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DESIGN OF CONDUCTIVITY CELLS
FOR STRONG ELECTROLYTES

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DESIGN OF CONDUCTIVITY CELLS FOR STRONG ELECTROLYTES

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ABSTRACT

Design and operating characteristics of conductivity cells were examined to improve the accuracy and precision of conductance data from highly conductive process solutions. The characteristics investigated included cell dimensions, size and nature of electrodes, and frequency and voltage ranges. Cell designs that confined the solution in a long column (where length >> diameter) minimized the importance of constant electrode area and virtually eliminated the effect of fouling of electrode surfaces by entrained organic solvents. Satisfactory operation with simulated dissolver solution from the Purex process was demonstrated with several cells constructed from new design criteria.

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INTRODUCTION

Close control of process variables is required to minimize process losses in the Purex process. This control is maintained by laboratory analyses of samples that are withdrawn from process streams. Continuing effort is directed toward the use of in-line methods of analysis that utilize physical parameters as critical indices of the composition of multicomponent systems. In this sense the Purex dissolver solution is a two-component system (uranyl nitrate and nitric acid) requiring two critical indices. The concentration of these components may be determined by measurements of the electrical conductivity and specific gravity of the solution.

Some attempts to apply conductometric techniques to solutions of high conductivity have failed, either because of anomalies observed with dip-type cells, or because the effective electrode area is reduced by dissolved and suspended solvent in the process solution. Thus the cell must be designed to minimize these factors.

No references were found concerning the design of conductivity cells to minimize the effects of changes in the effective electrode area, although a three-electrode cell[1] has been proposed as a means for eliminating polarization effects. While the three-electrode design is probably adequate for some installations, its performance can be improved if the changes in the effective electrode area can be minimized. This work was undertaken in an effort to define the parameters that determine the response of a conductivity cell and to design a cell with a response that would be a true measure of the absolute conductivity of the solution without calibration.

SUMMARY

Design criteria were determined for the construction and in-line operation of conductivity cells in aqueous streams from the Purex process. In the new design concept, gross changes in electrode area due to adsorbed organic solvent have a minimum effect on the observed conductivity. The critical variable that minimizes the effect of electrode area was shown to be the dimensions of the column of solution between the electrodes.

The basic design philosophy was demonstrated for a cell of new design by deliberately flooding the cell with organic solvent, thereby simulating a breakthrough of solvent into

the aqueous stream. When the aqueous phase was flushed through the new cell, the conductivity readings returned promptly to normal with less than 1% error resulting from this drastic treatment. The effect of electrode area can be eliminated completely from the conductivity measurements by incorporating this principle into the design of a three-electrode cell[1] or by utilizing a technique based on electrode separation as established in this report. The latter technique provides a means for determining the absolute conductivity of solutions.

DISCUSSION

The original criteria for obtaining reproducible measurements of electrical conductivity were proposed by Kohlrausch in 1875. In order to obtain the consistent results, Kohlrausch found it necessary to: (1) design the cell so that the effective resistance was greater than 100 ohms, (2) incorporate large electrodes (1 cm^2 or larger), (3) increase the frequency of the applied voltage to 1000 cycles per second, and (4) platinize the electrodes. The above criteria were established on an empirical basis[2]. The success of the Kohlrausch method lies in platinization of the electrodes to minimize polarization effects that are in turn a function of the electrochemical processes which occur at the electrode. In an effort to make further improvements, the above variables were re-examined in the light of contemporary theories of faradaic admittance.

Contemporary theories of the faradaic admittance of a polarized electrode[3,4] are well established, and the AC impedance of a polarized electrode can be represented by an equivalent circuit that contains elements of pure resistance and capacitance[3,5]. Since a conductivity cell contains two electrodes, it is convenient to represent the AC impedance of the cell in terms of an electrical analog:
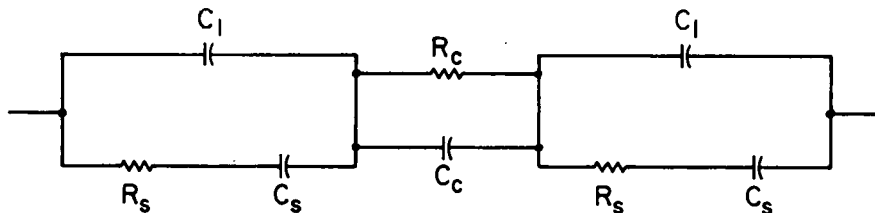
where C_1 = double layer capacity of the electrode-solution interface

R_s = polarization resistance

C_s = pseudocapacitance due to polarization

R_c = resistance of electrical path between electrodes

C_c = capacitance between electrodes with the solvent as the dielectric

However, the individual electrode impedances cannot be measured separately so that the circuit can be simplified as follows:
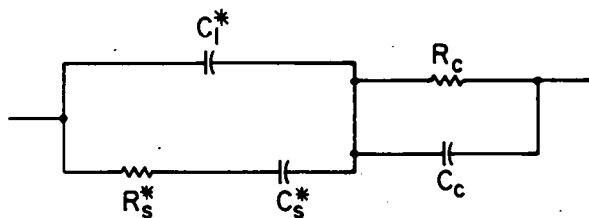
where C_I^*, R_S^*, and C_S^* represent the combined impedances for both electrodes.

In the case of strong electrolytes where the frequency of measurement is 1 megacycle or less and the cell constant is less than unity, the circuit can be simplified still further, since the shunting effect of C_c on R_c will be negligible. The capacitance of a cell with a constant of unity and water as the dielectric is approximately 7 picofarads. Thus the capacitance C_c can be eliminated, and the circuit becomes
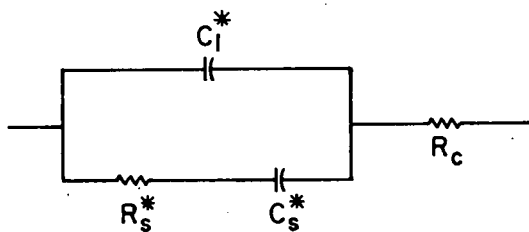
The flow of alternating current across the interface between the electrode and the solution is divided into two paths[3]; the nonfaradaic path through the charging and discharging of the electrical double layer, and the faradaic path which exists by virtue of the charge transfer due to an electrochemical process. The latter process is represented by the series combination of R_S^* and C_S^*. Since the resistance of the electrical path between the electrodes is independent of frequency, the response of a conductivity cell to changes in the applied frequency is determined by the capacitance of the

electrical double layer and the nature and magnitude of the electrochemical reaction. At frequencies above 10^4 cycles per second, the impedance of the electrode is determined primarily by the capacitance of the electrical double layer, which for most metals is approximately 10 microfarads per square centimeter[6]. Thus at high frequencies the electrical analog consists of a series combination of resistance and capacitance, and if the path of the current between the electrodes is such that R_c is much greater than the impedance of C_1, then the impedance of the cell should approach the true resistance of the current path between the electrodes.

