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PROJECT NO. 2372						
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REPORT NO						
DATESeptember 3, 1963						
NOTE BOOK						
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SIGNED Lloyd R. White						

CONTROL SYSTEM DESIGN FOR COULOMETRIC ANALYZER

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#### INTRODUCTION

Figure 1 shows a block diagram of the coulometric analyzer developed under Project 2067. Direct current for generating bromine in the electrolysis cell (B) is supplied by a constant current source (G) and is indicated on a stripchart recorder (A). A constant-rate pump (E) withdraws the bromine solution from the cell and combines it with a stream containing sample and NaOH, drawing them through the mixer (C). The e.m.f. of the effluent from the mixer is sensed using a platinum-saturated calomel cell (D). The control system (F) automatically adjusts the current level in the electrolysis cell to bring the e.m.f. nearer the equivalence point (O mv.).

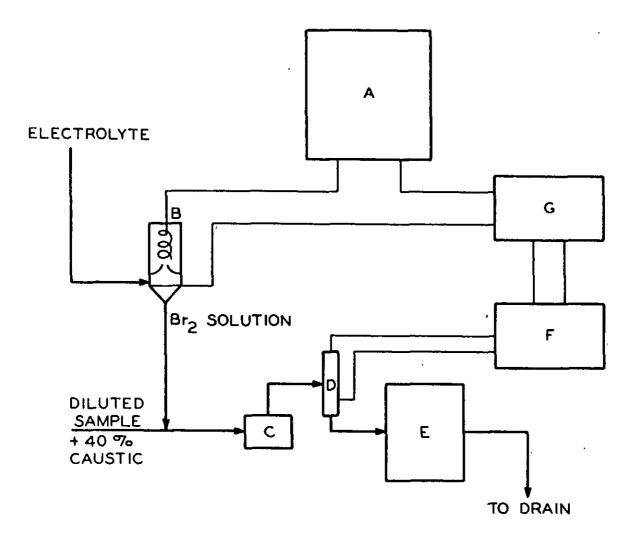
When the e.m.f. is maintained near the equivalence point (between ±150 mv.), the electrolysis current indicated on the recorder is an accurate measure of the strength of the unknown sample. The advantages of such a system are that a simple current-indicating device may be used to indicate sample concentration and electrolysis current is a linear function of sample concentration.

The control system previously designed for the analyzer provides:

1. Incremental changes in electrolysis current, each followed by a waiting period.

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- A CURRENT INDICATING RECORDER
- B ELECTROLYTIC CELL FOR BROMINE GENERATION
- C MIXER

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- D EMF CELL
- E MULTI-CHANNEL PERISTALTIC ACTION PUMP
- F CONTROL SYSTEM
- G D.C. CURRENT SUPPLY
- --- FLUID FLOW LINES

Figure 1. Block Diagram of Coulometric Analyzer

 Three different magnitudes of current increment adjustments-coarse, medium, and fine, and a mechanism for switching from one to the other.

This report describes an alternative control system of an entirely different character. It would consist of a motor (to drive the currentadjusting potentiometer) connected through a suitable amplifier to the e.m.f. cell. It would operate continuously to alter the current level in the electrolysis cell, obeying the following relationship:

$$\frac{dR_{l}}{dt} = \frac{k}{T_{l}} E$$
 (1),

where <u>R</u> is the concentration of hypobromite ion in the mixer,  $\underline{\underline{T}}_{\underline{1}}$  is the integral time, <u>E</u> is the value of the e.m.f. in mv., and <u>k</u> is a proportionality constant. In other words, the current-adjusting motor would turn at a rate directly proportional to the value of the e.m.f. If the e m.f. were zero, the motor would not turn. If it were +100 mv.,

$$\frac{dR_1}{dt} = + \frac{k}{T_1} (100) ,$$

and if it were -100 mv.,

$$\frac{dR_1}{dt} = -\frac{k}{T_1}(100) .$$

It was realized from the outset that this type of control system would require careful study; analog simulation was done because it appeared to be the fastest way of determining the feasibility of this system short of building and testing it.

Chapter Two, System Description, of this report is a mathematical description of the problem and provides a theoretical basis for the study. Chapter Three, Results, gives the findings of the analog simulation, and Chapter Four, Specification of Control System, provides specifications of a broad nature for design of the control system.

# SYSTEM DESCRIPTION

Figure 2 is a block diagram of the system.

The electrolysis cell is represented by (A), a combined mixer-e.m.f. cell by (B), and a control system by (C). This is the only portion of the analyzer of interest for the purpose of this study.

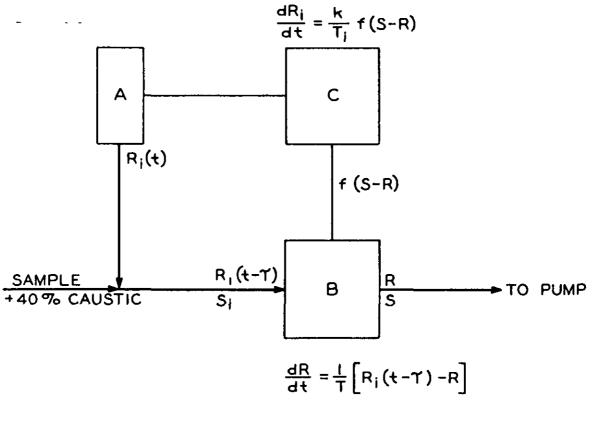
The line going from (B) to (C) represents the e.m.f. signal from the mixer-e.m.f. cell. Figure 3 gives the relationship between  $\underline{E} = f(\underline{S} - \underline{R})$  and  $\underline{S} - \underline{R}$ . This was prepared from data obtained in batch titrations of thicsulfate solutions with hypobromite ion.

The control system,  $\underline{C}$ , maintains the following relationship between  $\underline{R}_1$  and  $\underline{S} - \underline{R}$ :

$$\frac{dR_i}{dt} = \frac{k}{T_i} f(S - R)$$
 (2).

