A COLORIMETER FOR IN-LINE ANALYSIS
OF URANIUM AND PLUTONIUM SOLUTIONS

by

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ABSTRACT

A colorimeter is described that can be used to
monitor process solutions continuously for
uranyl nitrate or plutonium nitrate concentration.
The instrument was tested under plant conditions
in the concentration range from 0.1 to 70 grams
of uranium per liter and 0.1 to 10 grams of
plutonium per liter. The instrument error was
±1% of the span, but errors of 15 to 20% can be
caused by other variables such as acidity and
other salts present.

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A COLORIMETER FOR IN-LINE ANALYSIS
OF URANIUM AND PLUTONIUM SOLUTIONS

INTRODUCTION

In the process of separating uranium and plutonium from spent reactor fuel elements, it is advantageous to monitor the concentration of these products in the various process streams. A gamma absorptometer was designed for this application[1] but only concentrations greater than about 10 grams per liter can be measured with this instrument. Furthermore, the gamma absorptometer cannot operate satisfactorily when the gamma radiation from the sample cell exceeds about 25-50 mr/hour.

A colorimeter was designed to satisfy the need for an instrument to monitor the lower concentrations and to operate in a field of high radiation.[2] This early instrument proved the feasibility of using a colorimeter to monitor a process stream continuously for uranium concentration. However, some design improvements were needed to decrease the zero drift, to provide a remote method of standardization, to compensate more effectively for turbidity in the solution, and to compensate for fouling of the optical components. This report describes a colorimeter that avoids these shortcomings of the earlier design.

SUMMARY

The new instrument uses the dual-beam principle to compensate for darkening of optical components and for turbidity in the solution. A pulsating light source and AC amplifiers are used in the measuring system to eliminate the drift that would result with a DC system. A method of remote standardization is included in the instrument, which permits a periodic check and readjustment of the calibration.

The colorimeter was used to measure the concentration of either uranyl nitrate or plutonium nitrate in solution. The instrument was tested under plant conditions with calibrations in the range from 0.1 to 10 grams of Pu(III) or Pu(IV) per liter and from 0.1 to 70 grams of uranium per liter. The accuracy of the measurements was found to be limited by the effects of extraneous solution variables rather than instrument noise or drift. The combined noise and drift produced an error of about ±1% of the recorder span, while variations in temperature, turbidity, and nitric acid concentration in the solution can produce errors of 15 to 20% of the span.

DISCUSSION

GENERAL PRINCIPLES

A colorimeter may be used to measure the concentration of a chemical in a solution if the chemical imparts a characteristic color to the solution. The colorimeter optical system isolates a narrow wave

band of light at a selected absorption peak for the chemical that is measured. The intensity of the transmitted light at the absorption wave length is a function of the concentration of the chemical in the solution. When only the light at this wave length is used, Beer's law is obeyed and maximum sensitivity is obtained for the instrument. Use of the narrow wave length band usually makes possible the elimination of the absorption effects of other chemicals in the solution. However, the effect of some chemicals cannot be eliminated if they change the complex ion formation of the chemical being measured. This is the case when uranyl nitrate is measured in a solution containing nitric acid.

A more stable colorimeter can be made if the dual-beam principle is utilized. This is usually accomplished by comparing the light intensity at an absorption wave length with the intensity of a reference beam from the same light source. The two beams are obtained by passing a beam of white light through the solution and then separating the beam into two parts. Filters are used to isolate an absorption wave length as well as a reference wave length. The reference filter is selected to pass only light at a wave length that is not absorbed by any chemicals in the solution. The two beams may then be compared by taking the ratio of their intensities to obtain an indication of the concentration of the chemical being measured. In this way, the instrument compensates for changes in the transmitted light intensity caused by darkening of the light bulb, fouling of optical components, and turbidity in the solution.

DESIGN OF THE INSTRUMENT

GENERAL DESIGN

The colorimeter described here is a dual-beam instrument that uses a pulsating light source. As a result, the instrument is unaffected by changes in phototube dark current and, since AC amplifiers can be used in the measuring circuit, the drift that usually results from using DC amplifiers is eliminated. The pulsating light is obtained by turning the light on and off with a synchronous multivibrator that operates at a frequency of 15 cycles per second. The light is collimated and passed through the sample cell. The light beam is then divided by a beam splitter to produce an absorption beam and a reference beam. These beams pass through interference filters that isolate a 7-10 mμ band of light at the specified wave lengths. The light beams then fall on phototubes, which produce electrical signals proportional to the light intensity. The resulting electrical signals are amplified by a preamplifier located in the optics housing and are then fed to a remotely located amplifier. The amplified currents are indicated on separate ammeters, and the ratio of the absorption to the reference current is indicated on a recorder. The recorder is wired so that an upscale deflection is obtained for increased concentration of the chemical being measured. The complete instrument is shown schematically in Figure 1.