There is almost universal agreement that the bridge utilized for AC impedance studies should have a series combination of resistance and capacitance in the measuring arm; however, a parallel combination can be employed provided the results are transformed to agree with the series circuit. Since bridges are not well adapted to in-line measurement, it appeared desirable to evaluate an alternative method for measuring the cell impedance. Therefore in this study, the impedance of the conductivity cell was determined by two methods: (1) bridge measurement in which the cell impedance is expressed in terms of a series combination of resistance (R_m) and capacitance (C_m) (Figure 1) and (2) a constant current technique where the impedance (Z_m) of the cell is determined directly.
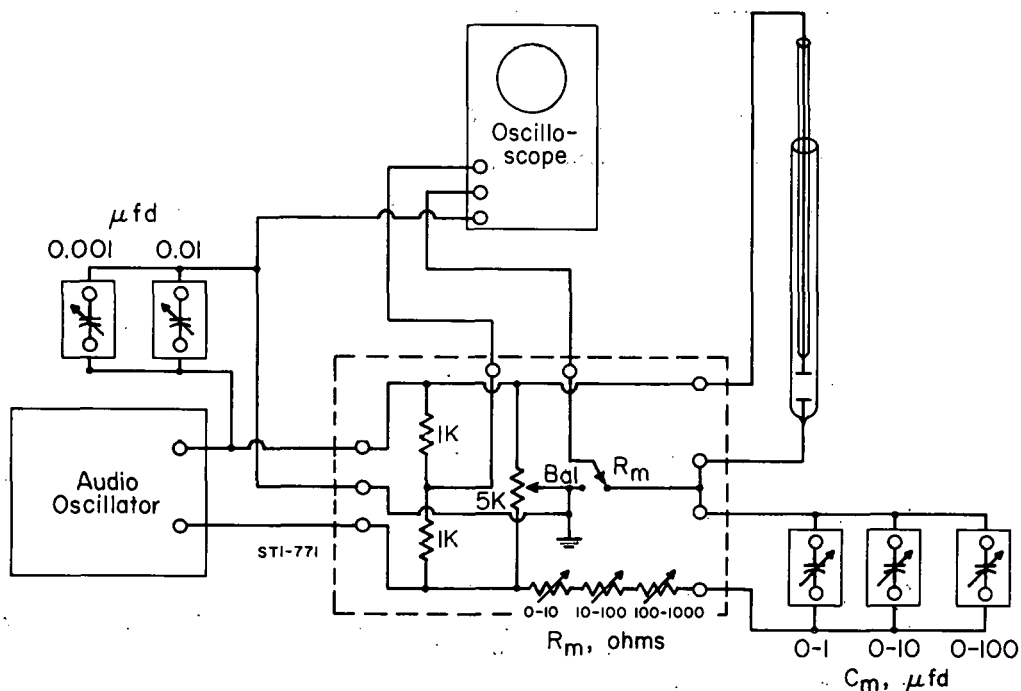
FIG. 1 BRIDGE APPARATUS

In the constant current technique, the current was supplied to the cell through a large voltage dropping resistor (10^5-10^6 ohms) so that the current flowing through the cell was essentially constant even though the impedance of the cell varied over a considerable range (0-200 ohms). The impedance of the cell was calculated from the voltage drop across the cell at constant current.

EQUIPMENT

The apparatus employed for the bridge measurements is shown in Figure 1, and the apparatus for impedance measurements is shown in Figure 2. A Jackson Model 655 audio oscillator served as the signal source for both measurements. A DuMont Model 304A oscilloscope served as the balance indicator for bridge measurements, and a Hewlett-Packard Model 400-C audio frequency voltmeter was utilized to obtain voltage measurements at constant current.
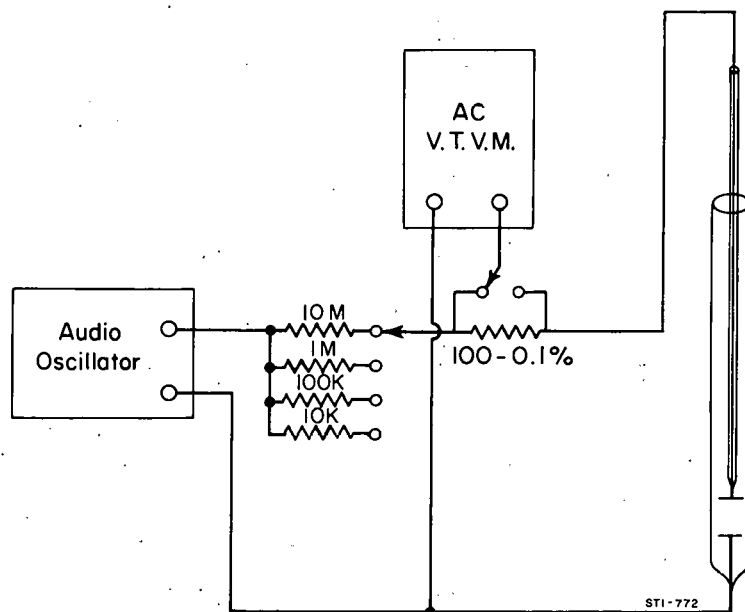
FIG. 2 APPARATUS FOR IMPEDANCE STUDIES

The output of the audio oscillator was balanced with respect to the bridge ground by means of a conventional Wagner circuit. The balancing arm (R_m-C_m) consisted of a series combination of resistance and capacitance to conform to the equivalent circuit concept of the conductivity cell.

Constant current measurements were made with the full output (50 volts) of the signal generator applied to the series combination of dropping resistor and conductivity cell. The

current was calculated from the voltage drop across a precision 100-ohm resistor.

Conductivity cells were constructed as shown in Figure 3. With the design shown in Figures 3a and 3b, both the electrode separation and the area of the upper electrode were varied. The effect of changes in cross-sectional area was studied with the design shown in Figure 3b by substituting tubes of different diameters.