The value of reagent concentration at time  $\underline{t}$  is represented by  $\underline{\underline{R}}_{\underline{i}}(\underline{t})$  and is the value at the electrolysis cell. There is distance-velocity lag between the electrolysis cell and the mixer and therefore  $\underline{\underline{R}}_{\underline{i}}$  at  $\underline{\underline{A}}$  is different from  $\underline{\underline{R}}_{\underline{i}}$ at  $\underline{\underline{B}}$ . This is very important and must be accounted for in the analysis. Thus,  $\underline{\underline{R}}_{\underline{i}}(\underline{t} - \gamma)$  refers to the reagent concentration at the input to the mixer and is

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 $\frac{dS}{dt} = \frac{1}{T} (S_i - S)$ 

Figure 2. Block Diagram of System

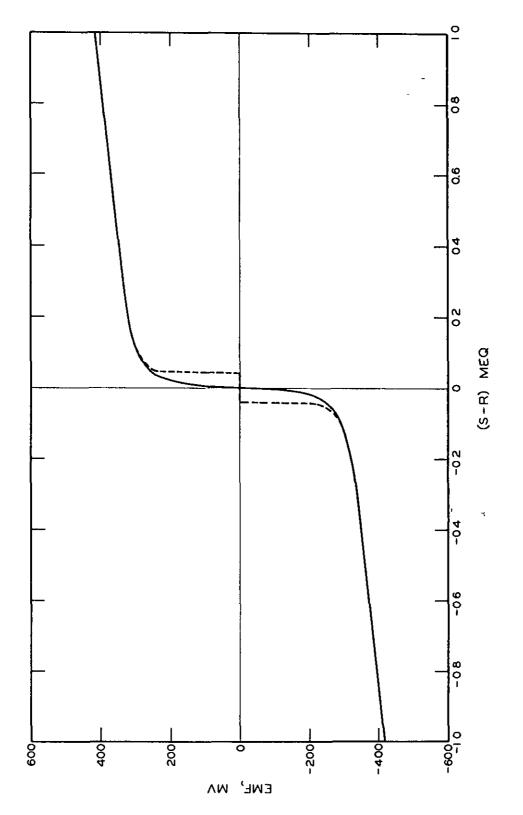


Figure 3. E.m.f. Versus Excess Reagent or Sample

simply the value which  $\frac{R}{-1}$  had at the electrolysis cell  $\gamma$  seconds earlier,  $\gamma$  being the time required to transport reagent from (A) to (B). Equations (3) and (4) describe the effect the mixer has on both reagent and sample.

$$\frac{dR}{dt} = \frac{1}{T} \left[ R_{1}(t - \gamma) - R \right]$$
(3)

$$\frac{\mathrm{dS}}{\mathrm{dt}} = \frac{1}{\mathrm{T}} \begin{bmatrix} \mathrm{S}_{1} - \mathrm{S} \end{bmatrix}$$
 (4).

In these equations  $\underline{T}$  represents the time constant of the mixer and is defined by the ratio  $\underline{V}/\underline{q}$ , where  $\underline{V}$  is the mixer volume, ml., and  $\underline{q}$  is the volumetric flow rate through the mixer in ml./sec.

We wish to determine the variation of  $\underline{R}$  with time for an arbitrarily defined variation in  $\underline{S}$ , the sample. Consider the following simplified case.

NO LAG ( $\gamma = 0$ ),  $f(\underline{S} - \underline{R}) = \underline{S} - \underline{R}$ 

With  $\gamma' = 0$  and with  $f(\underline{S} - \underline{R}) = \underline{S} - \underline{R}$ , Equations (2-4) may be solved by hand. This corresponds to a case where no distance-velocity lag exists between the electrolysis cell and mixer and where the typical e.m.f. curve as shown in Fig. 3 is replaced by a straight line passing through the origin. For this case, Equations (2) and (3) become

$$\frac{dR}{dt} = \frac{k}{T_{1}}(S - R)$$
(5)

$$\frac{\mathrm{d}R}{\mathrm{d}t} = \frac{1}{\mathrm{T}} \left[ R_{1} - R \right]$$
(6).

Differentiating Equation (6), we get

$$\frac{d^2 R}{dt^2} = \frac{1}{T} \begin{bmatrix} \frac{d R}{1} & \frac{d R}{dt} \end{bmatrix}$$
(7).

The variable  $\underline{R}_{\underline{1}}$  may be eliminated by substituting Equation (5) into (7), thus

$$\frac{d^2 R}{dt^2} + \frac{1}{T} \frac{dR}{dt} + \frac{k}{TT} R = \frac{k}{TT} S \qquad (8).$$

This equation may be solved for arbitrary values of S. Suppose

$$S = S_{sin} \beta t$$
 (9),

and that at  $\underline{t} = 0$ ,  $\underline{R} = \underline{R} = \underline{S} = 0$ .

For these conditions, Equation (8) may be solved to yield

$$P = R_{c} + \frac{kS_{o} \sin(\beta t - \theta)}{T_{i} \sqrt{\beta^{2} + (k/T_{i} - \beta^{2}T)^{2}}}$$
(10)  
$$\Theta = \arctan\left[\frac{\beta}{k/T_{i} - \beta^{2}T}\right],$$

where  $\underline{\underline{R}}_{\underline{\underline{C}}}$  is the solution to Equation (8) with  $\underline{\underline{S}} = 0$ . It will be noted that  $\underline{\underline{R}}_{\underline{\underline{C}}}$  includes the exponential factor,  $e^{-\underline{\underline{t}}/\underline{\underline{T}}}$ , which will decay rapidly. Therefore, the remaining term in Equation (10) is of interest.