The instrument is standardized by energizing two rotary solenoids that
rotate mirrors into the light beam to divert the beam around the
sample cell. In the standardizing position, the current indicated
on the ammeter in each channel and the recorder reading should be the
same value that they had at the initial calibration. If, during a
standardization check, the readings are observed to have changed, the
amplifier gain controls can be adjusted to obtain the readings
determined previously so that the instrument is readjusted to the
original calibration.

COMPONENT DESIGN

The colorimeter consists of two groups of components. The first
group is located at the solution sampling point and consists of the
optics housing and the power supply for the light source. The
optical system, sample cell, and preamplifier are all located in the
optics housing. A photograph of the optics housing is shown in
Figure 2. The second group of components may be located remotely
and include the amplifier, the recorder, and the solenoid power supply.
A photograph of these components is shown in Figure 3.

Optical System

A diagram of the optical system is shown in Figure 1. The light path
is indicated for both the measuring and the standardizing positions.
The light bulb is a GE #2331 prefocused headlight bulb, which should
last for at least three months provided it is well ventilated. The
transmission wave lengths of the interference filters depend on the
chemicals being measured. The table in Figure 1 gives the absorption
and reference wave lengths for $UO_2(NO_3)_2$, and for Pu(III) and Pu(IV).
The optical parts of the system can withstand gamma activity from the
sample of up to 16 roentgens per hour at one inch for one year if the
lenses and cell windows are made from nonbrowning glass and front
surface mirrors are used.

Light Power Supply

The voltage for the light source is obtained from a 6.3-volt 60-cycle
supply that is turned on and off 15 times per second. The power is
interrupted with a relay located in the plate circuit of a 6L6 vacuum
tube that is controlled by a synchronous multivibrator. A diagram of
the circuit is shown in Figure 4. The 10K adjustable resistor must
be adjusted to obtain the wave form shown on the circuit diagram.

Sample Cell

The sample cell was designed for in-line installation and consists of
a stainless steel block that contains a cylindrical sample compartment.
Inlet and outlet tubes are provided for continuous circulation of a
sample stream. Glass windows are used to cover the sample compartment

and allow transmission of the light beam through the solution. The cell is constructed so that the glass windows seat against the steel block to maintain a constant cell thickness. A leaktight seal is made with gaskets at the outside surface of the glass. A drawing of the cell is shown in Figure 5.

The thickness of the sample cell is dependent on the chemical to be measured and the concentration range to be covered. The thickness is usually made optimum for a concentration at the center of the absorption range to be covered. The cell thickness for maximum sensitivity at a given concentration may be calculated from the following equation, which is derived in the Appendix.

Cell thickness = (molar extinction coeff.)$^{-1}$ x (concentration)$^{-1}$

Preamplifier and Amplifier

The circuit diagram of the preamplifier is shown in Figure 6. This unit is located in the bottom of the optics housing and can be easily removed for replacement purposes. The circuit contains a stage of amplification and a cathode follower output for both the absorption and reference channels.

A circuit diagram of the amplifier is shown in Figure 7. This circuit contains a stage of amplification, a cathode follower, and a rectifier circuit for each channel. A twin "T" filter is used in a negative feedback loop to cancel out unwanted signals of other frequencies. After amplification, the absorption and reference signals are rectified and sent to the ratio recorder. A Brown recorder was converted to a ratio recorder as shown in the circuit diagram in Figure 7. A 5K potentiometer to adjust the recorder ratio is located in the amplifier circuit. A Helipot was geared to the recorder balance motor and used as the slide wire. A photograph of this modification is shown in Figure 8.

Solenoid Power Supply

A solenoid power supply is used as the voltage source to turn the rotary solenoids during standardization. When the "On" button is pushed, the solenoids are energized for a period of about three minutes. At the end of this time a thermal delay relay turns them off. The time delay is used because the solenoids produce excessive heat if used continuously, and in addition, the automatic cutoff prevents leaving the mirrors in the standardizing position. The voltage can be turned off before the three minutes is up by pushing the "Off" button. A diagram of this circuit is shown in Figure 9.