The apparatus employed in the AC impedance studies, Figure 4, was essentially that described by Silverman and Remick[7].
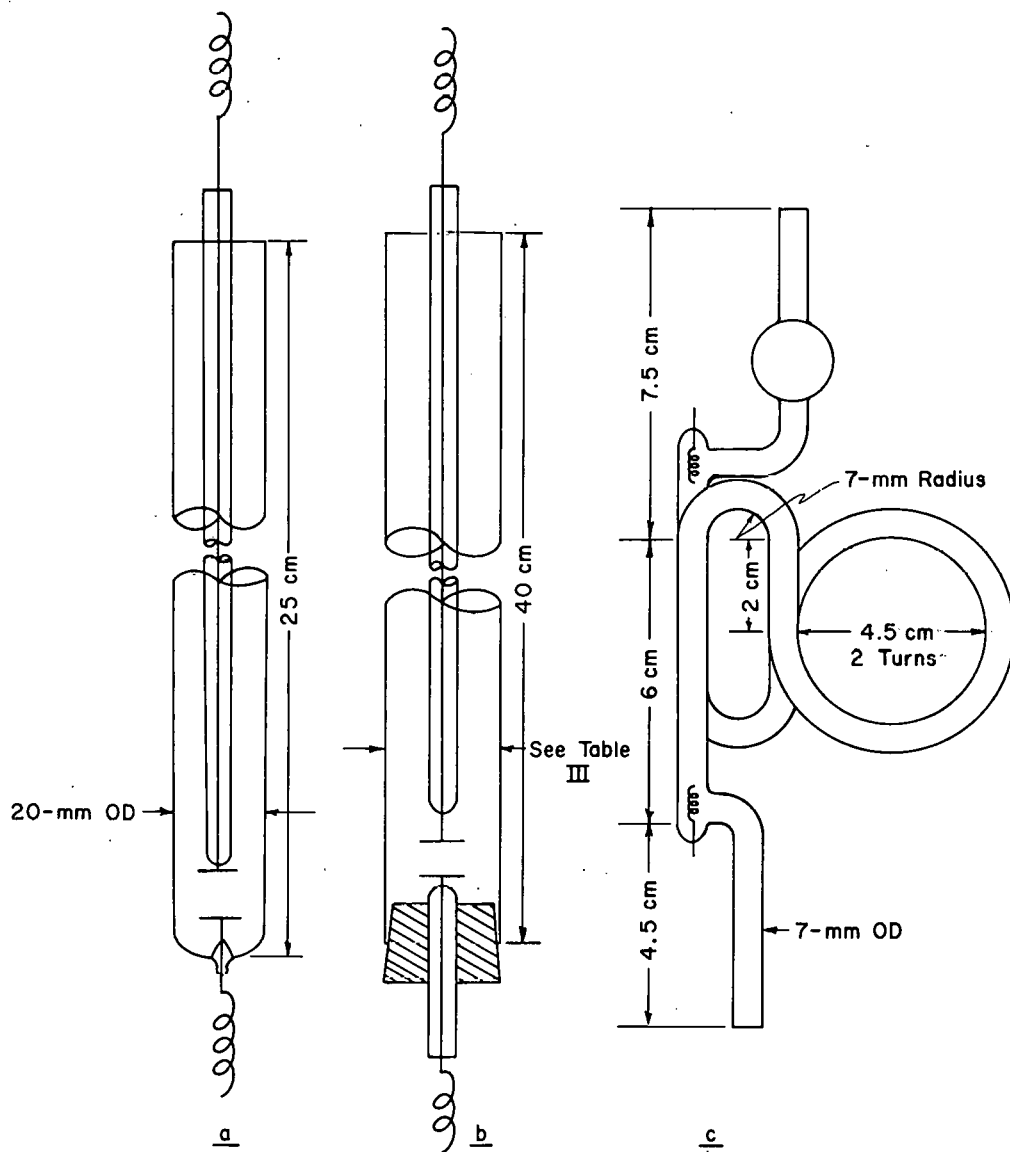
FIG. 3 CONDUCTIVITY CELLS
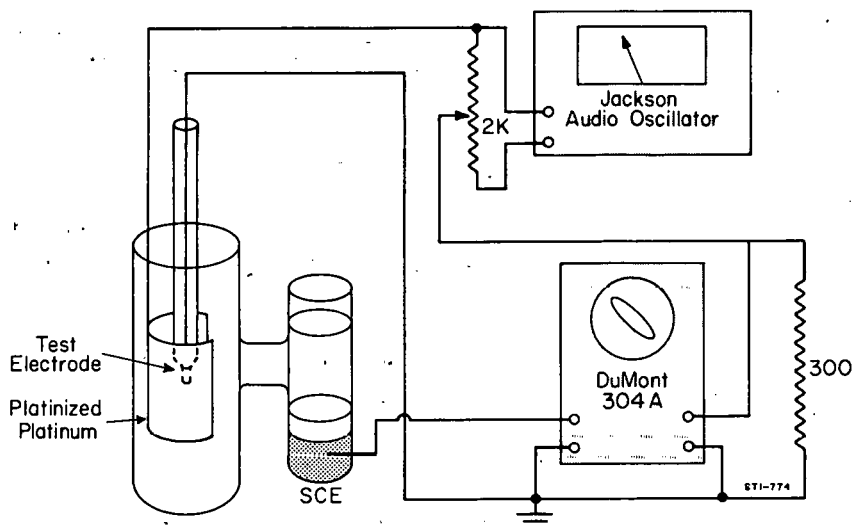
FIG. 4 ALTERNATING-CURRENT ELECTROLYSIS APPARATUS

ELECTRODE SEPARATION

The resistance of a column of solution of uniform cross section (R_c in the equivalent circuit) that was situated between two electrodes increased linearly with electrode separation; the effect was independent of electrode area and frequency as shown in Table I.

The data for the effect of electrode separation were obtained with the 20-mm-diameter cell shown in Figure 3a. The cell contained a solution of 0.14M uranyl nitrate that was 0.2M in nitric acid. The upper electrode was positioned with respect to a millimeter scale on the side of the cell, and the distance between electrodes was read from this scale. The position and area of the lower electrode remained fixed throughout the experiments. Initially, both electrodes were of the same area. After the effect of electrode area as a function of frequency was recorded, the upper electrode was reduced in area and the experiment was repeated. The final test was made with platinized electrodes.

Bridge measurements of R_m and C_m were made with approximately 5 millivolts applied to the cell, and a constant current of approximately 2 microamperes was used for the impedance studies.

The data in Table I were evaluated by the method of Miller[8,9]. However, in this work the cross-sectional area of the cell was larger than the areas of the electrodes so that Miller's equation could be rewritten in terms of the cross-sectional area of the cell. In the modified equation the

nomenclature of Miller was abandoned in favor of that used in recent texts[4]. The equation for a cell of uniform cross section is as follows:

$$R_m = R_s + \frac{\overline{R}1}{A}$$

where R_m = equivalent resistance of the cell as determined by bridge measurement (corresponds to R_s in the Miller equation)

R_s = electrode polarization resistance (corresponds to ΔR in the Miller equation)

$\overline{R}$ = specific resistance of solution

1 = length of column of solution between electrodes

A = cross-sectional area of the column of solution

$\frac{\overline{R}1}{A}$ = R_c in the equivalent circuit (corresponds to R_t in the Miller equation)

From the equation, plots of R_m versus 1 should be linear with a slope of $\overline{R}/A$ and an intercept equal to the value of R_s. The values for $\overline{R}/A$ and R_s were calculated from the data in Table I and the values are given in Table II. The data for

TABLE I

Effect of Electrode Separation

Values for R_m and Z_m in ohms (Ω) and C_m in microfarads (μfd) as functions of electrode area, electrode separation and frequency.

