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CONDUCTOMETRIC ACIDIMETRY IN THE PRESENCE OF HYDROLYZABLE IONS

by

R. C. Propst

Analytical Chemistry Division

June 1955

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E. I. du Pont de Nemours & Co.
Explosives Department --- Atomic Energy Division
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ABSTRACT

The sensitivity of the conductometric method for free acid in the presence of hydrolyzable ions was increased by employing an electrode system that had a large cell constant and by selecting a sample size that gave an optimum change in solution resistance per increment of titrant. The procedure that was developed was used to determine the free acidity of samples 0.01M in nitric acid and 1.5M in aluminum nitrate with a relative standard deviation of ± 14 per cent.

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CONDUCTOMETRIC ACIDIMETRY IN THE PRESENCE OF HYDROLYZABLE IONS

INTRODUCTION

An extremely sensitive analytical method is required to etermine very low levels of free acid in samples containing acid roduced by the hydrolysis of ions such as aluminum and uranium. This etermination has been the subject of many intensive investigations. lthough different approaches to this problem have been made(1)(2)(3) 4), none achieved the desired sensitivity.

A satisfactory method should possess the following qualifica- ions: adequate sensitivity, reproducibility, and accuracy; adapta- ility to both automatic and remote techniques; and adaptability to mall sample sizes. For radioactive solutions, the method should be perable at high dilutions so that shielding can be minimized.

With an increase in sensitivity, the conductivity method roposed by Pepkowitz et al.(1) would fulfill all of these require- ents. The conductivity method was selected for study with the ex- ectation that the sensitivity could be increased.

SUMMARY

Two variables, sample size and the cell constant of the lectrode system, were shown to have a pronounced effect on the ensitivity of the determination of acidity by conductivity. To btain reliable results, it was necessary to eliminate carbon dioxide rom the titration medium, and to control three variables: tempera- ure, electrode position, and concentration of complexing agent.

By proper control of the above variables, the free acidity f 25 µl samples 0.01M in nitric acid and 1.5M in aluminum nitrate was etermined with a relative standard deviation of ± 14 per cent.

The conductivity meter and procedure described here are used outinely in control laboratories for the determination of free cidity of radioactive samples. The technique has also served in a eferee capacity. The method is considered to be adaptable to remote nd semiautomatic recording techniques.

It was shown that the end point can be indicated in a new way by measuring the apparent capacitance of the electrode system.

DISCUSSION

Basically, this work was directed toward increasing the sensitivity of the conductometric method. The variables affecting th change in sensitivity were studied by measuring reproducibly and accurately the small changes in resistance that were experienced during titration.

Since phase shift decreases the sharpness of the null, the bridge was constructed so that it could be balanced for phase shift a well as for resistance. An audio-frequency source was employed to excite the bridge since a 60-cycle source may cause polarization effects.

The effect of the apparent capacity of the electrode system upon the measured resistance of the solution was investigated in a limited way. If the apparent capacity of the electrode system is large enough, this capacitance can cause the measured resistance to b low. In no case was the capacity of the electrode system large enoug to produce a detectable error in the measured resistance.

EQUIPMENT

Initially the bridge circuit shown in Figures 1, 2, 3, and 4 was used for conductivity measurements. The variable arm of the bridge consisted of a 50-ohm "Helipot" in series with a resistor decade having a range of 0-5000 ohms in 50-ohm steps. This arrangement permitted the variable arm to be adjusted to 0.05 ohm. A later modification of the bridge employed a 100-ohm "Helipot" and a decade having a range of 0-10,000 ohms in 100-ohm steps.

The bridge was excited at 2000 cycles by a Hewlett Packard Model 233-A audio oscillator. A Du Mont Model 304-A oscilloscope was used as the null detector by connecting the output terminals of the bridge to the vertical deflection system. Phase shift was detected by feeding the output of the oscillator to the horizontal deflection system of the oscilloscope. A condenser decade (0-10,000 mmfd in 100-mmfd steps) equipped with a 100-mmfd vernier, and connected as shown in Figure 1, was used to balance phase shift. Phase shift balance was readily accomplished with the vernier condenser of the decade.

With the equipment connected as shown in Figure 1, the trace on the face of the oscilloscope tube indicated the degree of balance of the bridge. In the absence of phase shift, the trace appeared as a straight line with resistance unbalance being indicated by the direction and degree of tilt of the trace. Phase shift across the arms of the bridge caused the trace to assume an elliptical shape. The width of the ellipse indicated the degree of capacitance unbalance. By careful adjustment the elliptical trace was reduced to a straight line which was then oriented horizontally. Both the resistance and capacitance balance could be obtained separately, the null point of the bridge being indicated by a straight line horizontal trace.

A second and more compact instrument, designed and built for he control laboratory, used the basic principle employed by Melville 5)and Fischer(6).

In this instrument, shown in Figures 5 and 6, the excitaion voltage is applied to the electrodes and a variable resistance is onnected in series. A balance is obtained by adjusting the variable esistor until the a.c. voltage developed across the resistor equals he a.c. voltage across the electrodes. At balance, the variable esistor is equal to the impedance of the electrode system. Since the oltages developed across the resistor and the electrode are rectified efore being compared, phase shift does not affect the sensitivity of he galvanometer null.

The titration vessel, Figure 7, was constructed from a tall-orm, 30-ml beaker and had an outer jacket through which water was irculated by means of a "LABLINE," Model 3052, constant-temperature ath. The vessel was closed with a rubber stopper through which the lectrodes, emptying tube, nitrogen inlet, and Gilmont buret were inerted. The solution was stirred by a magnetic stirrer with external peed control. The stirring bar was a half-inch length of 90-mil ickel wire sealed in glass.

Bright platinum electrodes were constructed as described by Pepkowitz et al.(1) During the course of the experiments, the cell onstant of the wire-type electrodes was increased by shortening the engths of the exposed wire to approximately 2 mm.

REAGENTS

A stock solution of 0.5M sodium fluoride was prepared from Baker's reagent grade sodium fluoride and was neutralized to a pH of 8.4.

A 1.5M aluminum nitrate stock solution was prepared from Fisher's reagent grade aluminum nitrate. The free acidity of this solution was determined by spiking 100 µl aliquots with various amounts of nitric acid and titrating with standard base according to the procedure of Pepkowitz et al.(1) The free acidity value was then used for a preliminary adjustment of the stock solution to neutrality. This procedure was repeated until the solution was neutral, as indicated by 100 per cent neutralization of the added acid. As a final check on the stock solution, 100 µl aliquots were complexed with fluoride and were titrated with 0.1M nitric acid and with 0.1M sodium hydroxide. Neither conductometric titration curve exhibited a detectable break, indicating that the solution was neutral.

For work at very low free acid concentrations, more sensitive neutralization of the stock solution was required. Accordingly, 25 µl samples of the 1.5M aluminum nitrate stock solution were spiked with 25 µl of 0.01M nitric acid for titration. The stock solution was then adjusted as previously described.

A one per cent aqueous thorin solution was prepared from Eastman Kodak, No. 6748 thorin, o(2-hydroxy-3, 6-disulfo-1-naphthylazo) benzene arsonic acid, and neutralized to a pH of 5.8.

PROCEDURE

The following procedure, which is a modification of that proposed by Pepkowitz et al. was used throughout this study.

Assemble the equipment as indicated in Figure 1. Adjust th constant temperature bath to room temperature and position the titration vessel 2-3 mm above the magnetic stirrer.

Fill the titration vessel with distilled water to within 0.5 cm of the rubber stopper and add a suitable sample aliquot (25 - 100 µl). Add the calculated amount of sodium fluoride required to complex the hydrolyzable ions, based on a molar ratio of 3 fluorides to 1 aluminum and 2 fluorides to 1 uranium.

Start the stirrer and allow nitrogen to bubble through the solution for 5 minutes. Shut off the nitrogen supply and titrate the solution by adding standard 0.1M sodium hydroxide in small increments from the Gilmont microburet, measuring the solution resistance after each addition. The increment size should be selected so that a minimum of five points are obtained before and five after the equivalence point.

Empty the vessel by applying vacuum to the emptying tube an flush several times with distilled water. Leave the titration vessel filled with distilled water when not in use.

Plot the solution resistance vs. volume of titrant on rectilinear graph paper, and draw the two best straight lines through the resulting points. In the case of samples containing high concentrations of acid, the conductivity ($1/_R$) should be plotted against microliters of titrant in order to obtain a straight-line plot. The point of intersection of the two straight lines designates the end point.

THE EFFECTS OF VARIABLES

Effect of Electrode Position

The cell constant of the electrode assembly varied with the geometrical position of the assembly within the titration vessel. This variation is related to parasitic currents(7) and, for absolute measurements, is eliminated by fixed geometry and calibration with known standards. In this work relative data were sufficient so calibration was unnecessary. The electrode was held in a fixed position by means of the rubber stopper closure for the titration vessel.

The measured resistance of the solution also changed cyclically with the rotation of the stirring bar. This effect was minimized by positioning the electrodes at least 1 cm above the stirring bar.

Effect of Carbon Dioxide

At low acid concentrations dissolved carbon dioxide causes ignificantly high results. This error was demonstrated by the titraion of 25 µl aliquots of 0.1M nitric acid with and without the use of itrogen to remove dissolved carbon dioxide. Correct acid recovery as obtained when nitrogen was used to remove the carbon dioxide; when o nitrogen was bubbled through the solution, the acid recovery was 09 per cent.