CALIBRATION

Before a colorimeter is placed in operation, the instrument must be adjusted and calibrated for the desired range of the chemical to be

measured. The general method of calibration is to obtain solutions
that cover the concentration range of the chemical to be measured
and contain the normal concentration of any other interfering chemical
that will be in the solution to be measured. Then, with alternate
flow through the cell of two solutions that have the minimum and
maximum concentrations, the instrument may be adjusted so that these
concentrations produce, respectively, zero and nearly full-scale
readings on the recorder. This is accomplished by adjusting the gain
controls and the recorder ratio control. The current in the absorption
channel should be near, but should not exceed, the full-scale meter
reading with the lowest concentration in the sample cell. The
reference current should be adjusted to produce a mid-scale current
reading. If a full-scale recorder deflection cannot be obtained for
the desired concentration range, the sensitivity may be increased by
inserting an appropriate resistor in series with the Helipot slide
wire in the recorder. The resistor should be connected on the ground
side of the Helipot. After these adjustments have been made, the
calibration curve can be completed with the remaining solutions.
Calibrations have been made with uranyl nitrate in the range from
0.1 to 70 grams of uranium per liter and with plutonium(III) nitrate
and plutonium(IV) nitrate in the range from 0.1 to 10 grams of
plutonium per liter. These calibration curves are shown in Figures
10 and 11.

In practice, the above calibration must be made in the laboratory.
Therefore, it was necessary to devise a procedure for recalibrating
an instrument after installation on a process stream. Calibration
points were obtained by substituting standard optical filters in the
light path in place of the solution immediately after the instrument
is calibrated with standard solutions. The filters selected should
have the same absorption characteristics as the material being
measured so that on-scale current and recorder readings may be
obtained. Two such filters may be selected to correspond to concen-
trations near each end of the recorder scale. With the filters in
place the current and recorder readings should be taken. The
instrument may be recalibrated after installation by inserting one
of the filters in the light beam and readjusting the amplifier gain
and recorder ratio controls to reset the current and recorder readings
to the values obtained with the filter during the initial calibration.
The second filter may then be inserted to determine if the range of
the instrument is correct. In practice it was easier to make the
filter checks with the sample cell removed to eliminate the necessity
of cleaning and drying the cell.

STANDARDIZATION

A method of standardization was included in the instrument so that a
calibration check could be made without removing the sample cell from
the optics housing and without the standard filters used as outlined in
the previous section. During standardization, the light beam is diverted

around the sample cell. The current and recorder readings for this
condition should be recorded immediately after the instrument is
calibrated. These values should be reproduced each time the
instrument is standardized. If the instrument readings are not
reproduced the gain controls may be adjusted to obtain the correct
readings. However, some method must be provided to obtain an
on-scale recorder reading in the standardizing position if zero
concentration of the chemical being measured does not fall on the
recorder scale. This may be accomplished by inserting a filter in
the standardizing light path that has the same absorption properties
as the chemical to be measured.

An alternate method of obtaining an on-scale recorder indication
during standardization is to switch a second set of gain controls
into the circuit at the same time the light beam is diverted around
the sample cell. These controls should be adjusted after the
instrument is calibrated to produce a convenient recorder reading.
The instrument readings obtained may be used during subsequent
standardization checks. If the instrument readings are not reproduced
during standardization, the fine gain controls may be adjusted to
obtain the correct readings. These fine gain controls are in the
circuit during both measuring and standardizing so that if they are
adjusted during standardization they produce a similar effect when
the switch is returned to the measuring position. The instrument is
thus returned to the original calibration.

EVALUATION OF THE INSTRUMENT

The colorimeter has been tested under actual plant conditions for use
in measuring uranyl nitrate and plutonium nitrate. The precision and
accuracy of the measurements were found to be limited by the effect
of other variables in the solutions rather than instrument noise or
calibration drift. With the instrument calibrations shown in Figures
10 and 11, the combined instrument noise and drift is about ±1% of
the recorder span. However, the effects of temperature, turbidity,
and acid concentration may produce a much larger error. The effects
of these variables have been determined in the laboratory for uranyl
nitrate solutions.

The temperature effect was determined by calibrating the instrument
with solutions at 28, 40, and 50°C. The 22°C increase in temperature
caused the reading for uranium to increase about 7%. The effect will
probably vary with sample cell thickness. This test was made with a
cell thickness of 1-3/4 inches. The calibration curves obtained at
the different temperatures are shown in Figure 12.