Frequency, cps	Electrode Separation, cm	Area of Upper Electrode, cm²														
		1.00			0.45			0.01			0.06			0.06 Platinized		
		R_m	C_m	Z_m	R_m	C_m	Z_m	R_m	C_m	Z_m	R_m	C_m	Z	R_m	C_m	Z_m
10^2	1	13.4	35.2	92.0	21.2	26.6	109	24.3	28.4	67.7	27.3	22.0	121	10.6	8000	9.4
	2	18.5	31.9	92.0	26.0	26.0	118	29.3	29.7	84.0	32.1	21.3	129	15.8	8000	13.6
	3	23.3	31.0	93.0	31.0	25.3	119	33.3	28.1	91.0	35.3	21.0	132	20.4	8000	14.4
	5	32.7	29.9	94.0	41.0	24.9	122	42.7	27.4	88.0	46.2	20.5	132	29.6	7500	27.4
	7	42.2	29.2	94.0	50.8	24.6	122	51.8	26.6	96.0	55.6	20.5	129	39.8	7500	37.8
	10	56.4	28.5	102	64.2	24.4	127	65.8	26.3	105	69.3	20.4	136	54.1	6500	52.5
10^3	1	8.4	20.4	10.6	11.6	15.1	15.5	14.2	18.8	15.2	17.5	14.4	19.4	10.4	2500	9.3
	2	13.3	20.6	14.0	16.5	15.0	19.3	19.7	18.6	19.2	22.1	14.2	23.1	15.8	2500	13.6
	3	18.2	20.7	18.4	21.0	14.6	22.3	23.6	18.6	23.3	27.0	14.2	28.0	20.3	2500	18.8
	5	27.6	20.9	27.4	30.5	14.5	30.8	33.2	18.4	31.8	36.7	14.2	36.6	29.6	2500	28.1
	7	37.3	21.0	36.8	40.5	14.3	40.2	42.4	18.4	41.3	46.2	14.1	41.1	39.5	2500	37.6
	10	51.0	20.8	48.0	54.2	14.5	52.5	56.9	18.4	50.0	60.1	14.1	59.2	53.9	2500	52.0
10^4	1	7.3	12.3	5.8	8.6	8.2	7.9	10.8	7.2	9.1	13.3	5.3	11.2	10.4	1000	8.7
	2	12.1	14.5	10.8	13.5	9.0	12.0	15.8	7.0	11.8	17.9	5.3	18.8	15.4	1000	13.3
	3	16.8	12.5	15.0	18.1	8.0	16.2	20.3	7.0	18.9	22.4	5.3	20.9	20.3	1000	18.1
	5	26.5	12.6	23.3	27.7	7.7	26.1	30.3	6.6	27.8	32.2	5.2	29.8	30.1	1000	27.3
	7	35.6	13.7	33.4	37.3	7.9	35.0	39.7	6.6	36.5	41.0	5.2	38.6	39.3	1000	38.0
	10	50.0	12.0	45.6	51.0	7.5	47.6	53.7	6.6	50.8	55.5	5.2	51.0	53.4	1000	52.2
10^5	1	9.3	0.5	5.9	8.6	0.6	6.4	9.3	0.5	8.4	10.0	0.4	9.3	10.4	1.0	9.3
	2	12.1	5.0	10.6	13.8	1.8	9.1	14.4	0.8	12.2	16.0	0.5	10.4	15.2	1.0	12.7
	3	16.7	0.9	14.6	17.7	0.7	15.7	18.0	0.5	16.8	20.4	0.5	17.2	20.3	0.6	17.3
	5	25.7	0.8	23.4	27.0	0.7	25.0	28.9	0.4	25.9	30.3	0.4	27.9	30.3	0.5	26.8
	7	35.6	0.8	32.2	37.1	0.7	34.5	37.6	0.5	35.9	39.7	0.4	36.4	39.3	0.6	36.5
	10	51.0	0.5	45.8	51.0	0.5	50.0	51.0	0.4	47.5	54.0	1.0	48.8	53.8	0.8	51.8

TABLE II

Effect of Electrode Area

a. Values for $\bar{R}/A$ and $\bar{Z}/A$

Frequency, cps	Area of Upper Electrode, cm²									
	1.0		0.45		0.21		0.06		0.06 Platinized	
	$\bar{R}/A$[a]	$\bar{Z}/A$[a]	$\bar{R}/A$	$\bar{Z}/A$	$\bar{R}/A$	$\bar{Z}/A$	$\bar{R}/A$	$\bar{Z}/A$	$\bar{R}/A$	$\bar{Z}/A$
10^2	4.75	(b)	4.82	1.1	4.61	(b)	4.67	(b)	4.83	4.8
10^3	4.70	4.3	4.70	4.1	4.70	3.7	4.70	4.4	4.83	4.7
10^4	4.75	4.4	4.70	4.5	4.67	4.5	4.68	4.2	4.70	4.8
10^5	4.75	4.4	4.70	4.5	4.65	4.4	4.71	4.4	4.82	4.7

b. Values for R_s and Z_s

	R_s[c]	Z_s[c]	R_s	Z_s	R_s	Z_s	R_s	Z_s	R_s	Z_s
10^2	8.9	91.6	16.8	115.3	19.6	(d)	22.6	(d)	5.9	3.0
10^3	3.8	6.3	7.0	11.0	10.0	12.7	13.0	14.6	5.9	3.0
10^4	2.6	1.6	4.0	3.4	6.5	4.9	8.7	8.6	5.9	3.0
10^5	2.6	1.6	4.0	1.7	4.9	3.8	5.8	5.5	5.9	3.0

(a) Values for $\bar{R}/A$ and $\bar{Z}/A$ in ohms-centimeters (Ω-cm) were calculated from data in Table I.
(b) Plots of Z vs l were nonlinear.
(c) Values for R_s and Z_s in ohms (Ω) were obtained from data in Table I by extrapolation of R_m and Z_m to zero interelectrode distance.
(d) Data exhibit too much dispersion to permit accurate estimate.

cell impedance (Z_m) versus electrode separation were evaluated in a like manner. In this case, the intercept corresponds to the combined impedance of the electrodes. These results are also given in Table IIa.

The data on the uranyl nitrate — nitric acid system show that the calculated values of $\bar{R}/A$ for a cell of constant cross section were independent of electrode area and frequency. The calculated values of $\bar{Z}/A$ were also a function of electrode separation and were independent of electrode area and applied frequency above 1000 cycles per second. However, the values for $\bar{Z}/A$ were lower than the corresponding values of $\bar{R}/A$ except in the case of platinized electrodes. This result is in accord with the equivalent circuit concept of a conductivity cell. Therefore bridge measurements are required where accurate values of $\bar{R}/A$ must be obtained.