It will be useful to recall what these variables refer to. The electrolysis current is related linearly to  $\underline{R}$ , and  $\underline{S}$  is the unknown sample concentration we are seeking. We hope that  $\underline{R}$  will not be unreasonably different from S. Therefore, let us compare R and S.

Sample concentration is given by Equation (9)

$$S = S_{o} sin(\boldsymbol{\beta}t)$$
 (9).

Let

$$\frac{k}{T_{1}\sqrt{\beta^{2} + (k/T_{1} - \beta^{2}T)^{2}}} = K$$
(11),

then

$$R = K S_0 \sin(\beta t - \theta)$$
 (12),

and it will be noted that  $\underline{\mathbb{R}}$  differs from  $\underline{S}$  by the phase lag,  $\Theta$ , and the factor  $\underline{K}$ , the amplitude ratio. It would be desirable to have  $\underline{K}$  as nearly equal to unity as possible and  $\Theta$  as small as possible. It may be seen from the defining equations for  $\underline{K}$  and  $\Theta$  that if  $\underline{k}/\underline{T}_1 >> \beta$ ,  $\underline{K} \cong 1$ , and  $\Theta$  is negligibly small. This would correspond to having the current adjusting motor turn very rapidly as a function of the e.m.f. signal. In practice, this cannot be done because there are always lags in any real system and if very high values of  $\underline{k}/\underline{T}_1$  were used, instability would result. Usually, however, up to a certain frequency, a given value of  $\underline{k}/\underline{T}_1$  may be used which would keep  $\underline{K}$  very close to unity and  $\Theta$  small, and therefore, it would be possible to rely on  $\underline{R}$  as an indicator of  $\underline{S}$ 

Now consider the more interesting case expressed by Equations  $(2-l_+)$ . LAG AND TYPICAL E.M.F. CURVE

It would be a tedious, lengthy task to solve Equations (2-4) by hand even with the aid of a digital computer. It is possible to solve them conveniently

using an analog computer. The details of the problem setup are given in the Appendix. The solutions represent simulations of what should actually happen if the analyzer were built and operated so that the values used in the equations correspond to the actual situation in the analyzer.

There is one point somewhat aside from the main problem which must be considered, i.e., the effect the mixer alone has on fluctuating values of the sample concentration at the input. For this purpose, define

$$S_{i} = S_{o} \sin \beta t \qquad (13),$$

and substitute into Equation (4) to give

$$\frac{dS}{dt} = \frac{1}{T} \left[ S_0 \sin\beta t \cdot S \right]$$
(14)  
$$S_1 = 0 \text{ at } t = 0.$$

This may be solved to give

$$S = \frac{S_0}{\sqrt{1 + (\beta T)^2}} \left[ \sin(\beta t - \theta) + \sin \theta e^{-t/T} \right]$$
(15)

 $\theta$  = arctan ( $\beta$ T).

As before, the transient term involving  $e^{-\underline{t}/\underline{T}}$  will be ignored. It will be observed that the amplitude ratio and phase lag depend upon  $\underline{T}$ , the time constant of the mixer.

Equation (15) will be used to help make a somewhat arbitrary decision concerning the frequency range we wish to study. We will choose to restrict our

attention to frequencies at which the effect of the mixer alone on <u>S</u> is negligible. This is an arbitrary, but nevertheless reasonable choice since the analyzer will not be particularly useful in any case for rapidly oscillating sample concentrations. Using a value of <u>T</u> = 6 sec. (<u>q</u> = 0.1 ml./sec., <u>V</u> = 0.6 ml.), it can be shown that  $\frac{1}{\sqrt{1 + (\beta T)^2}}$  will be greater than 0.9 for all values of  $\beta$  less than about 0.003 cycles/sec. We will, therefore, limit the frequency of <u>S</u> to about 0.003 cycles/sec.

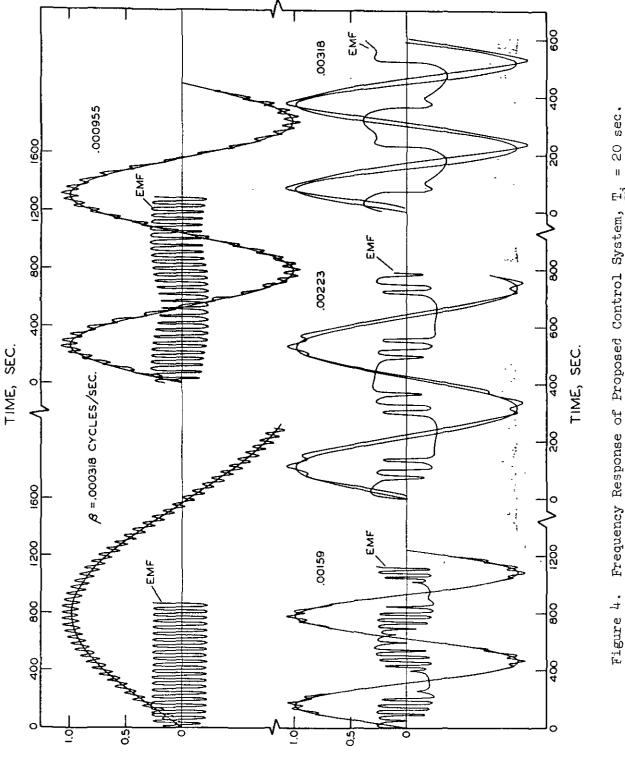
### RESULTS

The following values for system constants were used in the study.

T = 6 sec.,  $\gamma = 6 \text{ sec. and } 3.46 \text{ sec.},$   $\beta = 0.000318 \text{ to } 0.00318,$   $\frac{T_{1}}{R} = 10 \text{ to } 30 \text{ sec.}, \text{ and }$ k = 0.01 meq./mv.