The turbidity effect was determined by adding organic solvent to the
uranyl nitrate solutions. The solvent was beaten into the solution
and circulated rapidly through the colorimeter. The turbidity, which
resulted from an addition of 0.3% solvent, caused the current at the

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absorption wave length to decrease by about 50%. However, the reference current also decreased so that the ratio circuit compensated for most of the change. The resulting change in the uranium indication was a maximum of about 5%. The amount of solvent was increased to 0.6%, which resulted in further decrease of the currents and increased the error to a maximum of about 10%. The results of this test are plotted in Figure 13.

The effect of the organic solvent was reduced to less than 1% by installing a separator-degasser in the inlet sample line. This device, which contains a decanting system, is similar to a degasser described in a previous report[3].

The acid effect on the instrument was determined by varying the nitric acid concentration from 0 to 1 molar in the uranyl nitrate solutions. The results as shown in Figure 14 indicate that an increase of one molar acid increases the uranium indication by 15%. Therefore, when nitric acid is present in a uranyl nitrate solution an accurate measurement cannot be obtained unless the acid concentration is held relatively constant and the instrument is calibrated with solutions that contain the normal acid concentration.

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APPENDIX

CALCULATION OF OPTIMUM CELL THICKNESS

The transmission of light through a solution at an absorption wave length of the chemical in the solution may be expressed by the equation

$$I_A = I_O e^{-ECT} \qquad (1)$$

The symbols are defined as follows.

I_A = intensity of the light beam emerging from the solution

I_O = intensity of the light beam emerging when the chemical concentration is zero

E = molar extinction coefficient of the chemical, liter/(mol)(cm)

C = concentration of the chemical, mol/liter

T = thickness of the cell, cm

In the colorimeter, the intensity of the absorption beam is compared with a reference beam that is not attenuated by the chemical to be measured. The intensity ratio of the two beams is taken and indicated on a recorder that is wired to produce an upscale deflection for increased absorption.

Recorder indication, $R = - \dfrac{I_A \text{ (Intensity of Absorption beam)}}{I_R \text{ (Intensity of Reference beam)}}$

or

$$R = - \left[\frac{I_O e^{-ECT}}{I_R} \right] \qquad (2)$$

The sensitivity of the instrument may be defined as

$$\frac{dR}{dC} = \frac{I_O}{I_R} ETe^{-ECT} \qquad (3)$$

To find the cell thickness for a maximum $\dfrac{dR}{dC}$ and a given E and C the following expression may be used.

$$\frac{d\left(\dfrac{dR}{dC}\right)}{dT} = 0$$

- 11 -

or

$$\frac{d\left(\frac{dR}{dC}\right)}{dT} = \frac{I_O}{I_R} Ee^{-ECT} (1-ECT) = 0$$

and

$$T = \frac{1}{EC} \tag{4}$$

It may be shown that this is a maximum by substituting values of $T <$ and $> \frac{1}{EC}$ in equation (3).

If the molar extinction coefficient is unknown for the chemical being measured, the optimum thickness may be found with the instrument by using a standard cell of known thickness and filling the cell with the concentration of the chemical for which the optimum thickness is to be found.

Solving equation (1) for E and substituting for the cell thickness, T_1, used in the measurement yields the equation

$$E = \frac{1}{CT_1} \ln \frac{I_O}{I_A}$$

$$I_O = K_1 i_O$$

$$I_A = K_2 i_A$$

i_O = current in measuring channel at zero concentration

i_A = current in measuring channel at concentration for optimum thickness

K_1 and K_2 are constants and $K_1 = K_2$ if the instrument gain controls are not changed during the measurement. Therefore