CROSS-SECTIONAL AREA OF SOLUTION

In view of the linear dependence of R_m on electrode separation, it appeared desirable to establish the relationship between R_m and A. Since it was logical to conclude that the relationship of R_m to A would fail for large values of A and small electrode areas, tubing of the largest diameter immediately available was utilized in the fabrication of one of the cells.

The type of cell utilized for the area studies is shown in Figure 3b. All cells were 400 mm in length except for the

90-mm cell, which was 500 mm long. The cross-sectional areas arc given in Table III. The electrodes were bright platinum plates 1 cm in diameter. The applied frequency was 10 kc.

TABLE III

Effect of Cross-Sectional Area of Cell

$f = 10^4$ cps, 0.1N KCl - Electrodes (see Figure 3b)
Values of R_m in ohms (Ω)

Increase in Electrode Separation, cm (a)	Cross-Sectional Area, cm²				
	1.224	2.416	5.409	16.32	56.46
	R_m	R_m	R_m	R_m	R_m
1	253	181	79	77	102
2	319	213	93	82	103
3	386	243	108	87	104
4	448	275	122	92	106
5	509	309	137	97	107
6	576	341	151	101	108
7	642	372	165	106	110
8	704	405	180	111	111
9	770	437	195	116	113
10	831	469	210	121	114
15	1159	630	281	145	121
20	1480	794	353	169	128
25	1799	950	425	193	135
30	2110	1113	500	217	142
34	2370	1250	556	237	147
$R_m/1$	64.33	32.17	14.50	4.850	1.393

(a) Readings at an initial electrode separation of
2-5 cm depending on the diameter of the tube.

The cross-sectional areas of the cells were determined by adding measured volumes of water to each cell and recording the increase in height from the millimeter scale. The coefficient of variation of this method was 1%. Data for the effect of electrode separation on R_m for cells of different cross sections are given in Table III.

Calculated values for $\overline{R}/A$ obtained from the data in Table III, cross-sectional areas of the cells, and the calculated values for $\overline{R}$ are given in Table IV.

The results show that the value for R_c in the equivalent circuit can be calculated from the geometry of the solution between the electrodes and the specific resistance $\overline{R}$, and that the technique of electrode separation permits the specific resistance of a solution to be determined within 1%, independent of electrode area.

TABLE IV

Effect of Cell Cross Section

f = 10 kc, 0.1N KCl - Electrodes (see Figure 3b)

Cell No.	1	2	3	4	5
Cross-sectional area of cell, cm^2	1.23	2.42	5.41	16.3	56.5
$\overline{R}/A$, Ω-cm	64.3	32.2	14.5	4.85	1.39
$\overline{R}$, Ω-cm	79.1	77.9	78.4	79.0	78.4
$\overline{R}$(avg), Ω-cm			78.6 ±0.5		

ELECTRODE AREA

The impedance of the conductivity cell increased with decreasing area of the upper electrode; however, the 50% change in impedance was considerably less than anticipated in view of the 1600% change in the area of the upper electrode.

Data for the effect of electrode area are given in Tables I and II, and curves for the effect of electrode area at zero separation are shown in Figure 5. These data were obtained as previously described, and the areas given in the tables are for the upper electrode only. The area of the lower electrode was 1 cm^2.
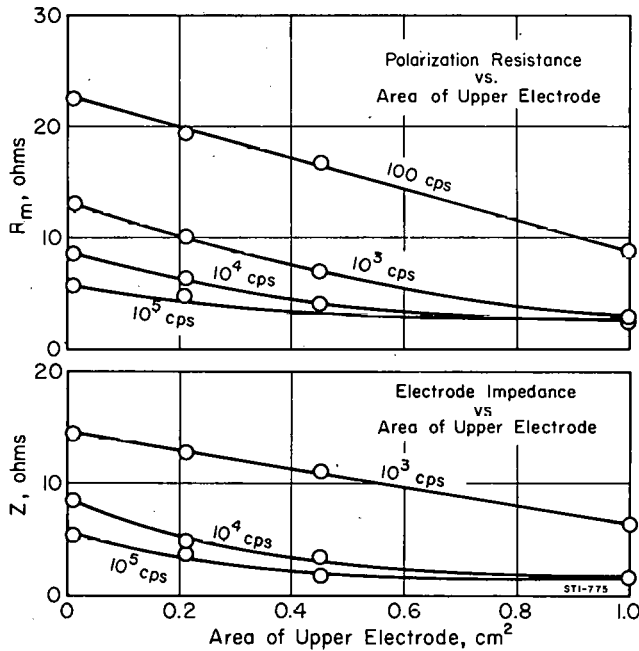

FIG. 5 EFFECT OF ELECTRODE AREA AT
ZERO INTERELECTRODE DISTANCE

Results from data given in Table I

The results show that the electrode impedance and polarization resistance decrease nonlinearly with increasing area, and that the effect, which was a function of the applied frequency, decreased as the frequency was increased. Normally the polarization resistance R_s and reactances of C_s and C_1 are expected to be inverse functions of the electrode area[4]. Although the reasons for the anomalous behavior are not immediately apparent, the results indicate the importance of electrode area in the design of conductivity cells.

FREQUENCY

The response of a conductivity cell to changes in the applied frequency can be interpreted in terms of the contemporary theory of faradaic admittance[3]. In the design of conductivity cells, the impedances of the elements R_s, C_s, and C_1 in the equivalent circuit that are dependent on frequency must be minimized in order for the measured response to be truly indicative of the resistance of the current path. Therefore the results in Table I were evaluated in terms of the contemporary theory.

Values for the frequency-dependent term R_s were obtained from the data in Table I by extrapolating the curves of R_m versus electrode separation to zero distance. These results are given in Table IIb. Due to the dispersion of the values of C_m, no results for C_m at zero electrode separation are given in Table II. The dispersion in the values for C_m is not surprising since a lengthy pretreatment and extreme care are necessary to obtain reproducible results for C_m with solid electrodes[7]. No special treatment was given to the electrodes during this study since one of the objectives was to demonstrate that the electrodes in a conductivity cell do not have to be scrupulously clean for in-line conductivity measurements.

The results show that the polarization resistance R_s and the electrode impedance (Z_s at zero separation) decrease with increasing frequency and approach constant values at 100 kc. Curves of R_s versus the reciprocal of the square root of frequency were linear in agreement with the theory of faradaic admittance.

In view of the dispersion in the observed values of C_m which did not permit extrapolation to zero electrode separation, this variable was studied at a separation of 5 mm. Curves of C_m versus log frequency were essentially linear with the capacity decreasing with increasing frequency.

The above results are consistent with the contemporary theory of faradaic admittance, and indicate that the effects of electrode impedance on the response of a conductivity cell can be minimized by utilizing frequencies in the range of 10^4 to 10^5 cycles per second.

PLATINIZED ELECTRODES

A platinized electrode behaves as a reversible hydrogen electrode[6], and the contemporary theory of faradaic admittance predicts that the impedance of an electrode will be minimum at the half-wave potential of the electrochemical reaction.