Effect of Temperature Variations

A 25 µl sample of 0.01M nitric acid in 1.5M aluminum nitrate as titrated according to the procedure on page 8. The initial esistance of the electrode system was approximately 3000 ohms, and he change in resistance from start to end point was approximately .5 ohms. Heating the titration vessel, however, caused a change in esistance of approximately 57.5 ohms per degree C. Thus, a change in olution temperature of 0.1°C during the titration would have produced change in resistance nearly as large as that observed from the start o the end point of the titration. Therefore, the temperature of the olution should be held to within ±0.01°C during a titration.

One of the sources of heat that can produce a significant emperature change during a titration is the magnetic stirrer if it is quipped with an internal rheostat for speed control. A magnetic tirrer equipped with an internal speed control produced a 0.25°C per inute rise in solution temperature with a 30-ml beaker as the titraion vessel. When the stirrer speed was controlled with a Variac, the bserved temperature rise was 0.05°C per minute. This temperature ise was minimized by circulating water at constant temperature hrough the jacketed titration vessel and by maintaining a 2-3 mm air ap between the top of the stirrer and the titration vessel. Under hese conditions, it was possible to hold the solution temperature onstant to within ±0.01°C.

Effect of Sample Size

When samples of various sizes are diluted to the same volume rior to titration, the initial resistance of the solution is, among ther things, a function of the sample size. Since the sensitivity, efined for purposes of this study as change in resistance per increent of titrant, is a function of this initial resistance, the effect f sample size upon the sensitivity was investigated.

Aliquots of the 1.5M aluminum nitrate stock solution were ipetted into the titration vessel, which contained for each titration pproximately 30 ml of distilled water. Each solution was spiked with known amount of nitric acid, and the stoichiometric amount of sodium luoride was added to complex the aluminum. The titrations were made, he results were plotted, and the slopes of the lines representing eutralization of the acid were determined in terms of the change in esistance per microliter of 0.1M sodium hydroxide titrant.

A logarithmic plot of $\Delta R/\Delta V$ (representing the slope of the acid neutralization curve) versus initial solution conductivity ($1/R$) Figure 8, gave a straight line. From these data, the slope of the neutralization curve was predicted and confirmed for a 25 µl sample o 0.0268M nitric acid in 1.5M aluminum nitrate diluted under the same conditions. The results are given in Table I.

Sensitivity Versus Sample Size

The relationship between the slope of the neutralization curve and the initial resistance of the solution can be explained on the basis of the following equation for a typical conductometric neutralization curve; a and b are constants, R is the solution resistance, and f is the fraction titrated:

$$\frac{1}{R} = a - bf \qquad (1$$

Differentiating and stating the resulting solution in terms of logarithms, one obtains:

$$\log \frac{dR}{df} = \log b - 2 \log \frac{1}{R} \qquad (2$$

Equation 2 indicates that the slope of the neutralization curve in terms of $\Delta R/\Delta V$ can be increased by using a smaller sample size. There is a limit to the size of sample which can be taken, since the volume of titrant used becomes less as the sample size is decreased; also, the overall resistance increases with a correspondin increase in sensitivity to temperature changes.

Effect of Cell Constant

The effect of cell constants upon sensitivity was studied because the measured resistance of a solution is a function of the cell constant.

The relationship between the cell constant (k) of an electrode assembly, the observed solution resistance (R) and the specific resistance of the solution ($\overline{R}$) is as follows:

$$R = k\,\overline{R} \qquad (3$$

When two sets of electrodes are immersed in the same solution and the measurements are taken simultaneously,

$$R_1/k_1 = R_2/k_2 \qquad (4)$$

and

$$R_1 = (k_1/k_2)R_2 \qquad (5)$$

This relationship indicates that the electrode assembly with the larger cell constant will give a greater change in resistance per increment of titrant, by the ratio of the cell constants.

To demonstrate this relationship, the wire and foil electrode assemblies, Figure 7, were used for conductivity measurements in the same titration. The approximate cell constants of the two electrode assemblies were 0.253 for the foil and 0.392 for the wire when measured in 0.1M potassium chloride solution. The ratio of the cell constants, k_w/k_f, was 1.55. As shown in Table II, the ratios of the resistances measured during the titration agree with the ratios of the cell constants. The calculated sensitivities in terms of ohms per µl of 0.1M NaOH were 0.1012 for the wire and 0.065 for the foil assemblies. The ratio of the sensitivities was 1.56.

On the basis of these results, the ratio of the cell constants was increased to seven by reducing the area of the wire electrode. The cell constant of the wire electrode could not be reduced further without damage to the glass seal. The length of the exposed wire that remained was approximately 2 mm. Since the wire electrode assembly had the higher sensitivity, it was used in subsequent studies.

Effect of Fluoride to Aluminum Ratio

The effect of a relatively large excess or deficiency of sodium fluoride upon the shape of a typical conductometric titration curve was discussed by Pepkowitz(1). His work was extended by studying the acid recovery as a function of the fluoride to aluminum ratio at a single acid concentration.

For this work, 25 µl samples of 1.5M aluminum nitrate, 0.1075M in nitric acid, were titrated according to the standard procedure with the exception that the fluoride to aluminum ratio was varied from approximately 2:1 to 3:1.

The data given in Table III show that at this acid concentration the amount of sodium fluoride used to complex the aluminum had no consistent effect on the acid recovery within the range studied. Although these results indicate that the ratio of fluoride to aluminum is not critical, a ratio of 3:1 is recommended in view of the dependence of the fluoride complex upon acid concentration as shown in the following section.

DETERMINATION OF FLUORIDE REQUIREMENTS BY A CONDUCTOMETRIC TITRATION

It is often impossible to estimate the hydrolyzable ion concentration of a sample as closely as desired; in these cases, a rapid determination of the fluoride requirements is desirable.

Several sample sizes of 1.5M aluminum nitrate containing various concentrations of acid were titrated conductometrically with 0.5M sodium fluoride. The titration curves exhibited typical conductometric end points with results as given in Table IV.

The results indicate that the sodium fluoride required in the titration is a function of the acidity as well as the aluminum concentration. This technique is limited to low concentration of acid ($<0.05M$). The curve shown in Figure 9 is typical of those obtained at high acid concentrations.

A successful method for adding complexing agent was to titrate 25 µl samples with fluoride to the "fluoride break," being careful not to exceed the end point by more than 20 per cent. The solutions were then titrated with base in the usual manner. The resulting titration curves gave sharp end points.

EFFECT OF MERCURIC NITRATE IN SAMPLE

Mercury is present in some samples that contain major amounts of aluminum and uranium. Such samples may be approximately 0.005M in mercuric nitrate, 1.5M in aluminum nitrate, 0.01M in uranyl nitrate and may contain nitric acid in various concentrations.

Preliminary results with this system indicated that severe electrode polarization, which could be attributed to the mercuric ion, took place when a frequency of 60 cycles was used to excite the bridge. By increasing the frequency to 2000 cycles the polarization effects were eliminated.

The fact that high acid recoveries were obtained by the procedure indicated that the mercuric ion was not complexed by fluoride. Several inorganic complexing agents for mercury were investigated, but none proved satisfactory. Although sodium iodide can be used to complex mercury in a potentiometric titration, the addition of a sufficient quantity of this reagent to complex the mercuric ion increased the conductivity of the solution to such an extent that the sensitivity of the method was greatly diminished.

Exploratory experiments with organic complexing agents indicated that thorin, o(2-hydroxy-3, 6-disulfo-1-napthylazo) benzene arsonic acid, could be used to complex mercury. To demonstrate this complexing action, 50 µl samples of 1.5M aluminum nitrate were pipetted into 50 ml of distilled water and spiked with 250 µl of 0.1M nitric acid 0.007M in mercuric nitrate. The samples were titrated potentiometrically with standard base using 1 ml of one per cent reagent in one case to complex the mercury. In the case where thorin was used, the correct result was obtained, Figure 10; in the absence of thorin, the acid recovery was high.

In another experiment, a 25 µl sample of 0.1M nitric acid 0.007M in mercuric nitrate was titrated conductometrically with the one per cent thorin reagent and the results were compared with a like titration containing no mercury. The break in the titration curve obtained in the presence of mercury, as shown in Figure 11, corresponds to a ratio of about two moles of thorin per mole of mercury.

To determine the required concentration of thorin and the effect of the thorin to mercury ratio on the acid recovery, experiments were conducted in which 50 µl samples of 1.5M aluminum nitrate plus 50 µl of 0.1033M nitric acid were titrated at varying ncentrations of thorin, first without and then with the addition of 35 μ moles of mercuric nitrate. High acid recoveries 118 - 122 per nt were obtained when mercury was present and thorin was not, but e addition of as little as 0.25 mg or as much as 4 mg of thorin gave rmal results of 100 to 105 per cent recovery of acid. The results e given in Table V.

Experiments where uranyl nitrate was substituted for alumi- m nitrate at comparable concentrations indicated that the thorin agent could not be used to eliminate the interference of the mer- ric ion. However, since the solutions of interest are normally not er 0.1M in uranyl nitrate, samples of this concentration were trated using thorin to complex the mercury. The average acid re- very was 102 per cent; therefore, thorin performs satisfactorily as complexing agent for mercury where the sample contains only small ncentrations (0.1M) of uranyl nitrate.

PACITANCE EFFECT OF ELECTRODE SYSTEM

During work with the bridge equipment, a large change in parent capacitance of the electrode system was observed near the end ints of titrations at several acid concentrations. The observed pacitance continued to increase after the end point had been reached, dicating that the change in capacitance was related to changes in e solution during the titration. If the trend in the observed pacitance had reversed at the end point, then the effect could have en attributed to the bridge circuit.