$$E = \frac{1}{CT_1} \ln \frac{i_O}{i_A}$$

Substituting for E in equation (4) yields the equation

$$T = \frac{T_1}{\ln i_O - \ln i_A}$$

Therefore, if values of i_O and i_A are determined with any convenient cell thickness, T_1, the optimum thickness, T, may be calculated.
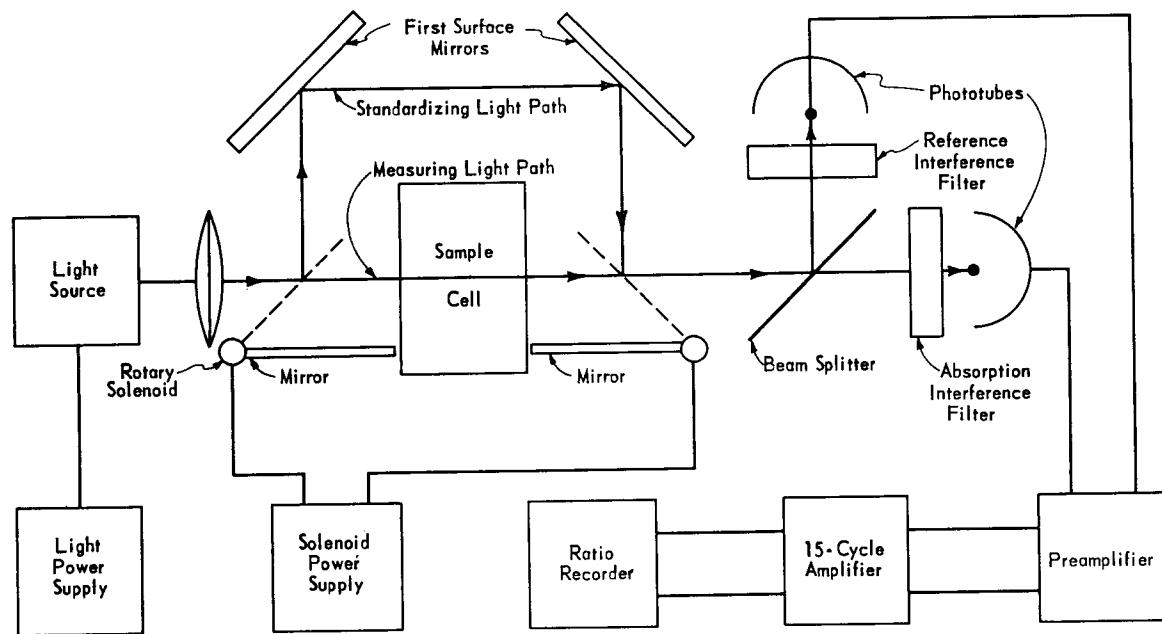
| Compound | Wave Length of Interference Filters | |
	Absorption	Reference
$Pu(NO_3)_3$	564 mμ	490 mμ
$Pu(NO_3)_4$	476 mμ	515 mμ
$UO_2(NO_3)_2$	416 mμ	542 mμ

FIGURE 1 – FUNCTIONAL DIAGRAM OF THE COLORIMETER
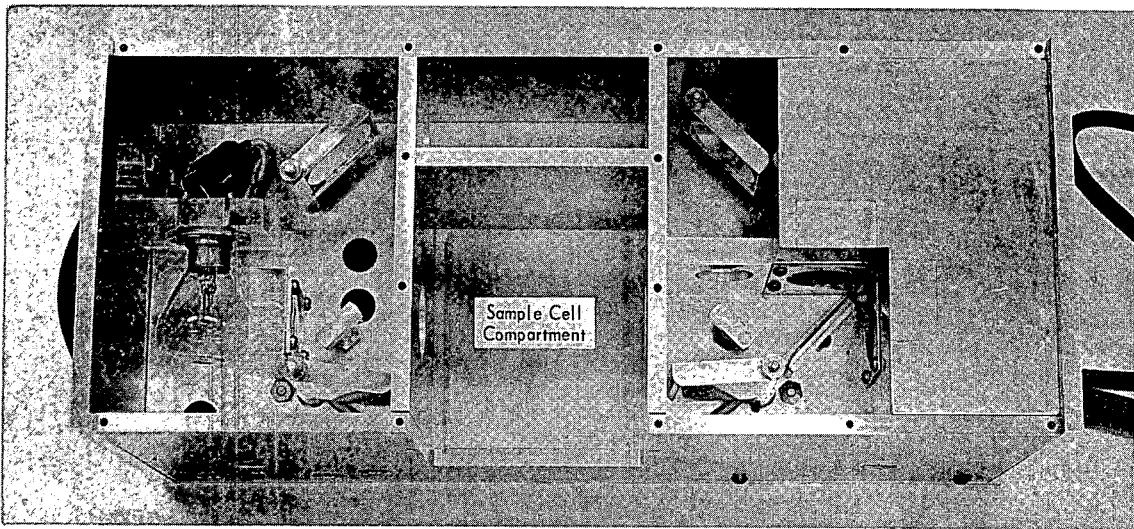
Top View
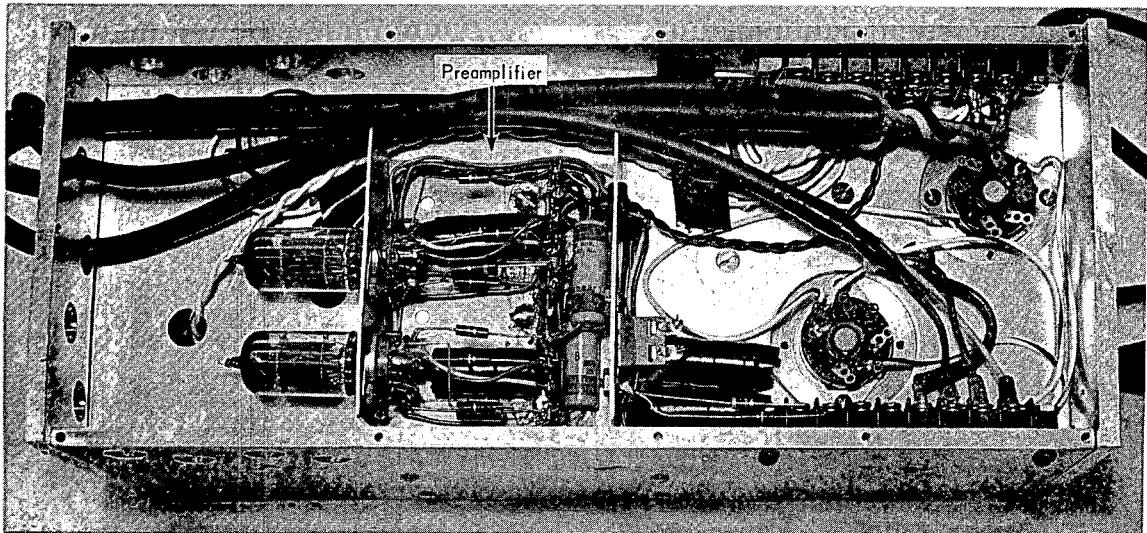
Bottom View