Data for the effect of electrode platinization are given in Table I. The area of the upper electrode was 0.06 cm². Curves for R_s and C_s at zero separation versus $f^{-\frac{1}{2}}$ are shown in Figure 6, and extrapolated values for R_s and Z_s at zero separation are given in Table II.

The theory for alternating current electrolysis[4] predicts that the polarization resistance of an electrode is minimum at the half-wave potential of the controlling electrochemical reaction and that the pseudocapacitance (C_s) will be maximum at that potential. The theory also predicts that for fast reactions both R_s and C_s will decrease as a function of $f^{-\frac{1}{2}}$. The curves in Figure 6 show that C_s decreased as a function of $f^{-\frac{1}{2}}$, whereas R_s was essentially constant. This behavior of R_s was indicative of a slow reaction.
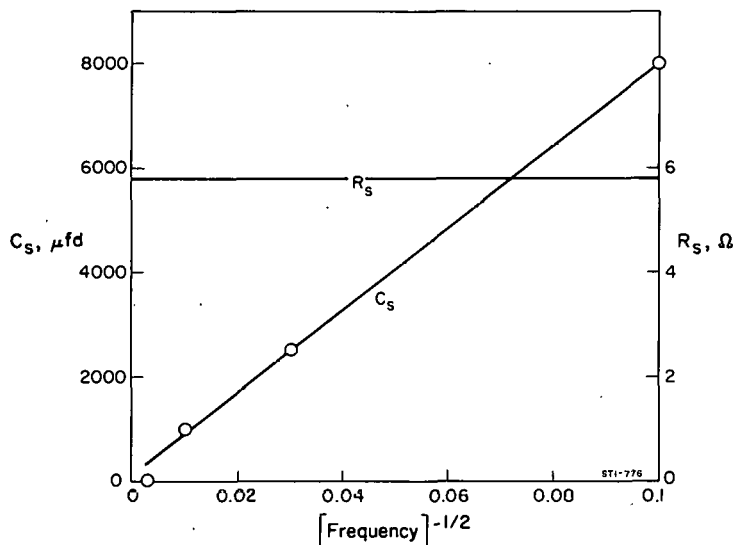

FIG. 6 EFFECT OF PLATINIZED ELECTRODES
Values of R_s and C_s versus $f^{-1/2}$
Results calculated from data given in Table I
by extrapolating R_m and C_m to zero inter-
electrode distance.

The results indicate that platinized platinum electrodes are desirable for conductivity cells; however, the results observed with bright platinum electrodes at 10^5 cps agree with those obtained with platinized electrodes. Therefore the necessity for platinized electrodes can be eliminated by utilizing high frequencies.

AMPLITUDE OF CELL VOLTAGE

Since the amplitude of the cell voltage is one of the factors that determines the extent of the electrochemical reaction that occurs at the electrodes, the effect of the amplitude variable was studied at four frequencies with the cell shown in Figure 3a. The areas of the upper and lower electrodes were 0.06 and 1.0 cm², respectively, and the electrodes were positioned 1 cm apart. Cell voltages were monitored by means of an AC voltmeter; and R_m, C_m, and Z_m were determined as a function of cell voltage. The results are given in Table V.

TABLE V

Effect of Amplitude of Cell Voltage

Area upper electrode 0.06 cm², Area lower electrode 1 cm²
Interelectrode distance 1 cm, Cell shown in Figure 3a
0.14M UNH - 0.2M HNO_3

| Frequency, cps | Platinized Electrodes | | | | | Bright Platinum Electrodes | | | | |
| | Bridge | | | Constant Current | | Bridge | | | Constant Current | |
	E_{cell}, V, RMS	R_m, Ω	C_m, μfd	E_{cell}, V, RMS	Z_m, Ω	E_{cell}, V, RMS	R_m, Ω	C_m, μfd	E_{cell}, V, RMS	Z_m, Ω
10^2	0.0042	10.4	8000	0.00012	11.5	0.0082	25.7	24	0.00012	72
	0.016	10.4	8000	0.00054	9.1	0.027	25.9	24	0.00032	50
	0.08	10.4	8000	0.0027	10.8	0.092	26.8	25	0.0099	51
	0.29	10.7	6000	0.023	10.6	0.29	20.3	58	0.034	52
	1.00	10.7	6500	0.084	9.2	0.92	13.4	215	0.22	28
	1.74	10.7	6500	0.39	10.5	2.25	11.5	390	1.1	15
10^3	0.0062	10.4	1500	0.00024	10.6	0.008	11.2	25	0.00030	12.6
	0.040	10.4	2000	0.00072	10.3	0.029	11.2	24	0.0010	11.9
	0.020	10.4	3000	0.0026	10.5	0.096	11.2	25	0.0036	14.6
	0.70	10.4	7000	0.026	10.3	0.29	11.2	30	0.011	12.4
	1.92	10.4	24000	0.26	10.4	0.90	10.4	55	0.11	12.7
				0.58	10.5	2.1	10.0	100	1.0	11.2
10^4	0.0074	10.4	4000	0.00019	10.4	0.0071	10.0	15	0.00027	10.7
	0.022	10.4	4000	0.00084	9.5	0.029	10.0	14	0.00095	10.5
	0.09	10.4	4000	0.0026	10.6	0.096	10.0	14	0.0050	11.1
	0.27	10.4	8000	0.0084	9.7	0.30	10.0	13	0.040	10.9
	0.81	10.4	20000	0.029	10.7	1.0	9.7	13	0.098	10.8
				0.59	10.5	1.8	9.7	13.5	0.65	10.8
10^5	0.0066	10.4	3	0.00024	10.9	0.0025	10.0	0.4	0.00030	11.0
	0.027	10.4	7	0.00082	11.6	0.0092	10.0	0.5	0.00082	11.4
	0.091	10.4	8	0.0030	11.1	0.030	10.0	0.5	0.0095	10.5
	0.24	10.4	8	0.029	10.7	0.10	10.0	0.5	0.098	10.8
	0.30	10.4	8	0.12	10.5	0.29	10.0	0.5	0.129	10.8

The results indicate that the resistance (R_m) and impedance (Z_m) of a cell with bright platinum electrodes were essentially independent of cell voltage in the frequency range of 10^3 to 10^5 cps. Below 10^3 cps, the values for R_m and Z_m decreased with increasing voltage and approached the values obtained at higher frequencies. An explanation of this behavior, which is in accord with the theory of faradaic admittance, was given by Silverman and Remick[7].

For platinized electrodes, the values of R_m and Z_m were independent of frequency and applied voltage, while the values of C_m increased with applied voltage except at 10^5 cps where the values for C_m abruptly decreased in value. This behavior of the platinized electrode system is in accord with the concept of polarized electrodes operated at the half-wave potential of the electrochemical reaction that occurs at the electrode surface. The decrease in C_m at 10^5 cps was characteristic of the behavior of platinized electrodes (see Figure 6).