Trials were conducted as follows: A value of  $\underline{T}_{\underline{1}}$  was selected and a set of five curves drawn as illustrated by Fig. 4. After a set of curves was finished, a new value of  $\underline{T}_{\underline{1}}$  was selected and another set of curves prepared. Each curve represents a certain frequency. First the plot of  $\underline{S}$  versus time is drawn, then the plot of  $\underline{R}$  versus time, and in one case, the e.m.f. versus time is also shown (Fig. 4).

Figures 4 and 5 show the results for  $\underline{T}_{\underline{1}} = 20$  and 28.6 sec. respectively. The S curve is the smooth sine wave, the R curve is the distorted waveform trying to follow the S curve. The frequency for S is indicated near each curve. All X axes are labeled time in seconds. The Y axes are labeled in

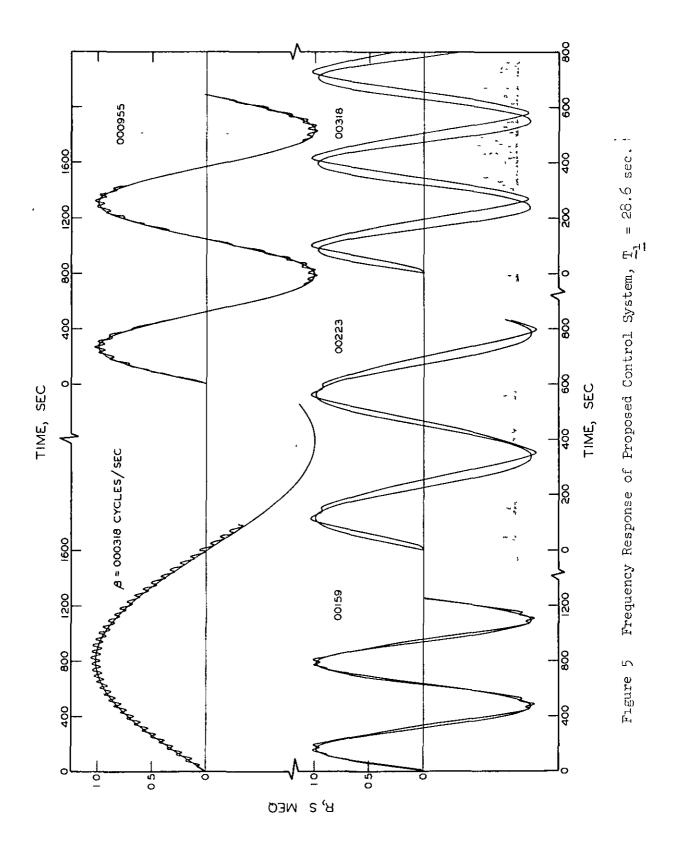


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Frequency Response of Proposed Control System,  $\underline{\underline{T}}_{\underline{\underline{L}}}$ Figure 4.



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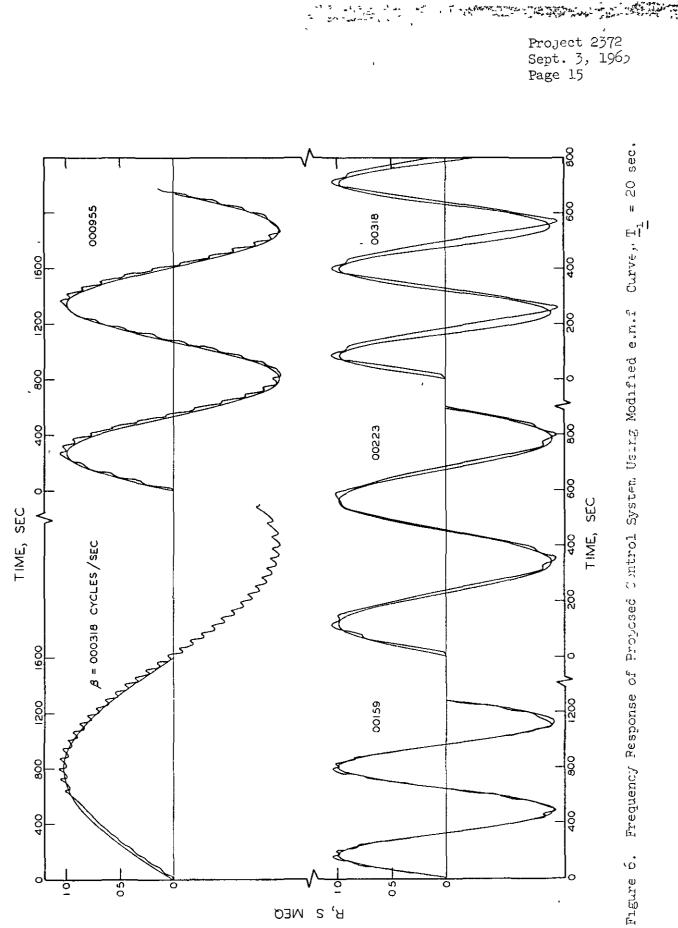
meq. (milliequivalents). For typical values of the flow rates used, a 1-meq. change corresponds to a 5-ma. change in electrolysis current.

Figure 6 shows the results for  $\underline{T}_{\underline{i}} = 20$  sec., using a modified e.m.f. versus  $\underline{S} - \underline{R}$  curve. The modification is indicated by the dashed curve on Fig. 3. Comparison of these results with those obtained using the unmodified e.m.f. curve show, perhaps, a slight improvement with the modified e.m.f. curve, especially at low frequencies where the amplitude and frequency of oscillation of the <u>R</u> curve about the <u>S</u> curve is reduced. This modification amounts to incorporating a dead zone into the e.m.f. signal (same as the dead band in the VHS relay of the control systems we have already used).

Response to a step change in sample concentration was also studied. The results, using the modified e.m.f. curve, are shown in Fig. 7. The <u>S</u> curve rises exponentially to its new value after the change is introduced. Because of the lag in the system, the <u>R</u> curve does not start to rise until some time after the step change has occurred.

The effect of decreasing lag has also been examined. Using a value of  $\tau$  = 3.46 sec. (compared with  $\tau$  = 6 sec. for the other case) Fig. 8 was prepared.