FIGURE 2 — PHOTOGRAPH OF THE COLORIMETER OPTICS HOUSING

Light Power Supply

Amplifier

Solenoid Power Supply
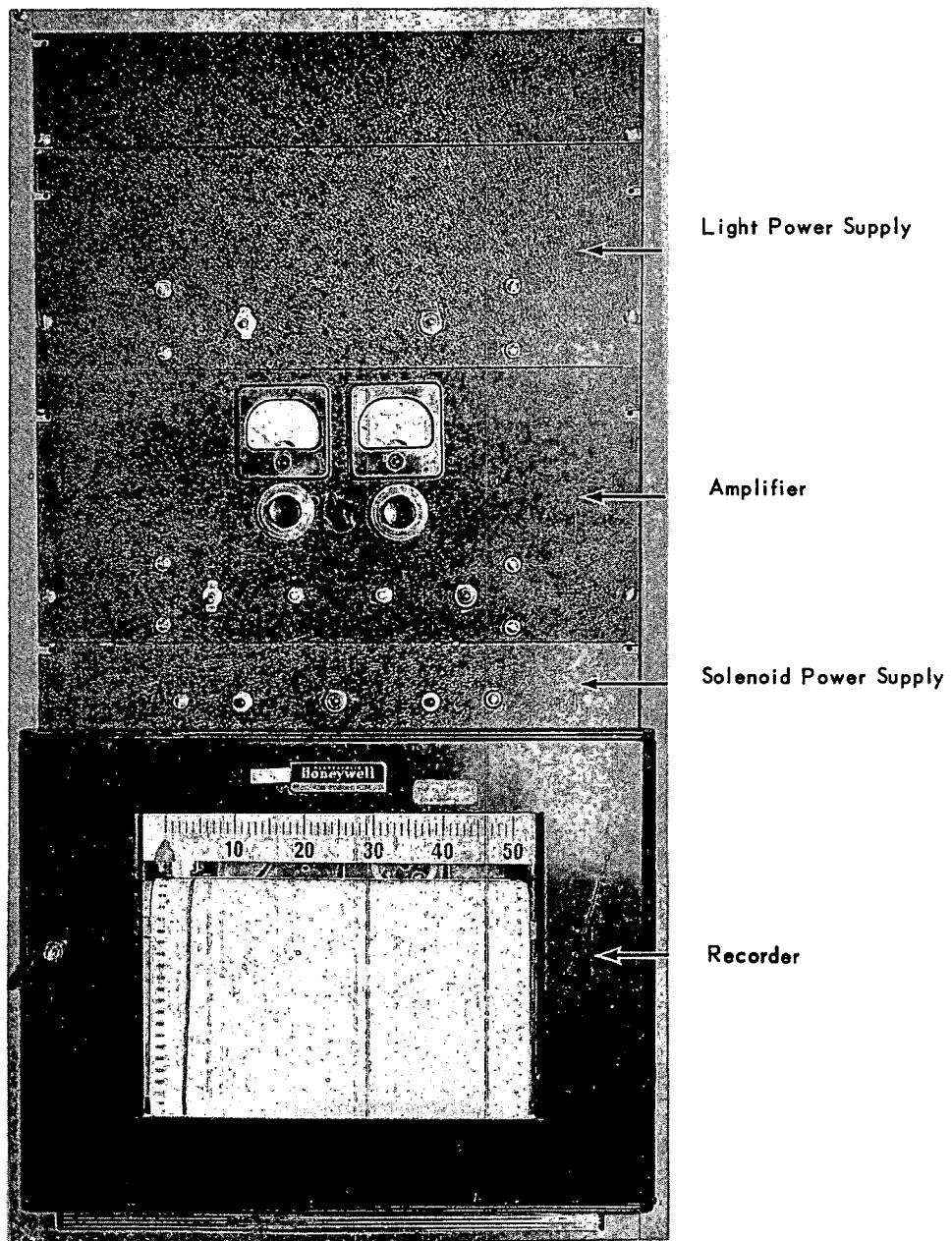