A typical plot of electrode capacitance versus volume of trant, Figure 12, resembles a potentiometric titration curve with a pid change in capacitance at the end point. Although this phenome- on offered a means of determining the equivalence point in this rticular system, there were no advantages over the conductometric d point. However, the method may be useful in other titrations.

EXAMPLES OF RESULTS

The precision and sensitivity of the method were determined y titrating aluminum nitrate and uranyl nitrate solutions of various cid concentrations. Aliquots of aluminum or uranium stock solutions, ere pipetted into the titration vessel and spiked with the desired mount of standard acid. The conductivity meter and the modified wire lectrode assembly were used with the procedure to titrate the solutions. The data are given in the following table and typical titration curves obtained at low acid concentrations are shown in Figure 13.

TITRATION OF FREE ACID IN THE PRESENCE OF ALUMINUM AND URANIUM

Number of Determinations	Sample Size, Microliters	Acid Taken, Millimoles	Avg. Acid Found, Millimoles	Standard Deviation, %
13	25-1.5M Al	0.000258	0.000281	±14
6	25-1.5M Al	0.000516	0.000520	± 5.6
5	25-1.5M Al	0.001033	0.001015	± 3.7
5	25-1.5M Al	0.00258	0.00260	± 1.6
5	25-1.5M Al	0.01033	0.00991	± 2.6
5	100-1.5M Al	0.0516	0.0512	± 1.3
5	*50-1.0M U	0.000516	0.000503	± 3.6
5	50-1.0M U	0.00258	0.00249	± 8.4

* The initial resistance of a 25 µl sample of 1.0M uranyl nitrate was excessively high, and a 50 µl sample was used in this case.

The titration curves obtained at the lowest acid level (0.01M) were defined well enough to permit the determination of the end point; however, extreme care was required to maintain constant temperature and to avoid contamination of the sample.

RC Propst

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Analytical Chemistry Divisio

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4. Carson, W. N., Jr. Microtitration of Free Acid in Uranyl Nitrate Solutions. HW-29455 (1953).
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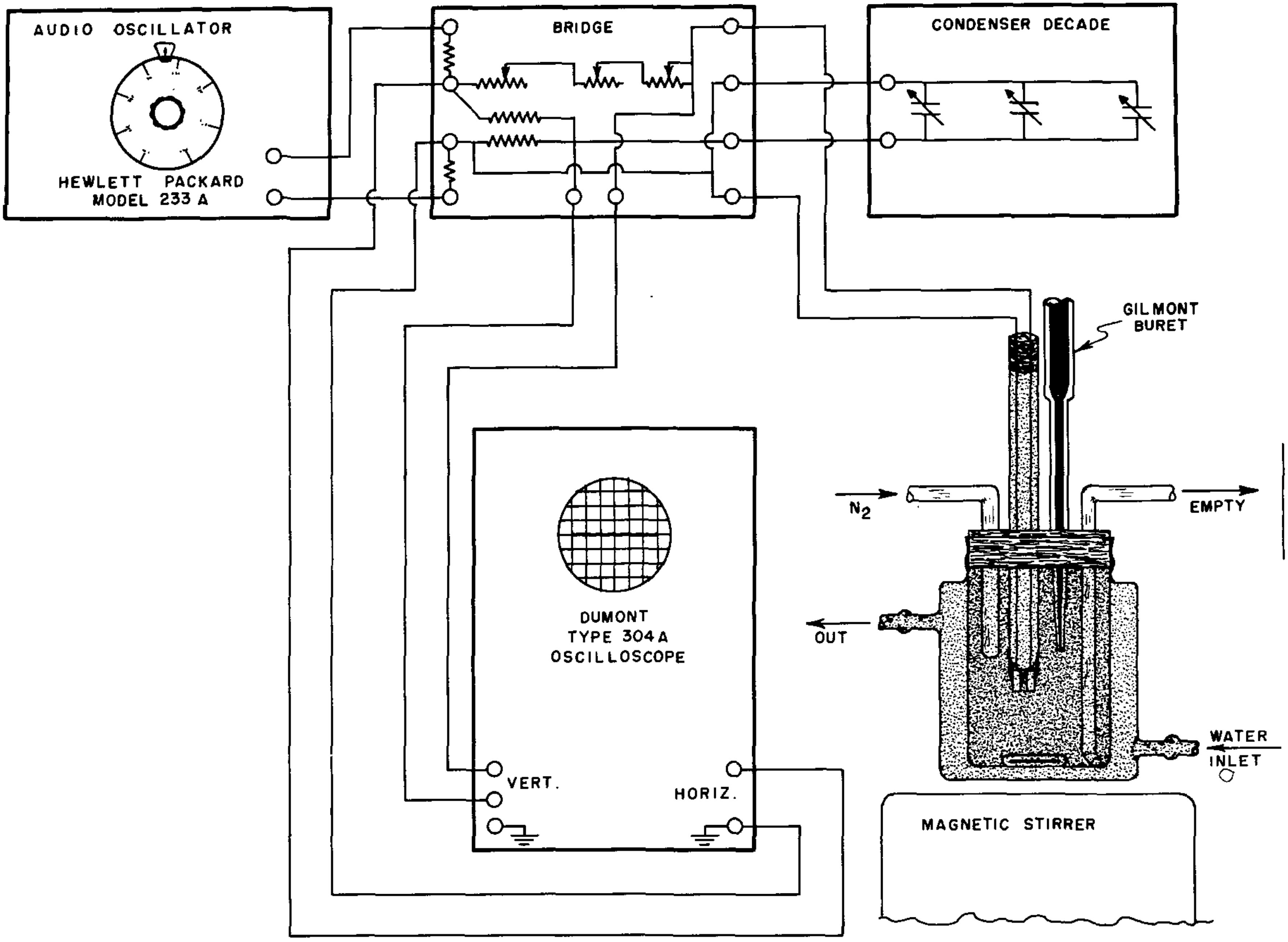
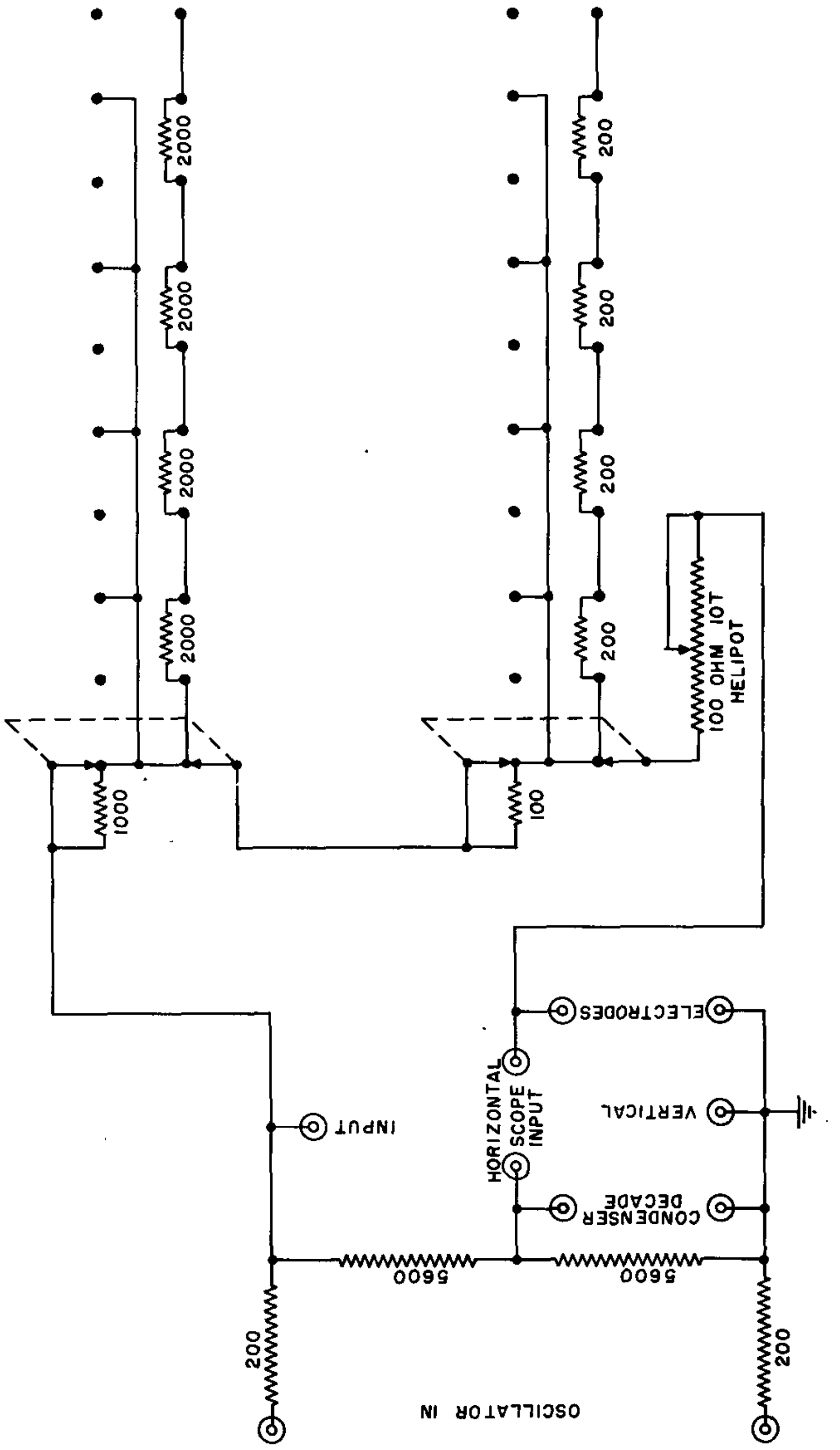
7. Jones, G. and Bollinger, G. M. J. Am. Chem. Soc. 53., 411 (1931).