The above results indicate that, with approximately 2 volts applied to the cell, the conductivity results would be independent of frequency. However, Silverman and Remick[7] have shown that at high current densities the electrode is polarized; therefore, for processes other than those involving reversible reactions, large errors can result due to polarization. Thus the high frequency — low voltage technique appears advantageous for use with those systems that do not involve reversible reactions at the electrodes.

ELECTRODE MATERIALS

The polarization impedance of various electrode materials in 0.14M uranyl nitrate — 0.2N nitric acid was studied qualitatively by the method of Silverman and Remick[7]. The impedance of the electrodes increased in this order: platinized platinum, platinum, stainless steel, and tantalum.

The apparatus utilized for these studies is shown in Figure 4, and typical cyclograms are shown in Figure 7.

At low current densities, the cyclograms were elliptical which indicates that the polarization resistance and capacitance did not change significantly with changes in cell current. If the reaction rate had changed significantly with voltage, the cyclograms would have been distorted. The impedance of the various electrodes was determined from the slope of the cyclograms. The cyclograms for platinized electrodes were essentially straight lines, while those for stainless steel were elliptical
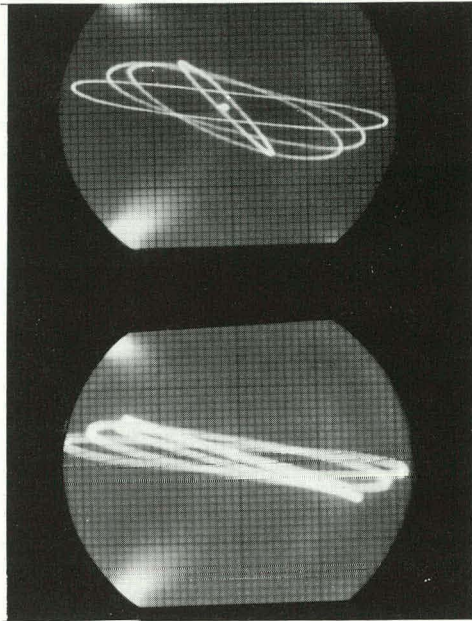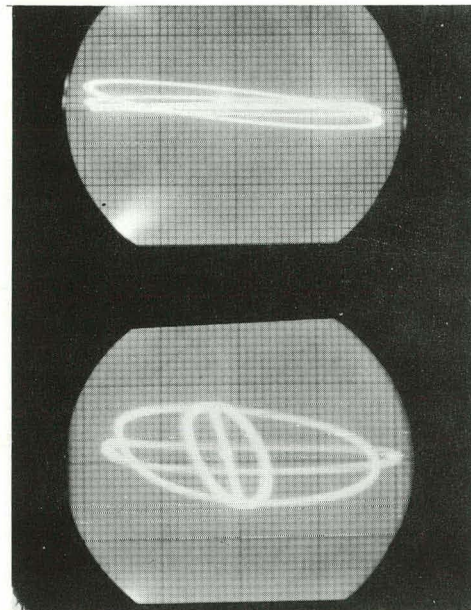
Platinum Electrode - 0.2 cm^2

Horizontal - 0.02 v per division
Vertical - 10^{-4} amperes per division

Frequency 10^2, 10^3, 10^4, 10^5 cps

Slope of major axis increases
with frequency

Platinized Platinum - 0.06 cm^2

Horizontal - 0.02 v per division
Vertical - 10^{-3} amperes per division

Frequency 10^2, 10^3, 10^4, 10^5 cps

Slope of major axis increases
with frequency

ST I - 777

Tantalum Electrode - 1.0 cm^2

Horizontal - 0.02 v per division
Vertical - 10^{-4} amperes per division

Frequency 10^2, 10^3, 10^4, 10^5 cps

Slope of major axis increases
with frequency

Stainless Steel Electrode - 0.7 cm^2

Horizontal - 0.2 v per division
Vertical - 10^{-4} amperes per division

Frequency 10^2, 10^3, 10^4, 10^5 cps

Slope of major axis increases
with frequency

FIG. 7   CYCLOGRAMS OF 0.14M UNH — 0.2M HNO$_3$

traces. Platinum was intermediate between these two. The phase angle decreased with frequency for all electrodes. Tantalum electrodes exhibited high polarization resistance and small capacity at all frequencies.

The above results indicate that stainless steel electrodes can be utilized in conductivity cells, while tantalum should not be used due to the high polarization resistance.

WATER-INSOLUBLE ORGANIC SOLVENTS

Since Purex plant streams contain dissolved and suspended organic solvent that is nearly insoluble in water, the effect on the response of conductivity cells of coating the electrodes with solvent was studied for three different cell designs: a commercial dip-type cell with 1-cm^2 disc electrodes spaced 3 cm apart and centered inside a 2.8-cm cylindrical glass sleeve, and the two designs shown in Figures 3b and 3c. The commercial dip-type cell was included for comparative purposes. Cell response was determined with the equipment shown in Figure 2.

The cells were cleaned with acid-dichromate cleaning solution and rinsed with distilled water prior to use. The electrodes were not platinized. The specific resistance ($\overline{R}$) of the test solution (0.14M uranyl nitrate − 0.2M nitric acid) was determined by the electrode separation technique in a cell of the design shown in Figure 3b. This value of $\overline{R}$ was used to determine the cell constants for the dip-type and flow cells. After the initial impedance measurements were made, the cells were flooded with solvent, rinsed three times with distilled water, once with the test solution, and finally filled with fresh test solution. The impedance of the test solution was then remeasured. In the case of the flow cell, the organic solvent was simply flushed from the cell with fresh test solution. The results are given in Table VI. Although the

TABLE VI

Effect of Organic Solvents on Cell Response

Test solution: 0.14M $UO_2(NO_3)_2$ - 0.2M HNO_3, f = 10^5 cps

	$\overline{R}$, ohm-centimeter		
Cell Treatment	Dip Type	A = 1.224 cm^2 (Figure 3b)	A = 0.16 cm^2 (Figure 3c)
Clean cell	11.76[a]	11.76	11.76[a]
Flood with 30/70 TBP	16.35[b]	11.76[b]	11.76
Flood with SAE 30 oil	21.48[b]	11.87[b]	11.76
Clean cell with detergent	12.28	-	-

[a] Corrected for geometry based on value of $\overline{R}$ obtained by electrode separation method.
[b] Flooded with solvent, rinsed three times with water, once with test solution; refilled test solution and redetermined $\overline{R}$.

SAE 30 motor oil will not normally be found in organic streams, such a condition might arise from a broken pump seal and was included to indicate the worst conditions.