Recorder

FIGURE 3 – PHOTOGRAPH OF THE COLORIMETER MEASURING SYSTEM
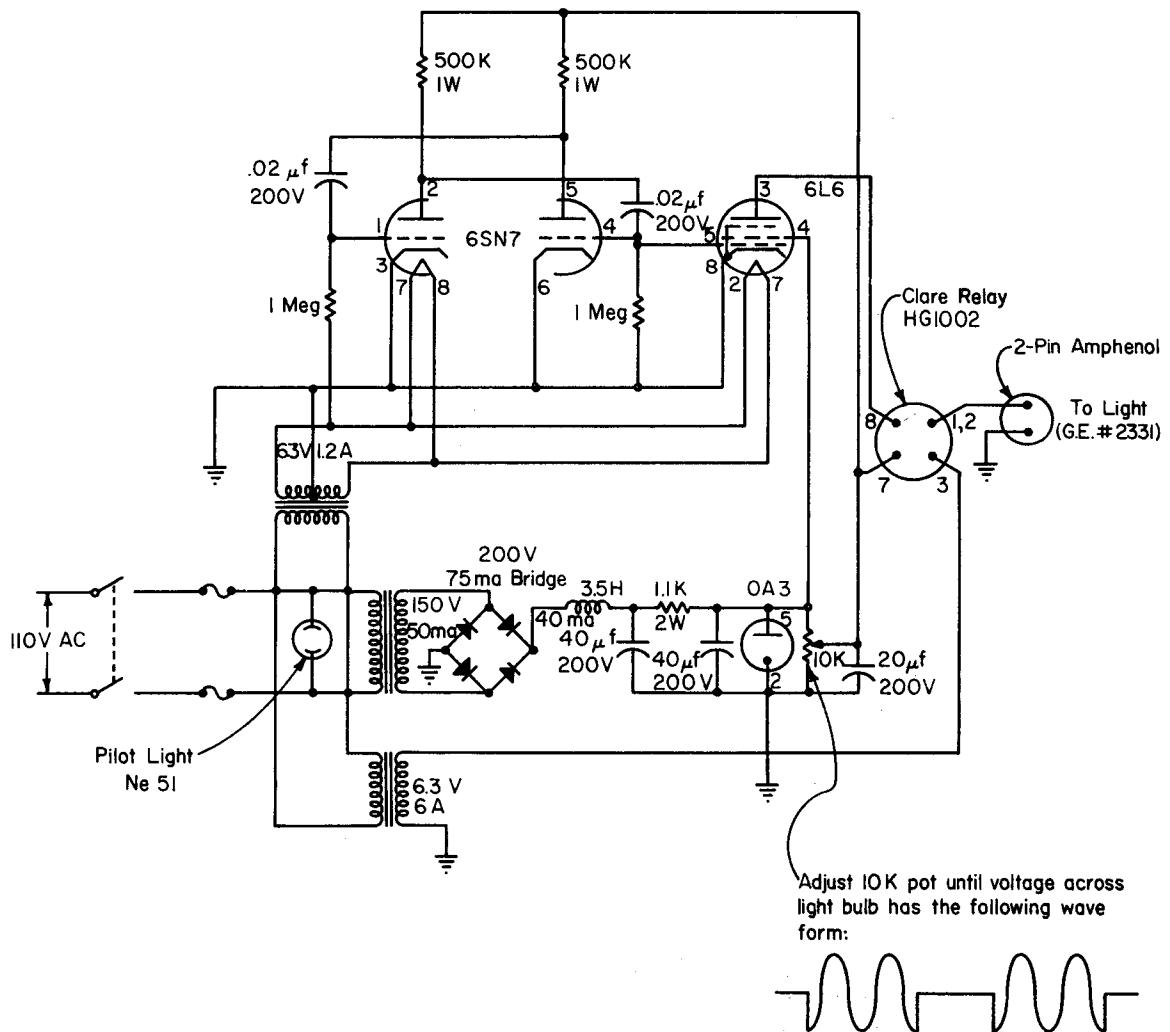
FIGURE 4 – LIGHT POWER SUPPLY