FIGURE 1



CONDUCTIVITY BRIDGE APPARATUS

FIGURE 2



DETAILS OF BRIDGE CIRCUIT

FIGURE 3

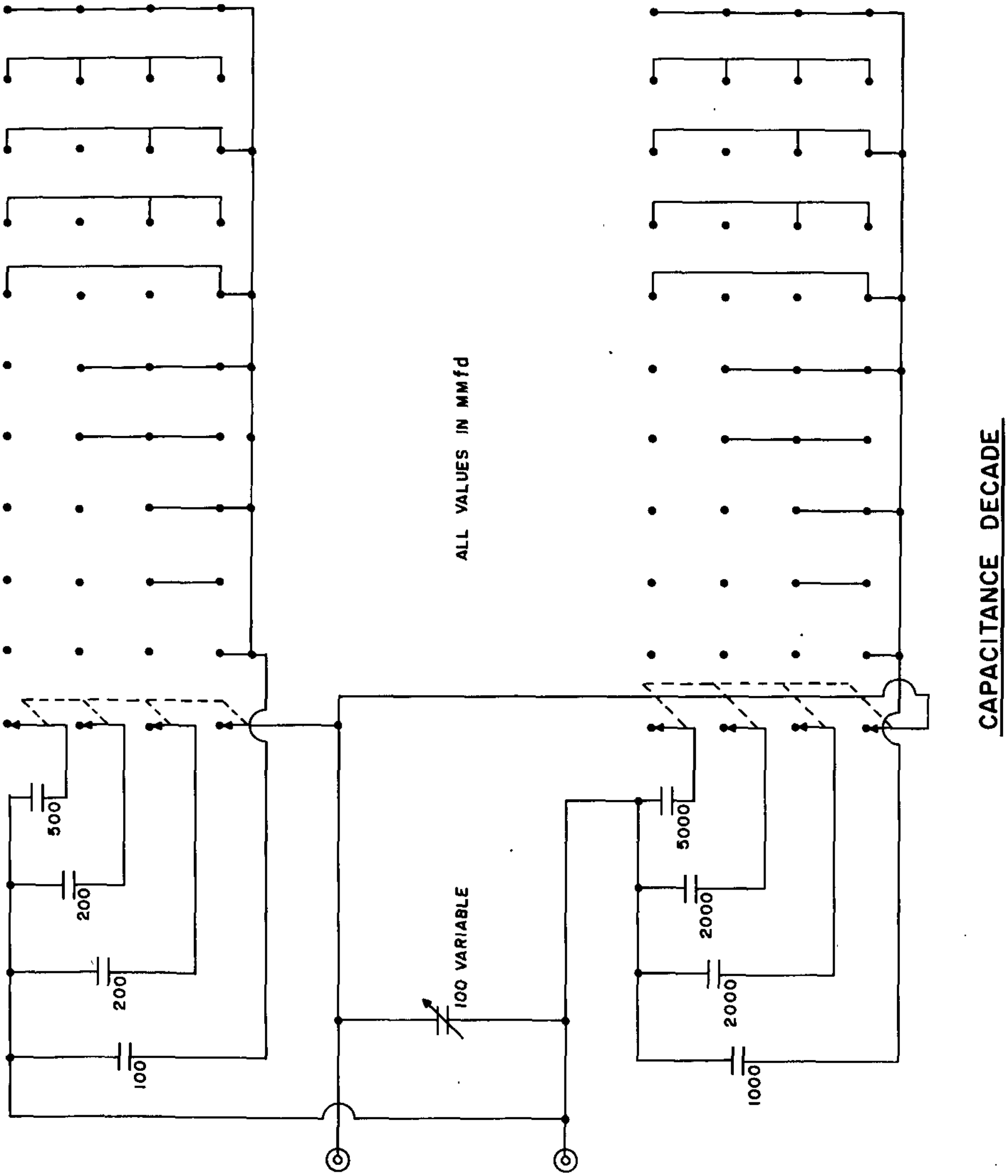
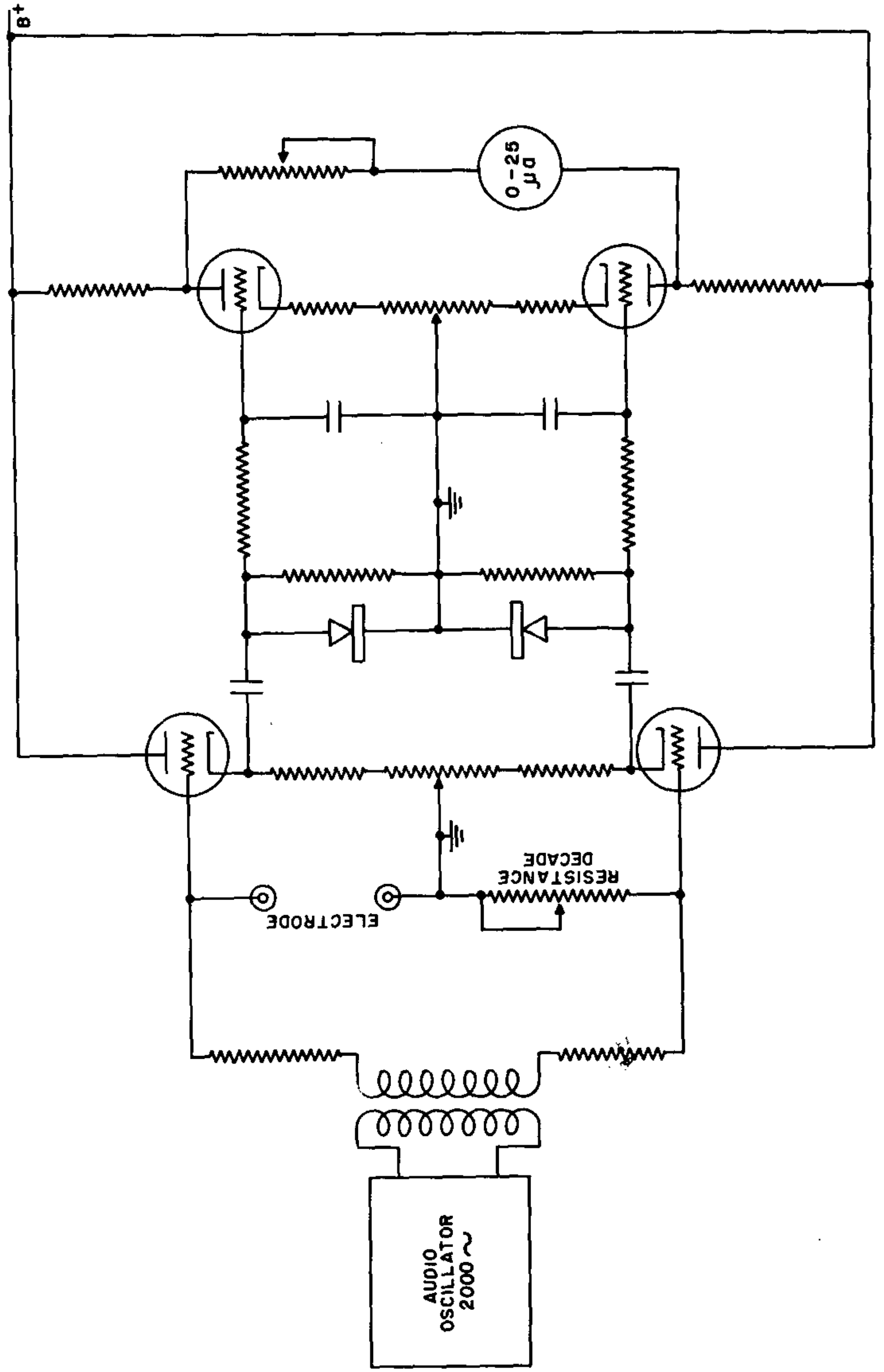
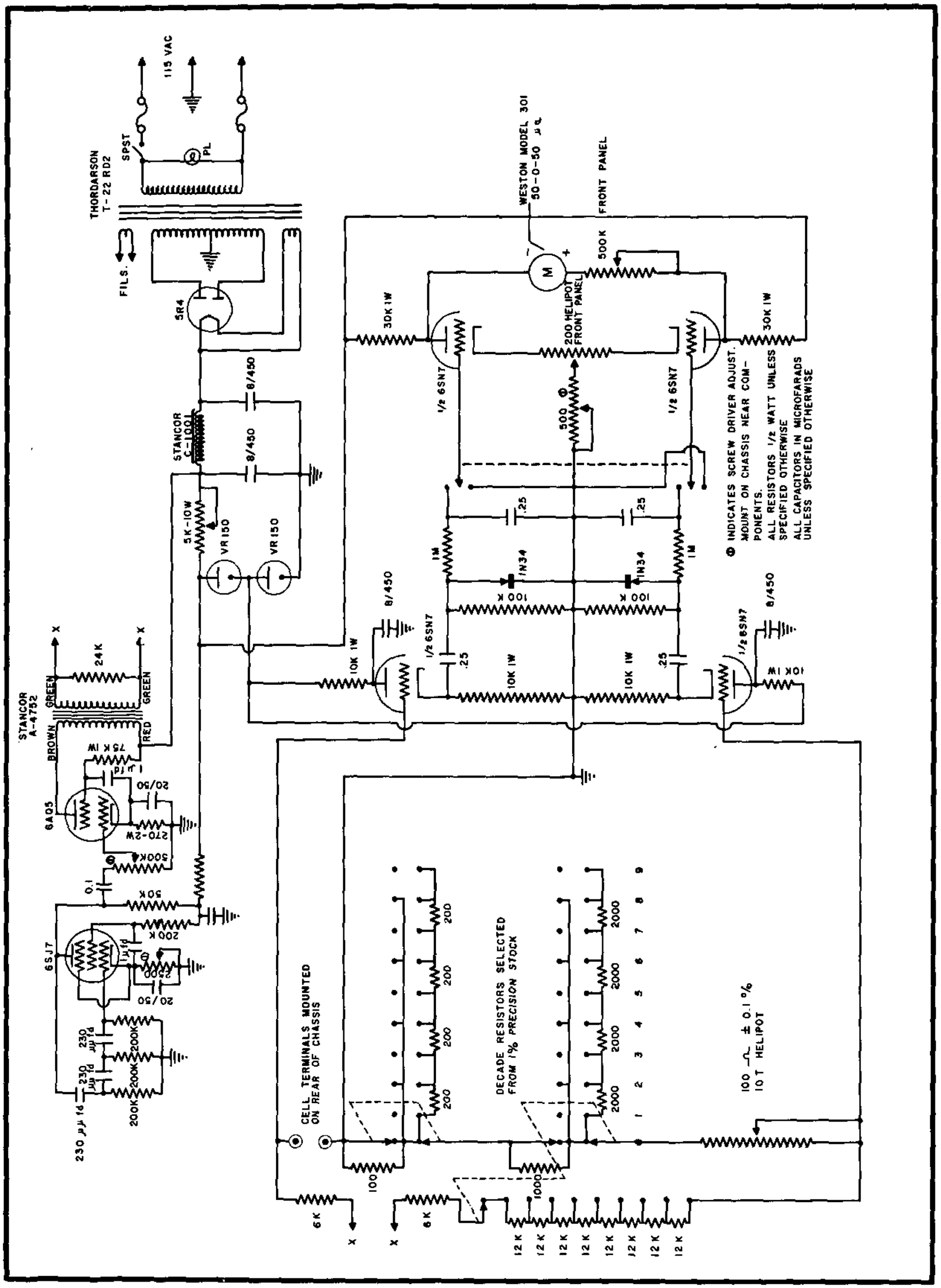