For this case,  $\underline{T}_{\underline{i}}$  was set at 20 sec. and the modified e.m.f. curve was used. To assess the improvement gained by decreasing the lag, Fig. 8 should be compared with Fig. 6. Response to a step function is shown in Fig. 9 ( $\underline{T}_{\underline{i}}$  = 20 sec.), and this should be compared with Fig. 7. A few curves were also prepared with  $\Upsilon$  = 0, Fig. 10. The result is remarkable; control is almost perfect.



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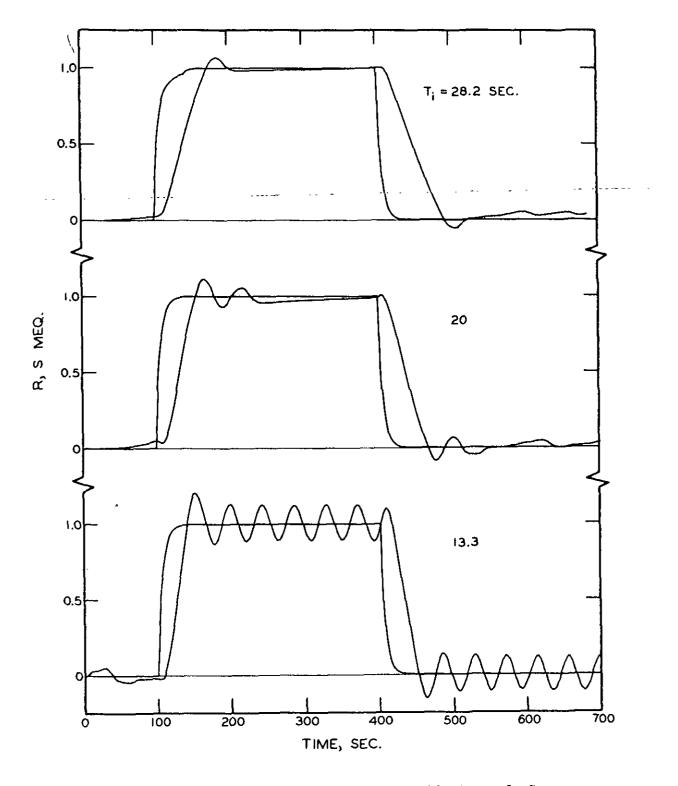
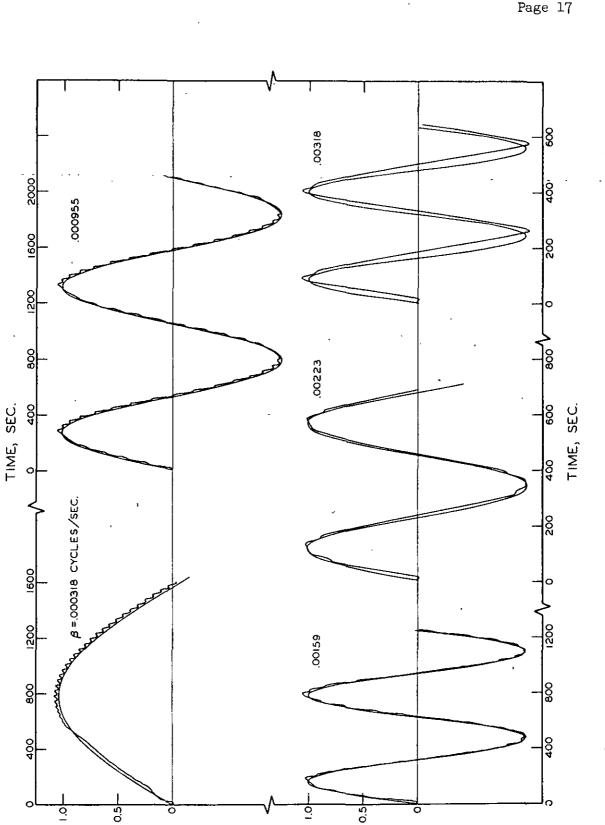


Figure 7. Response to a Step Function, Modified e.m.f. Curve

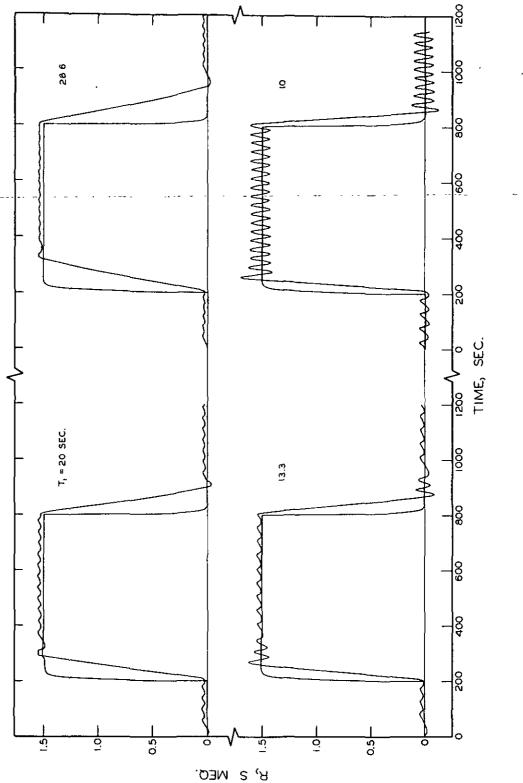


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= 3.46 sec. Frequency Response With Decreased Lag, Modified e.m.f. Curve,  ${\cal T}$ Figure 8.

