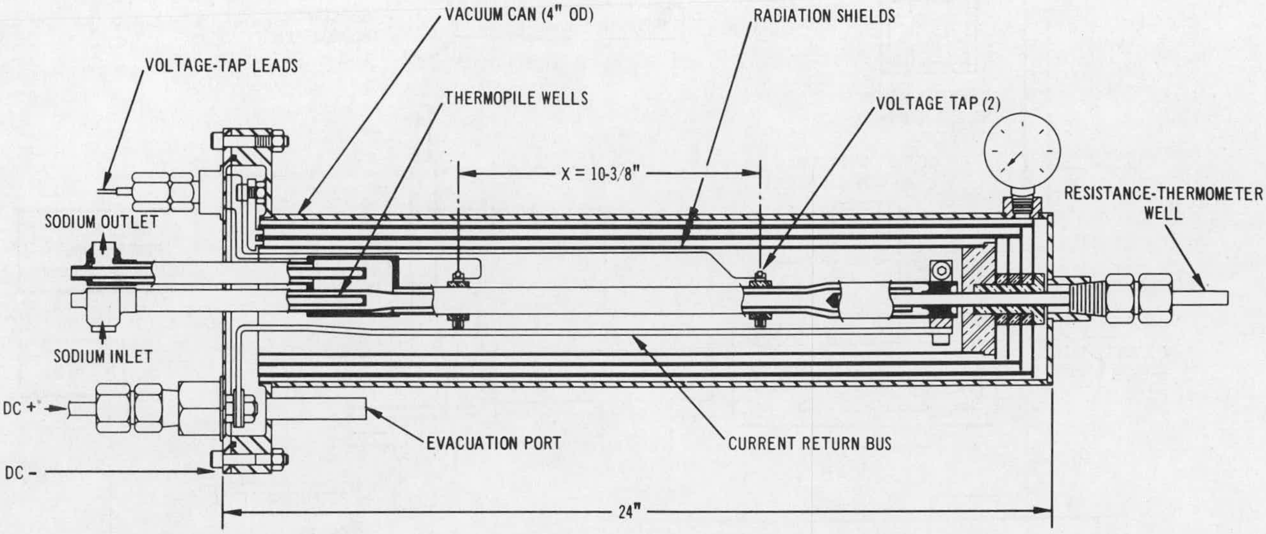

Fig. 16. DC Resistivity Meter

The section of the meter across which resistance is measured consists of a 3/8-in.-OD tube within a 5/8-in.-OD tube. Both tubes are made of Type 304 stainless steel. Sodium within the small tube flows countercurrently to sodium in the annulus between the tubes. The distance X (see Fig. 16) between the measuring-voltage taps was precisely set at $10\frac{3}{8}$ in. The total resistance measured is that of the branches of the parallel circuit formed by the sodium and the two tubes. The final sodium resistance is calculated from this total measurement and the separately measured resistances of the tubes before installation.

The total resistance was measured with a Kelvin bridge circuit (see Fig. 17) that used a regulated dc power supply set at 30 A and controlled at 0.5% constant current ripple. The Kelvin bridge consists of a low-resistance standard and a double-ratio box. A galvanometer was used for null indication of a resistance setting. The deflections of the null indicator were recorded on a two-pen recorder, and the variations from the set point were read from the strip chart. The temperature of the sodium was also recorded on the same strip chart and read as a deflection from a null setting of 600°F, which was measured by a calibrated platinum resistance thermometer through a Mueller bridge circuit. The final resistance reading was then temperature-corrected at 0.74 μΩ/°C to eliminate the effects due to temperature variations above and below 316°C. The temperature was normally precision-controlled at 316 ± 0.1°C. The differential temperature across the resistance meter was normally maintained at less than 0.025°C by heater control, and was measured by a Chromel-Alumel thermopile.

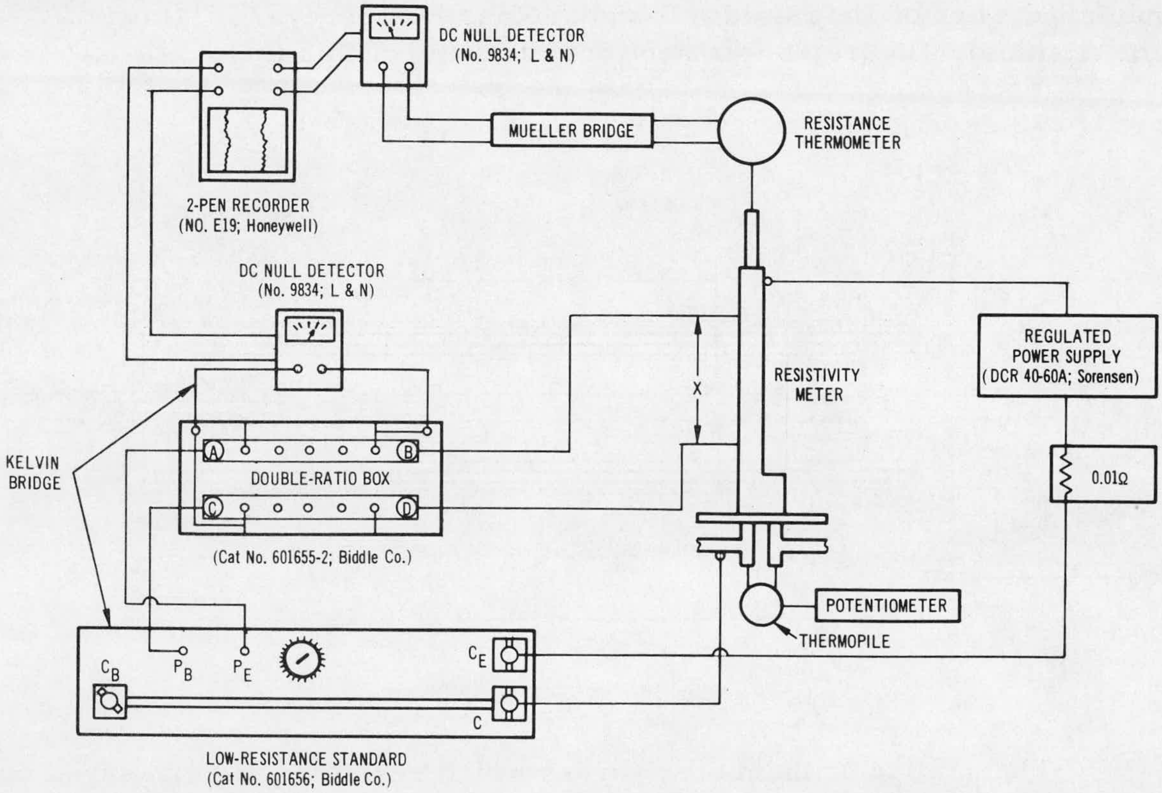

Fig. 17. Schematic Diagram of Bridge and Power Supply of DC Resistivity Meter

The temperature of the meter, the differential temperature, and the current were recorded on punched tape by the data-acquisition system and printed out by computer programming. The 30-A current was measured as a voltage divided by 0.01 Ω at the standard shunt.

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