CAPACITANCE DECADE
ALL VALUES IN MMfd
500
200
200
100
100 VARIABLE
5000
2000
2000
1000

FIGURE 4



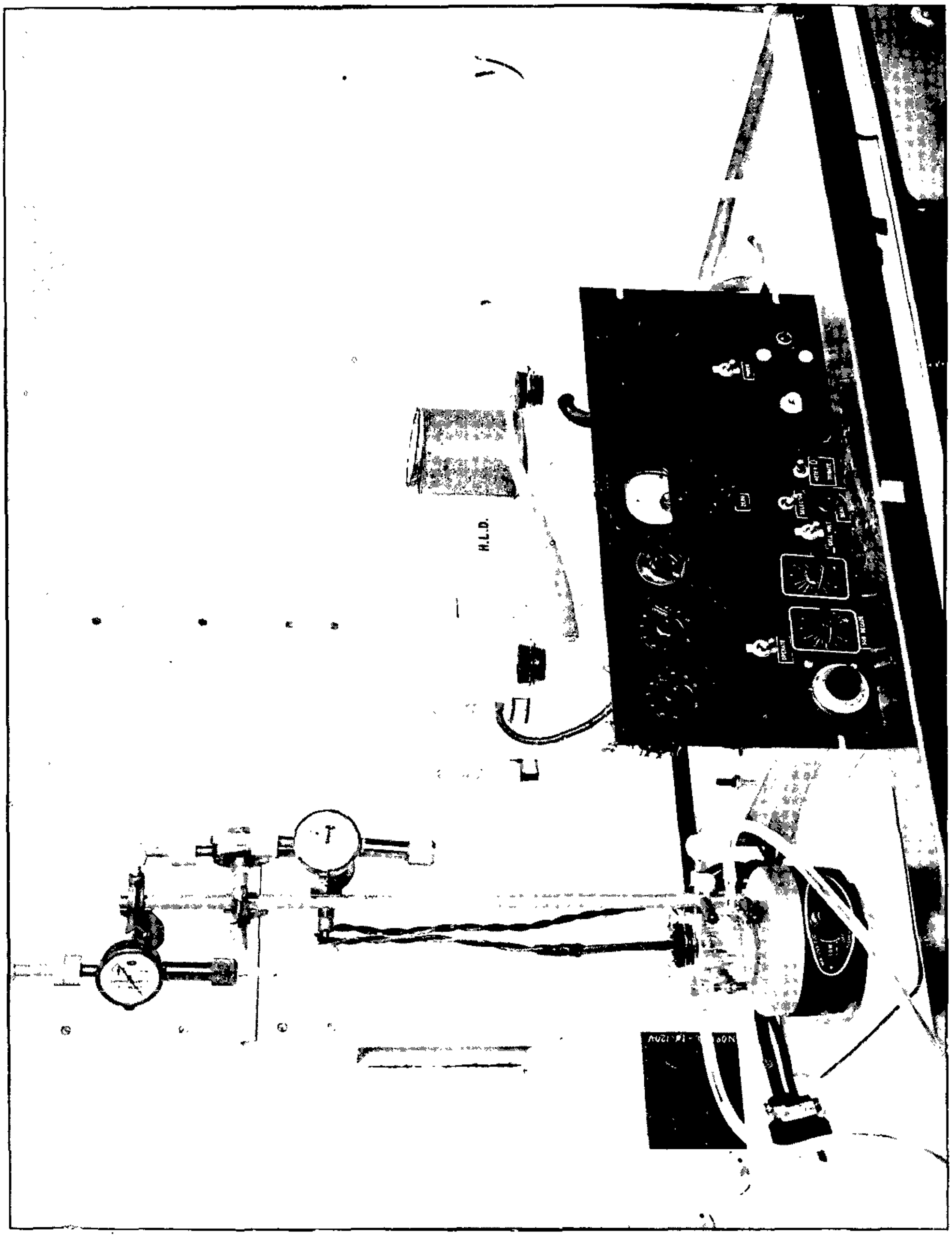
BASIC CONDUCTIVITY METER CIRCUIT

FIGURE 5

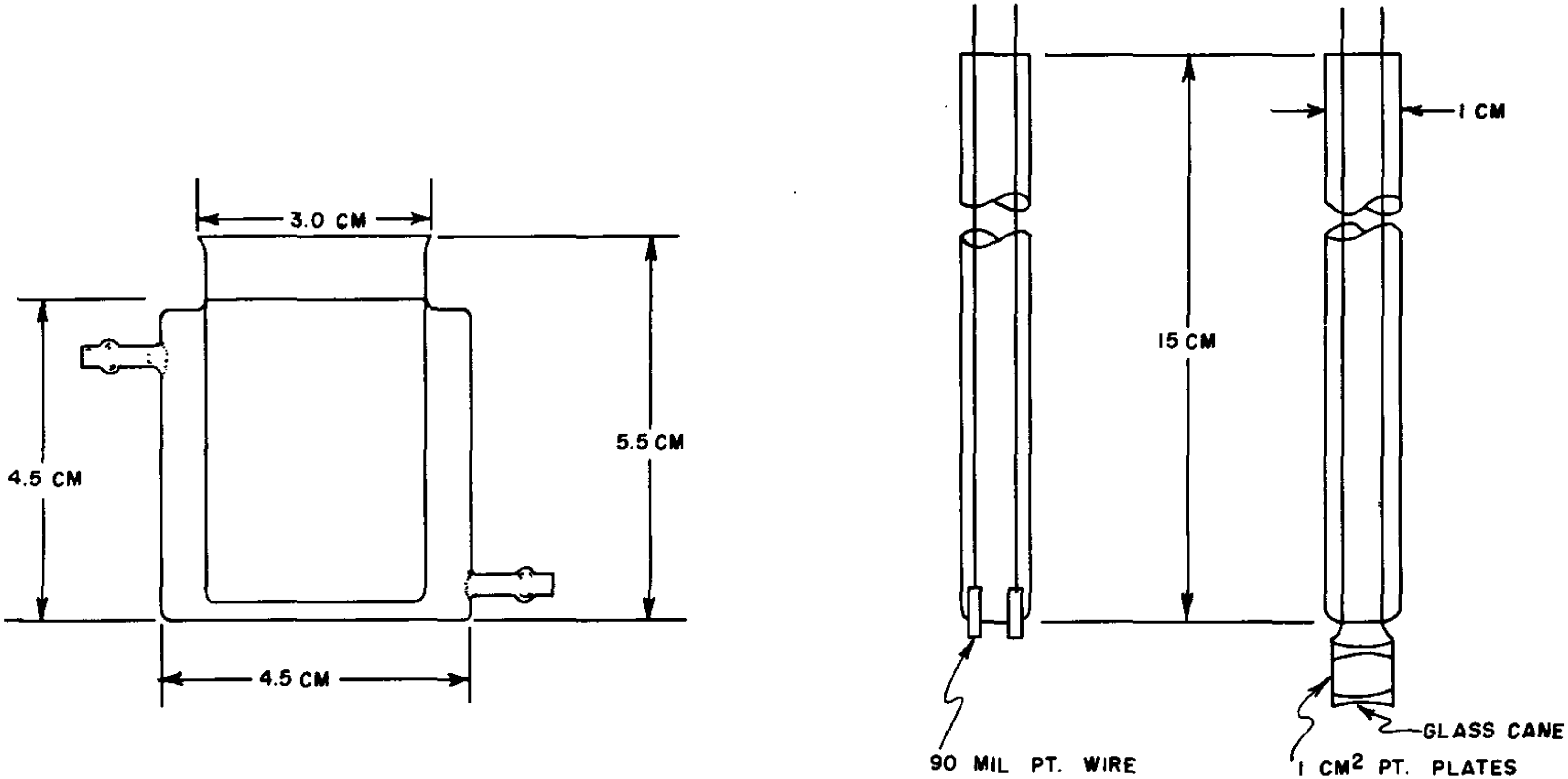


CONDUCTIVITY METER

FIGURE 6