The results indicate that the commercial dip-type cell would be unsatisfactory in this service, even if the cell could be flushed periodically with a detergent solution. The response of the long path cells returned to within 1% of the initial readings; however, the flow cell was superior in this regard due to a more favorable geometry. The coating of the electrodes with organic solvent will have a minimum effect on the response of a properly designed cell.

The flow cell was tested for sensitivity to flow in the range of 0 to 600 milliliters per minute. No sensitivity to flow rate was detected.

BRIDGE AND CONSTANT CURRENT METHODS

Examination of the results for R_m and Z_m obtained during this study (Table I) shows that at frequencies of 10^3, 10^4, and 10^5 cps the results were related by a proportionality constant. The slopes of the lines representing the ratios were as follows:

Frequency, cps	10^3	10^4	10^5
R_m/Z	1.12	1.06	1.05

The results show that the ratio decreased as the frequency was increased. The differences in R_m and Z are due to the effects of C_d and C_s as explained previously.

ABSOLUTE NATURE OF THE ELECTRODE SEPARATION METHOD

The absolute nature of the electrode separation method for the measurement of the specific resistance of solutions is evidenced in the work of Miller[8], Jones[2], and Remick[9]. Jones and Remick were primarily interested in the effects of electrode polarization phenomena, and utilized the method of Miller to determine both the specific resistance of the solution ($\overline{R}$) and the effective polarization resistance (R_s). Both workers report that the measured values for $\overline{R}$ were in agreement with those obtained by the classical Kohlrausch method and also noted the frequency independence of this term in the Miller equation. However, neither Jones nor Remick claimed the prodedure as a method for the determination of the absolute value of $\overline{R}$, perhaps because Jones proposed to correct conductivity results by extrapolating plots of R_m vs $f^{-\frac{1}{2}}$ to zero frequency. However, Remick[9] has shown that plots of R_m vs 1

extrapolated to zero distance give answers in better agreement with the Kohlrausch method.

Since the value for $\overline{R}$ as determined by the electrode separation technique is independent of R_s, whereas R_s is included in the results obtained by the Kohlrausch method, the electrode separation technique should provide a basis for the measurement of absolute values for $\overline{R}$.

The validity of the modified Miller equation for the measurement of $\overline{R}$ is illustrated by the results obtained for the effect of the cross-sectional area of the solution (see page 13).

The standard 0.1000N potassium chloride solution used in these experiments was prepared from the salt that had been previously dried to constant weight at 105°C. The literature value[10] for the specific resistance of this solution was 77.83 ohm-centimeters at 25°C, which extrapolates to 78.15 ohm-centimeters at 24.8°C, the temperature of the test solution.

The average result of 78.6 ±0.5 ohm-centimeters agrees with the extrapolated literature value of 78.15 ohm-centimeters within the limits of error of the experimental procedure. Thus the modified Miller equation is valid for the determination of $\overline{R}$ by the electrode separation method.

In view of the relative precision of the experimental techniques utilized in this study, further experiments of a more precise nature will be conducted in the near future to substantiate further the above results. However, the validity of the original Miller equation is demonstrated in the work of Jones[2], and it was the sole purpose of this section to demonstrate the validity of the modified equation of Miller as applied to in-line measurements at the 1% level.

APPLICATION TO THE URANYL NITRATE – NITRIC ACID SYSTEM

Conductivity and specific gravity are critical indices of the composition of the uranyl nitrate — nitric acid system, and provide a means for the continuous analysis of raw metal feed solutions. A typical graph of conductivity versus specific gravity for solutions of various uranyl nitrate — nitric acid compositions is given in Figure 8.

The analysis of raw metal feed solutions with an accuracy of 1% requires a corresponding accuracy in conductivity and specific gravity determinations. This requirement is within the scope of conductivity measurements; however, the current differential pressure technique for measuring specific gravity
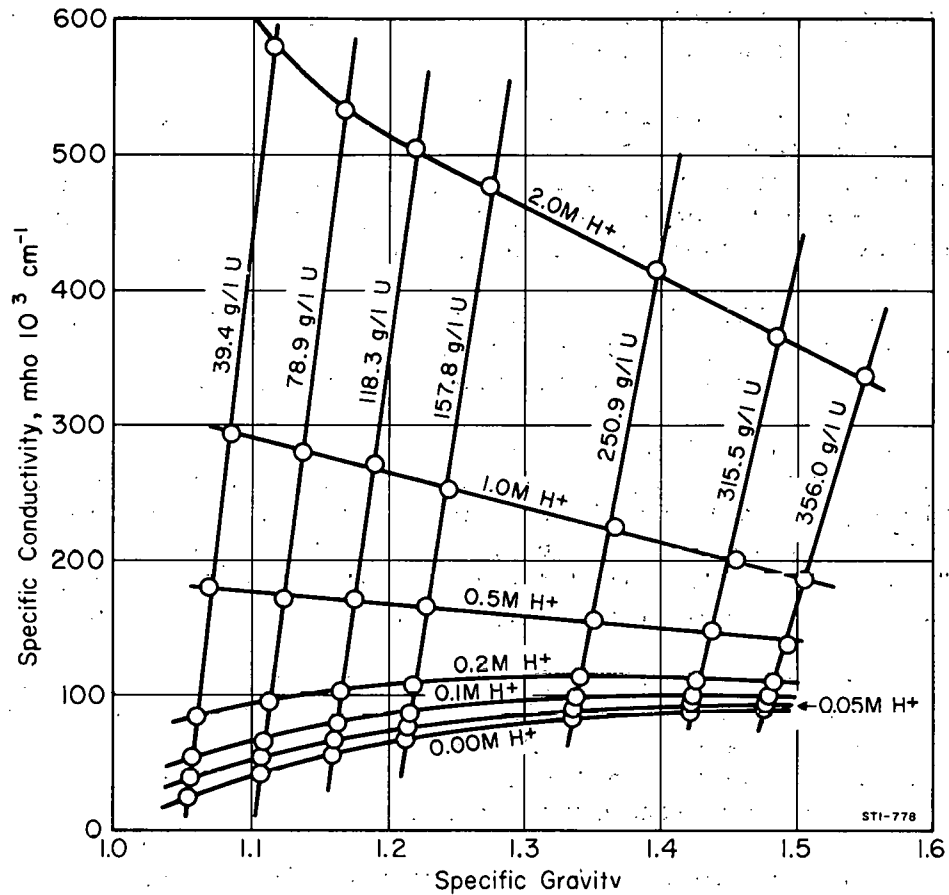
FIG. 8 SPECIFIC GRAVITY vs CONDUCTIVITY, $UO_2(NO_3)_2$-HNO_3 SYSTEM

in the Plant is sensitive to 0.01 specific gravity units when the distance between air bubble pipes is 10 inches. This corresponds to a 0.03M change in uranyl nitrate concentration. In order to obtain a sensitivity of 1%, the pressure differential will have to be increased to 30 inches H_2O, or another more sensitive method is needed.

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