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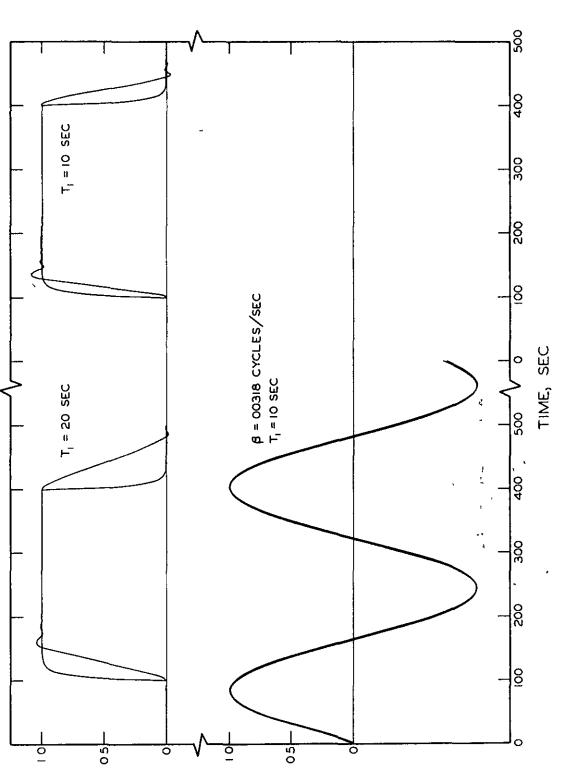
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Figure 10. Response With no Lag,  $\Upsilon$  = 0

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#### SPECIFICATION OF CONTROL SYSTEM

The purpose of this study was to determine whether or not such a control. system could work, and if so, to specify its characteristics.

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It is believed that the results of the study indicate that a control system of the nature simulated has real possibilities. It is also believed that use of the modified e.m.f. curve results in somewhat better performance.

Three components require specification:

- 1. An amplifier to receive the e.m.f. from the electrodes and convert it to the modified shape indicated by the dashed line of Fig. 3.
- 2. A power amplifier to receive the modified signal and drive a current-adjusting motor.
- 3. An appropriate motor.

The power amplifier should have an adjustable gain over a reasonable range and be able to provide a final rate of change of current of at least l ma./sec. Most likely, gears on the current-adjusting motor will have to be used to obtain rates of change in the desired range.

#### DESIGN OF MIXING CHAMBER

The study was carried out assuming the e.m.f. is measured in the mixing chamber. This may seem to be unreasonable but one of the basic assumptions underlying the mathematical development is that the solution in the mixer is homogeneous. If this is not true, the entire analysis is invalid. Therefore the mixer must provide adequate mixing. It should be possible to build a mixing

chamber into which very small calomel and platinum electrodes may be incorporated. If the e.m.f. is sensed in the tubing or in a separate chamber downstream from the mixer, the analysis of this report will not apply to the analyzer. Sensing the e.m.f. downstream from the mixer introduces another lag into the system which has not been accounted for.

It is also very desirable to minimize the mixer volume in order to minimize the time constant,  $\underline{T}$ . The analysis has been carried out assuming a mixer volume of 0.6 ml. and a flow rate through it of 0.1 ml./sec. (6 ml./min.). These are values which have been used.

#### REDUCTION OF LAG

Any effort made to reduce the distance-velocity lag between electrolysis cell and mixer will be worthwhile indeed. If this is reduced to a small enough value, most likely better performance would be achieved if the e.m.f. signal were used without a dead band at all (or at least with a very small dead band).

#### CONCLUSIONS

The study has demonstrated the promise of a truly continuous control system of the coulometric analyzer. It is believed that such a control system would be easier to trouble shoot and more reliable because fewer components would be required.

Specifications of a very broad nature have been given for the system.

# NOMENCLATURE

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E	z	$f(\underline{S} - \underline{R}) = e.m.f.$ signal from mixer, mv.			
<u>k</u>	=	proportionality constant, meq./mv.			
đ	Ξ	flow rate through mixer, ml./sec.			
<u>R</u>	н	hypobromite concentration in mixer, meq.			
Ri	=	hypobromite concentration upstream from mixer, meq.			
<u>s</u>	=	sample concentration in mixer, meq.			
<u>s</u>	=	zero to peak change in sample concentration, meq.			
<u>s</u> i	Ξ	sample concentration upstream from mixer, meq.			
<u>t</u>	Ξ	time, sec.			
$\underline{\mathbf{T}}$	=	$\underline{V}/\underline{q}$ = mixer time constant, sec.			
$\underline{T}_{i}$	=	integral time, sec.			
<u>v</u> _	=	mixer volume, ml.			
β	Ξ	frequency of oscillation of sample concentration, radians/sec. or cycles/sec.			
K	=	amplitude ratio, dimensionless			
Ð	÷	phase angle, radians			
7	=	distance-velocity lag from electrolysis cell to mixer, sec.			

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# APPENDIX

## ANALOG COMPUTER SETUP

The following equations were solved using a Heathkit computer (15 amplifiers):

$$\frac{dR}{dt} = \frac{1}{T} \left[ R_{1}(t - \gamma) - R \right]$$
(16),

$$\frac{dR_{1}}{dt} = \frac{1}{T_{1}} f(S - R)$$
 (17),

$$\frac{\mathrm{dS}}{\mathrm{dt}} = \frac{1}{\mathrm{T}}(\mathrm{S}_{1} - \mathrm{S}) \qquad (18),$$

 $S_{1} = S_{0} \sin\beta t \qquad (19).$ 

 $T = \gamma = 6 \text{ sec.}$  $\beta \stackrel{<}{=} 0.003 \text{ cycles/sec.}$ 

Because very low frequencies must be used, a time scale change is needed. Thus, let

$$\Theta = \frac{t}{10}$$
(20).