PHOTOGRAPH OF CONDUCTIVITY METER



TITRATION VESSEL

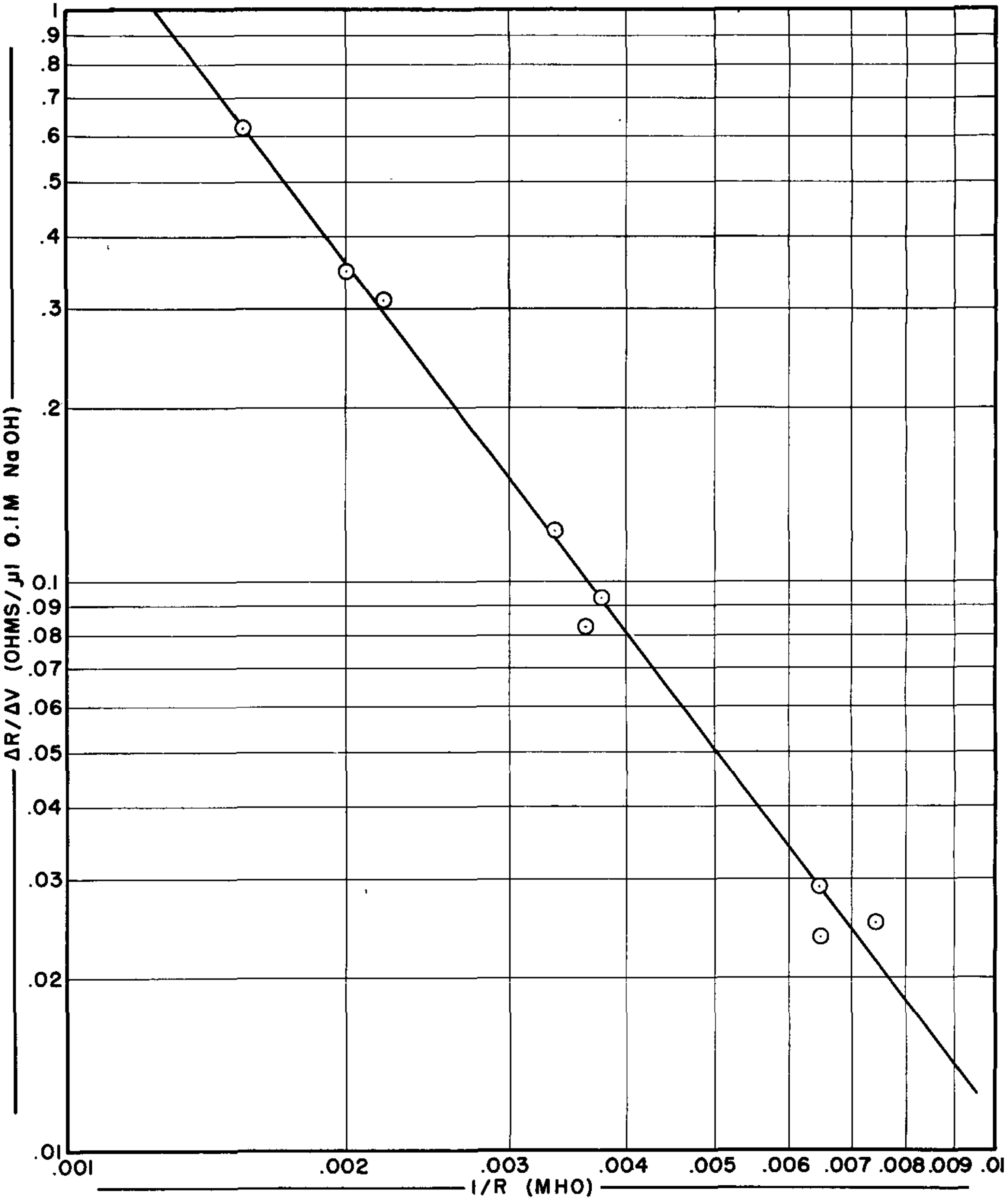
WIRE ELECTRODES

FOIL ELECTRODES

CELL AND ELECTRODE DETAILS

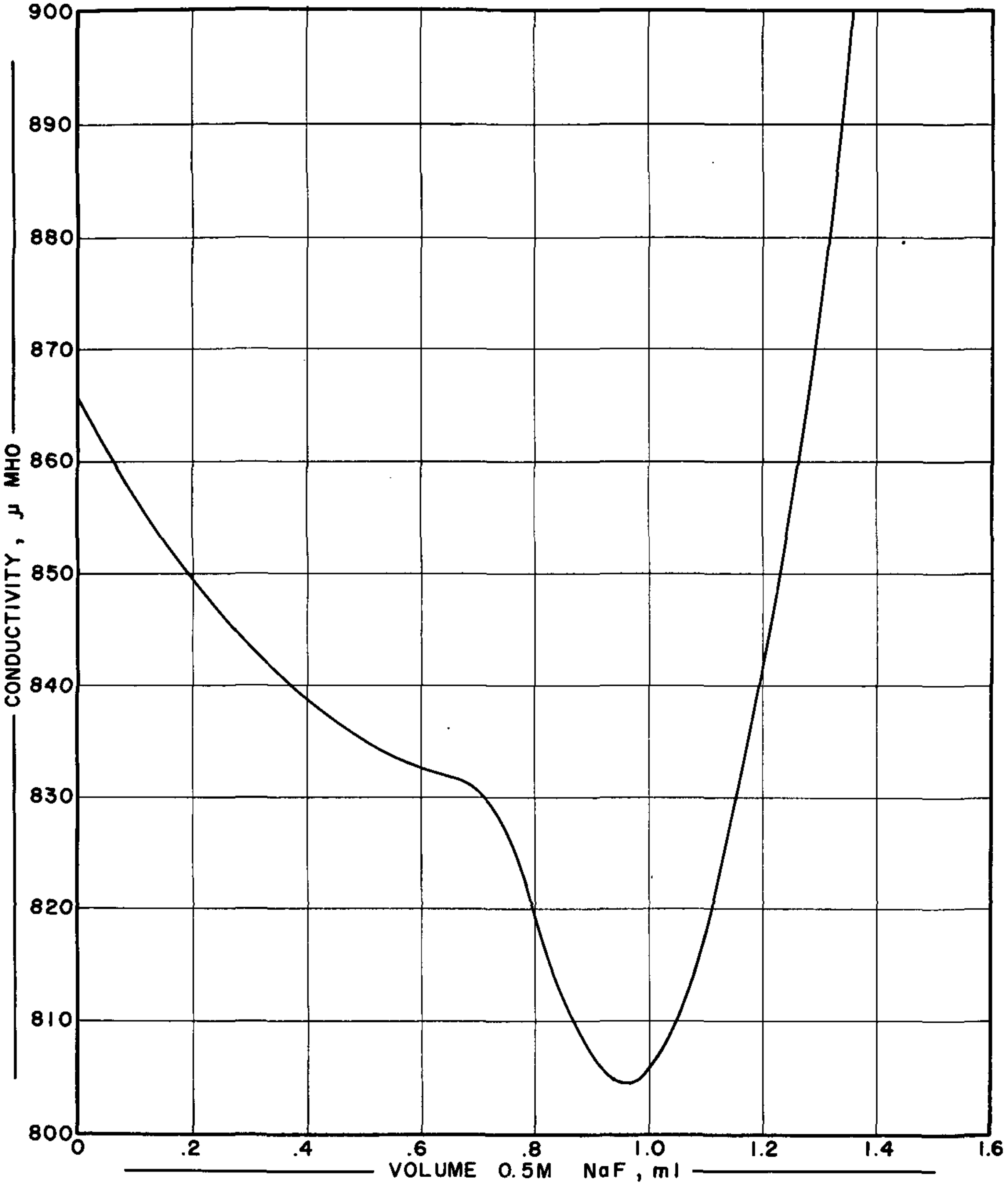
FIGURE 7

FIGURE 8



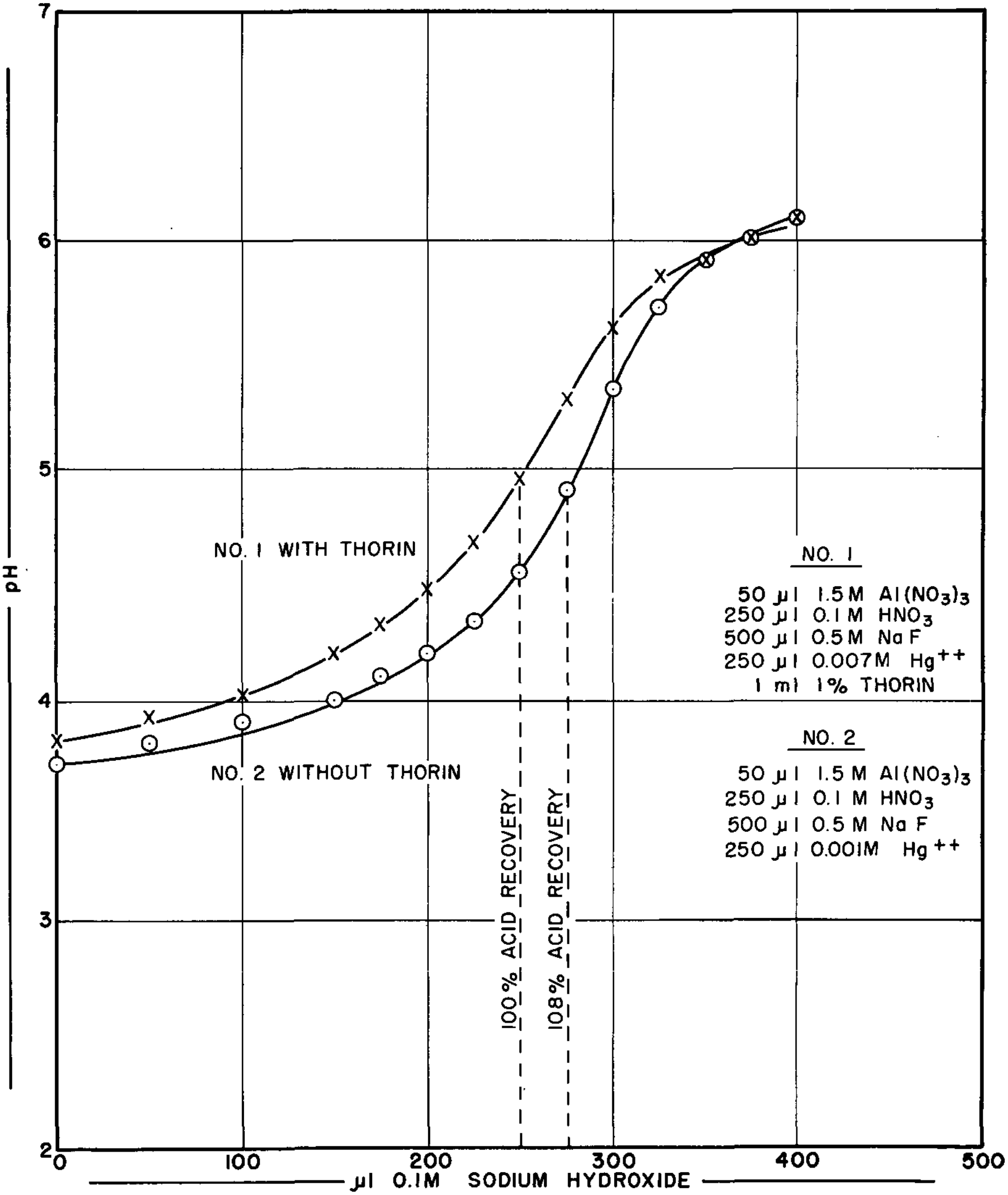
LOGARITHMIC PLOT - SENSITIVITY vs. INITIAL CONDUCTIVITY

FIGURE 9



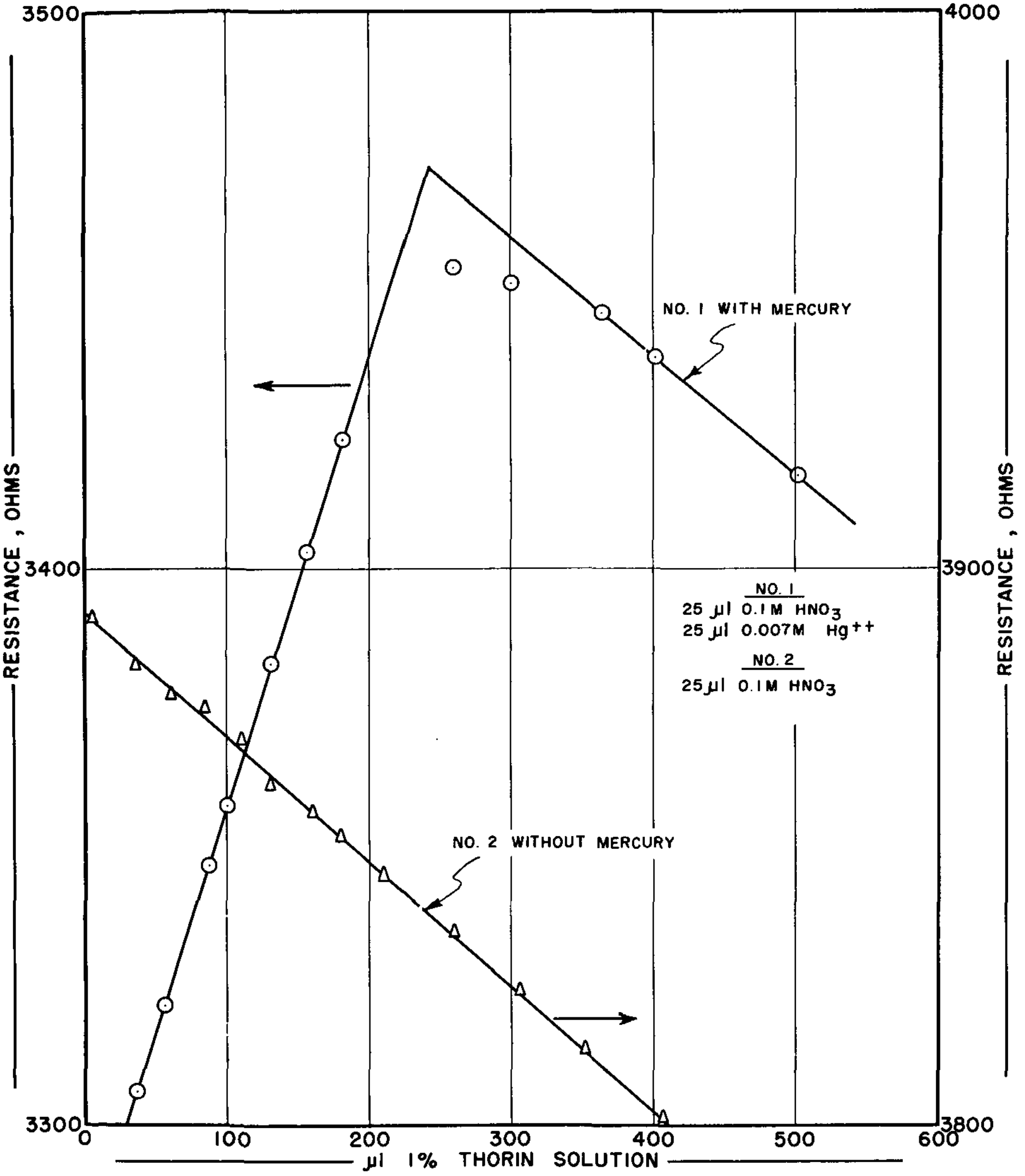
TITRATION OF 100 μl SAMPLE OF 0.05M HNO_3 IN 1.5M $Al(NO_3)_3$

FIGURE 10



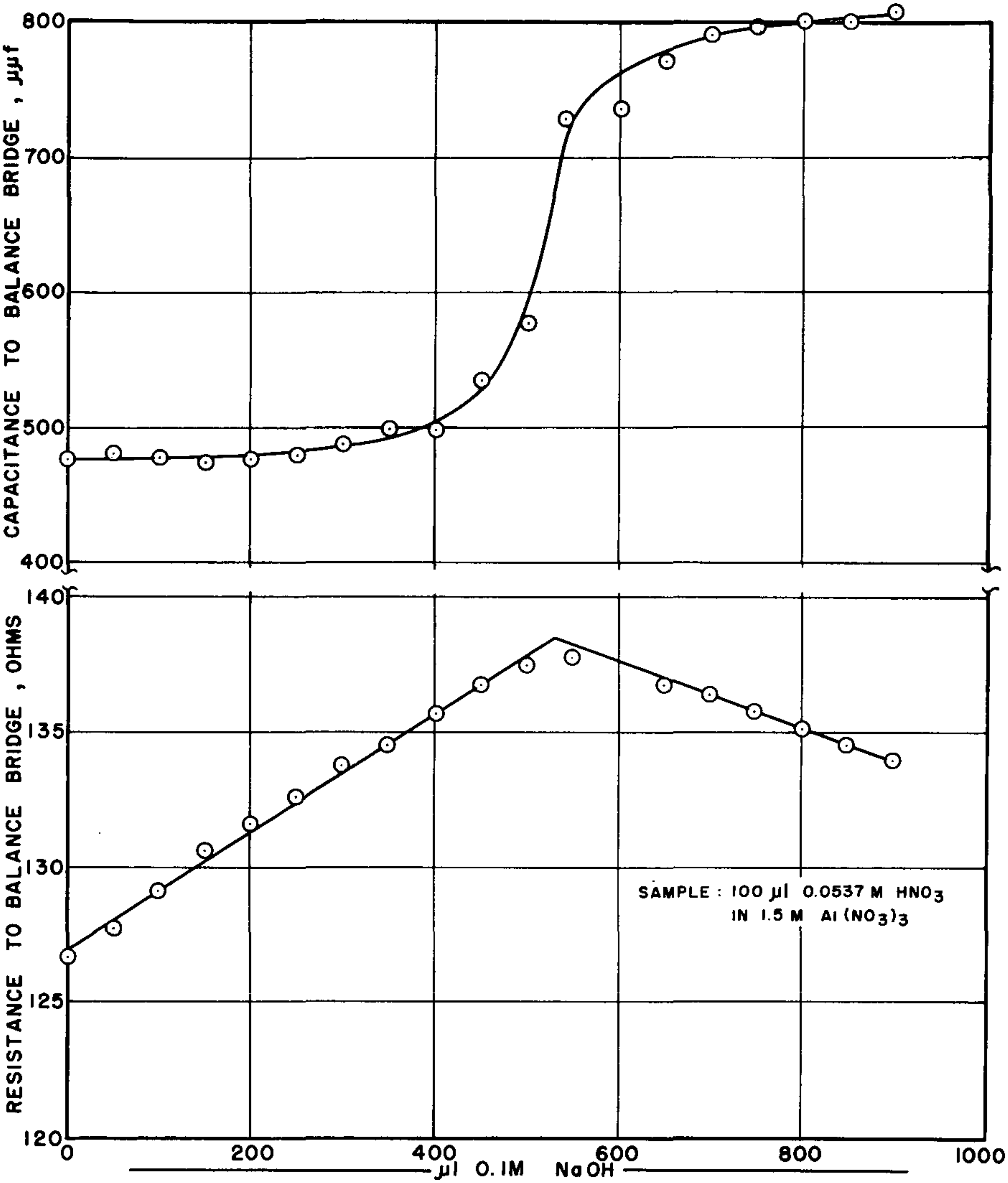
POTENTIOMETRIC TITRATION OF Al^{+3} --F^- --H^+ SYSTEM CONTAINING MERCURIC NITRATE