A change of t/100 would be more suitable. However, this cannot be done for a reason to be clarified later. Substituting Equation (20) throughout gives

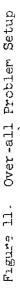
$$\frac{\mathrm{dR}}{\mathrm{d\Theta}} = \frac{10}{\mathrm{T}} \left[ R_1 \left( \Theta - \frac{r}{10} \right) - R \right]$$
(21),

$$\frac{dR_{i}}{d\Theta} = \frac{10}{T_{i}} f(S - R) \qquad (22),$$

$$\frac{dS}{d\theta} = \frac{10}{T}(S_i - S)$$
(23),

 $S = S_{o} \sin(10\beta \theta) \qquad (24).$ 

Figure 11 shows the over-all problem setup. (Values for all-resistors and condensers are listed in Table I.) Amplifier 2 solves Equation (21). Amplifier 1 sums <u>R</u> and <u>S</u> introducing a gain of 10 for convenience in setting up the function generator. The function generator was set up to provide  $f(\underline{S} - \underline{R})$  as shown on Fig. 3 (1 meq. = 10.0 volts, 100 mv. e.m.f. signal = l volt). Amplifier 5 solves Equation (21) providing  $\underline{R}_{i}(\underline{t})/\underline{k}'$ . The factor  $\underline{k}'$ is included to alleviate overloading the time delay network. The time delay network provides a true time lag for signals of frequency < 2 radians/sec. [Details about this network may be found in Johnson, C. L., Analog Computer Techniques, pages 128-131, McGraw-Hill (1956).] Inspection of Fig.12, which includes the circuit diagram for the time lag network, shows that very high gains must be used on Amplifiers 13 and 15 because of the factors  $\, \gamma \,$  and  $oldsymbol{\gamma}^2$  in the denominators of the coefficients. For small values of  $oldsymbol{\gamma}$  , the gains required become very high and unless small voltages are fed to the network, overloading results. This is also the reason for making the relatively small time scale change; a further reduction would have made  $\, \gamma \,$  too small. The time lag network provides  $\underline{R}_{i}(\underline{t} - \gamma)/\underline{k}'$  and the factor  $\underline{k}'$  is provided by the ratio  $\frac{R_{22}}{R_{21}}$  on Amplifier 2. When reading values of T from potentiometer setting 5A, this factor must be accounted for.



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A = FUNCTION GENERATOR FOR f(S-R), AMPLIFIERS 3 &

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DELAY NETWORK, AMPLIFIERS 11, 13-15 B = TIME

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# TABLE I

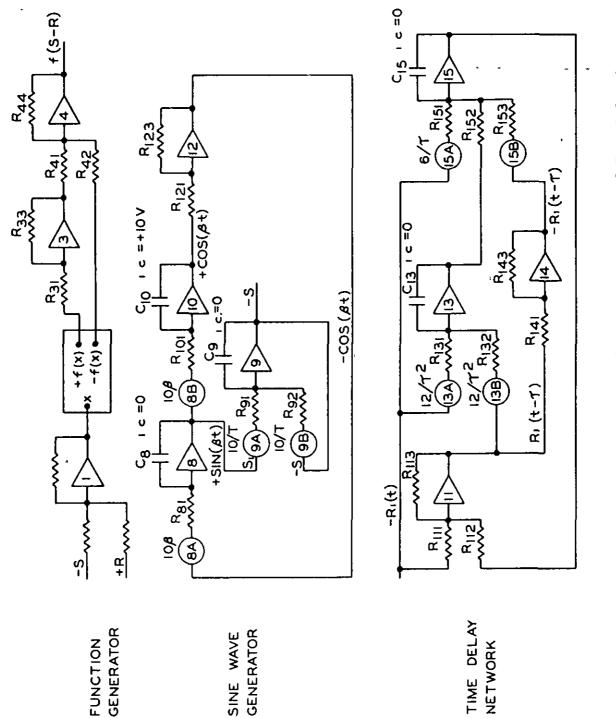
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TABULATION OF RESISTOR, CAPACITOR, AND POTENTIOMETER VALUES

Resis	tor	Capacitor	Potentiometer
R <sub>81</sub> = R <sub>101</sub> = R <sub>121</sub> =	5 M 1 M	$C_8 = 1 \mu f$ $C_{10} = 1 \mu f$	$8A = 8B = 0.1 - 1.0, (10\beta)$
R <sub>123</sub> ≠ .R <sub>91</sub> . ≠ R <sub>02</sub> =	l М _0.5 М 0.5 М		$9A = 9B = -0.833, -(\frac{10}{2T})$
$R_{131} =$	0.2 M	C <sub>13</sub> = 0.1 µf	$13A = 13B = 0.667, (\frac{12}{\gamma^2})$
R <sub>132</sub> = R <sub>151</sub> = R <sub>152</sub> =	0.5 M	C <sub>15</sub> = 0.1 µf	$15A = 15B = 0.5, (\frac{6}{7})$
<sup>R</sup> 153 <sup>≠</sup>	0.5 M		
R <sub>111</sub> = Basa =			s
R <sub>112</sub> = R <sub>113</sub> =			
R <sub>141</sub> =			
R <sub>143</sub> ≠ R <sub>21</sub> =	0.1 M	C <sub>2</sub> = lµf	$2A = 2B = 0.833, (\frac{10}{2T})$
$R_{22} = R_{51} = R_{11} = R_{11}$	5 M	C <sub>5</sub> = lµf	5A = 0.175 - 1.0
R <sub>12</sub> =	1 M		*
R_, ≠	10 M		
$\frac{1}{R}$	20 м 0.5 м	$c_7 = \pm \mu t$	7A = 0.1 - 0.2
R <sub>31</sub> = R <sub>33</sub> =	l M		
R <sub>41</sub> =	ΙM		
$R_{41} = R_{42} = R_{44} = R_{44} = R_{44}$	0.5 M 20 M		

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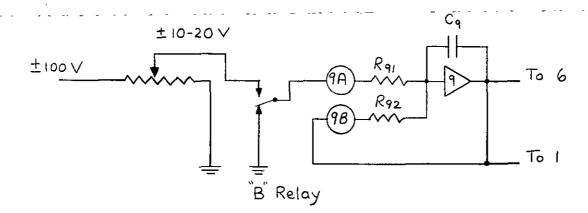
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Setup of Sine Wave Generator Function Generator, and Time Delay Circuit Figure 12.