FIGURE 11



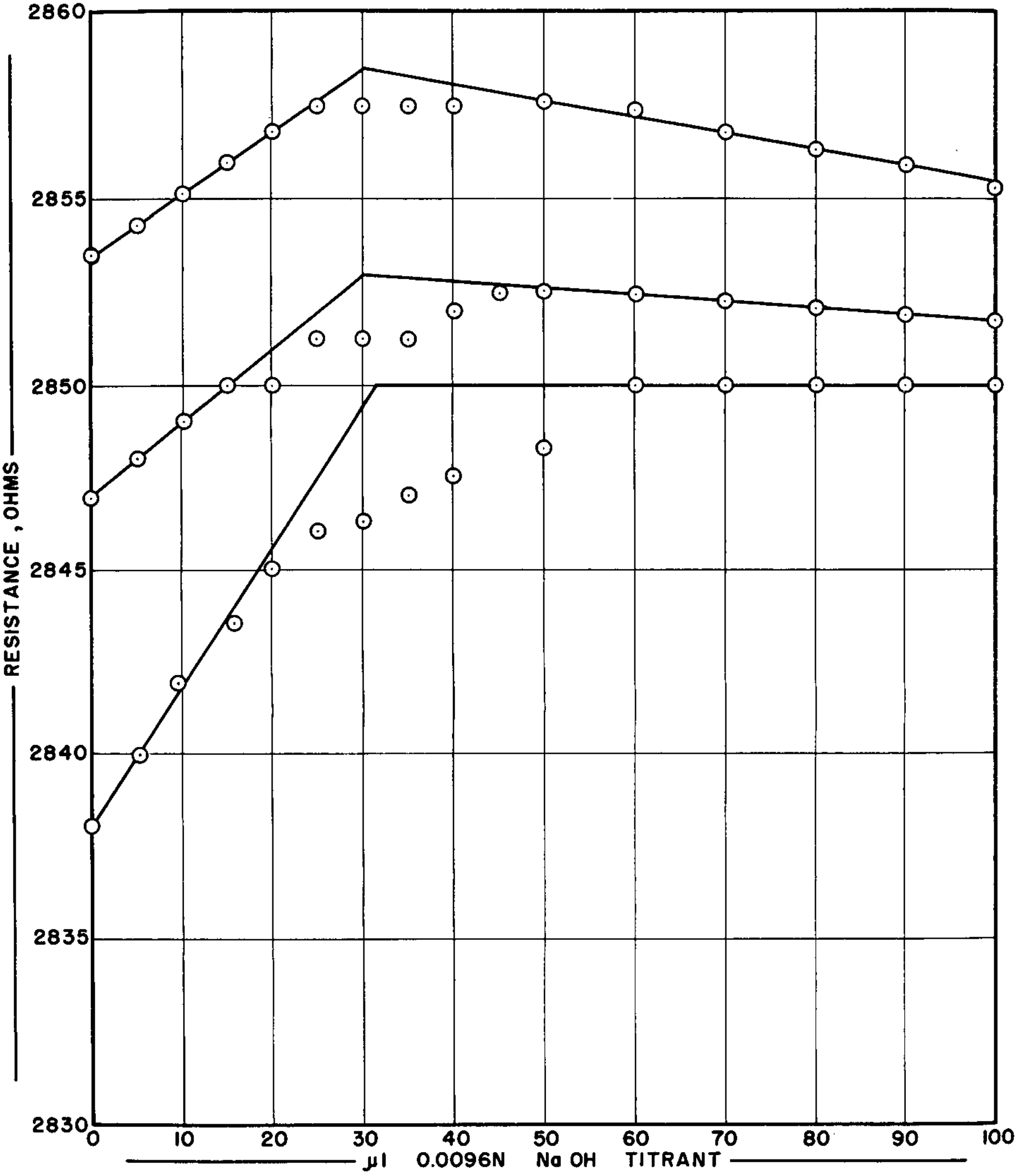
CONDUCTOMETRIC TITRATION OF MERCURY IN NITRIC ACID SOLUTION

FIGURE 12



PLOT OF RESISTANCE AND CAPACITANCE FOR A TYPICAL CONDUCTOMETRIC TITRATION

FIGURE 13



TITRATION CURVES FOR 25 μl SAMPLES OF 0.0103N HNO_3 IN 1.5M $Al(NO_3)_3$

TABLE I

SENSITIVITY VERSUS SAMPLE SIZE

Sample Size, µl	Acid Conc. in Sample, Molarity	Initial Conductivity, mho	ΔR/ΔV ohms/µl 0.1M NaOH
100	0.5375	0.00773	0.0256
50	0.5375	0.00381	0.0906
25	0.5375	0.00218	0.311
100	0.1075	0.00651	0.0295
50	0.1075	0.00340	0.121
25	0.1075	0.00200	0.346
100	0.0537	0.00652	0.0241
50	0.0537	0.00356	0.0835
25	0.0268	0.00153	0.625

TABLE II

RELATIONSHIP OF CELL CONSTANT TO SENSITIVITY

Volume 0.1M Sodium Hydroxide, ml	Resistance		Ratio Rw/Rf
	Wire	Foil	
0	310	200	1.55
0.5	335	215	1.56
1.0	362	232	1.56
1.5	395	254	1.55
2.0	435	280	1.55
2.5	481	310	1.55
3.0	541	350	1.55
3.5	615	400	1.54
4.0	715	460	1.55
4.5	845	550	1.53
5.0	1030	670	1.54
6.0	902	583	1.55
7.0	705	460	1.53
8.0	575	370	1.55
9.0	485	316	1.54
10.0	425	272	1.56

TABLE III

EFFECT OF FLUORIDE TO ALUMINUM RATIO

Ratio Fluoride/Aluminum	Acid Taken, Millimoles	Acid Found, Millimoles	Per Cent Recovery
2.0	0.00258	0.00259	100.4
2.1	0.00258	0.00264	102.2
2.2	0.00258	0.00259	100.4
2.4	0.00258	0.00268	104.1
2.5	0.00258	0.00259	100.4
2.7	0.00258	0.00259	100.4
2.8	0.00258	0.00259	100.4
2.9	0.00258	0.00249	96.6
3.1	0.00258	0.00259	100.4

TABLE IV

TITRATION OF ALUMINUM NITRATE WITH SODIUM FLUORIDE

$Al(NO_3)_3$ Taken, Millimoles	HNO_3 Taken, Millimoles	Fluoride Required, Millimoles	Ratio F/Al
0.0375	0.0	0.090	2.4
0.0375	0.00067	0.090	2.4
0.0375	0.00134	0.085	2.3
0.0375	0.00268	0.090	2.4
0.0375	0.0134	0.110	2.9
0.075	0.0	0.180	2.4
0.075	0.00134	0.175	2.3
0.075	0.00268	0.185	2.5
0.075	0.00537	0.190	2.5
0.075	0.0268	0.225	3.4
0.150	0.0	0.305	2.0
0.150	0.00268	0.305	2.0
0.150	0.00537	0.305	2.0
0.150	0.0107	0.310	2.1
0.150	0.0537	-	-

TABLE V

EFFECT OF THORIN ON ACID TITRATIONS

All solutions contained 50 µl of 1.5M $Al(NO_3)_3$ and 500 µl of 0.5M NaF

Experiment No.	0.1033M HNO_3, µl	0.007M $Hg(NO_3)_2$ in 0.1033M HNO_3, µl	1% Thorin, µl	Per Cent Acid Recovery
1		50		122
2	50		25	104.5
3		50	25	100.5
4	50		50	104.5
5		50	50	103.0
6	50		100	100.5
7		50	100	100.5
8	50		200	103.0
9		50	200	104.5
10	50		400	100.5
11		50	400	103.5
12		50		118