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Amplifiers 8-12 represent the standard technique for generating sine waves. Amplifier 9 is included to solve Equation (23). In most cases, its effect is negligible, but it has been included for the sake of completeness.

Two modifications to these circuits were made. The first was to provide a step function instead of a sine wave input to Potentiometer 9A. This is indicated schematically below.



Step Change Available Upon Actuating B Relays

The second modification was to provide a smaller value of  $\gamma$  (decreased lag). This was accomplished by changing some resistor and potentiometer values in the time delay network. The new values are tabulated below:

 $\gamma$  = 3.46 sec. corresponds to  $\gamma$  = 0.346 sec. in machine time.

and the second and th Project 2372 Sept. 3, 1963 Page 29 Resistor Capacitor Potentiometer °13 R<sub>131</sub> = 0.05 M = 0.1 µf 13A = 13B = 0.5R<sub>132</sub> = 0.05 M с<sub>15</sub> 15A = 15B = 0.866= 0.5 M R 151 0.1 µf = • •  $R_{153} = 0.5 M$ R 51 = 10 M ≃ 0.05 M R 21

From these listings of resistor, capacitor, and potentiometer values, the computation of values of the system constants should be straightforward.

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# PROJECT REPORT FORM

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PROJECT NO 2372							
COOPERATOR Institute of Paper Chemistry							
REPORT NO One March 5, 1963							
SIGNED K. M. Hardacher							
K. W. Hardacker							

### MODIFICATION OF COULOMETRIC ANALYZER SEQUENCING PATTERN

The coulometric analyzer developed for the automatic analysis of alkaline pulping liquors has been described in Progress Report 4, Project 2067. That report indicated that the performance of the instrument would be improved if the sequence of generator cell current increments were modified to permit the instrument to follow the liquor concentration changes more closely. This has now been done by replacing the stepping relay with an add-or-subtract relay chain for increment selection, adding a 10-second delay interval between the accumulation of an excess count and the shift to the next longer adjustment increment, and arranging to erase the countsaccumulated chain when the polarity signal relay stays open, that is, when the instrument is operating at the chemical equivalence point.

The attached block diagram indicates the present functional arrangement. The increment selection sequence is as follows. At start-up, the interrupting pulse will momentarily open the polarity signal relay. This relay will then close as dictated by the polarity of the emf. The coarse, medium, and fine increment relays will be energized simultaneously on the subsequent arrival of an incrementing pulse. The generator current adjustment motor will then run, in the direction determined by the polarity, for the longest increment energized (coarse). Successive coarse increments will continue to be made until the chemical equivalence point is passed, at which time the emf polarity will reverse. This polarity reversal will

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prepare the generator current adjustment motor for change in the direction of its rotation, erase all counts from the counting chain (counts of coarse increments are accumulated but have no effect on increment selection), and subtract one (removing the coarse increment relay) from the increment selection chain.

Medium increments of current adjustment will now be made. Assuming the equivalence point is passed again before an excess count has accumulated on the counting chain, the polarity signal will reverse. This will again prepare the generator current adjustment motor for change in the direction of its rotation, erase all counts from the counting chain, and subtract one (this time removing the medium increment relay) from the increment selection chain.

Fine increments of generator current adjustment will now be made as the instrument cycles about the equivalence point. Polarity change signals will erase all counts from the counting chain, but will have no effect on the increment selection chain since there are no more relays to be subtracted. Fine increment adjustments are made only when a + or - polarity signal is present. At the equivalence point, no polarity signal is present. In this latter situation, the incrementing pulse is diverted from the fine increment relay and is used instead to erase all counts from the counting chain. If the liquor concentration changes so rapidly that the equivalence point cannot be passed in five successive unidirectional fine increments, an excess count signal will leave the counting chain. After a 10-sec delay interval, this signal will add one (the medium increment relay) to the increment selection chain and erase all counts from the counting chain in preparation for counting

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the medium increments. (If, however, the last fine increment causes the equivalence point to be passed, the polarity reversal will subtract one from the increment selection chain before the next incrementing pulse. The instrument will then continue, uninterrupted, with fine increments.)

With medium increments being made, passage of the equilibrium point in less than the number of counts (3, 4, or 5) set on the medium increment count selection switch will return the instrument to operation in fine increments. If the equilibrium point is not passed in the set number of medium counts, an excess count signal will leave the counting chain and cause the coarse increment relay to be connected in the same manner as an excess fine increment count causes the medium increment relay to be connected. Operation with coarse increments will then continue until the equilibrium point is passed.

The Micropositioner relay (S126), which was blamed for occasionally causing the polarity relay (S107) to get irreversibly out of step, was replaced with a Sigma type 72A0Z-1000-TCP relay (S126a). Considerable improvement in performance was then obtained by additionally inserting the coil of a relay identical with the fine interlock relay (S103) in series with the coil of S126a. The emf generated by field collapse on interruption of current in this additional coil now bucks the emf generated by field collapse on interruption of current through the coil of S103, thereby preventing this latter emf from flowing through and momentarily energizing the coil of S126a in the reverse direction. (It is felt this momentary, unwanted current flow probably accounted for most of the difficulty with the Micropositioner.)

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Some minor changes in the functioning of the main switch (S101) have been made. Its present operation is tabulated below.

OFF	STANDBY	RUN
All off	J101 on	J101 on
	J102 off	J102 on
	J103 on	J103 on
	J104 on	J104 on
	J105 on	J105 on
	J106 on	J106 on
	+24V on	+24V on
	-24V on	-24V on
	Dummy load connected	Generator cell connected
	Counting chain reset to zero	Counting chain operative
	Increment selection chain reset to coarse	Increment selection chain operative
*		Clock timers energized
		Power to current adjustment motor