Side

Glass Windows

"Teflon" Gasket

3-1/16 in. Max.

Cross Section
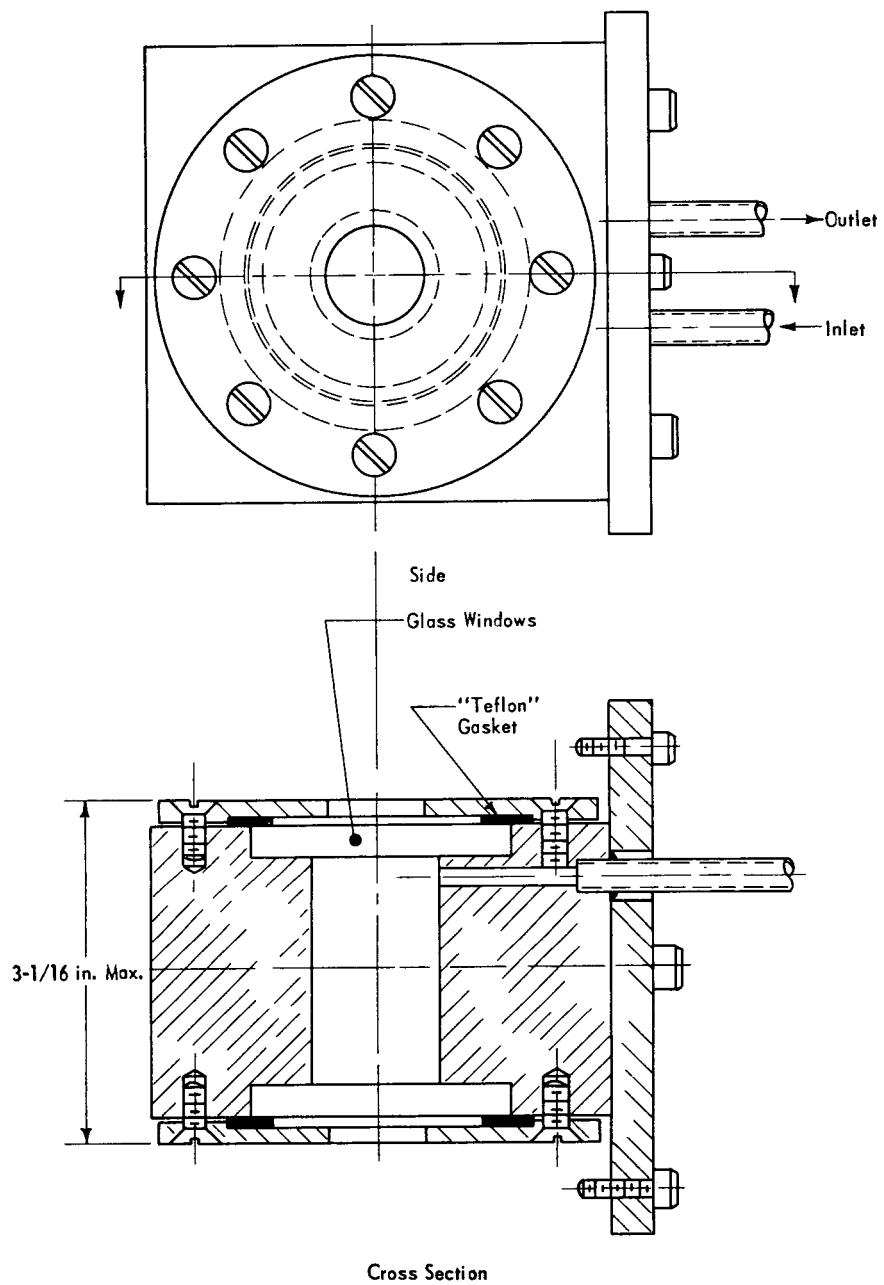
FIGURE 5 - SAMPLE CELL
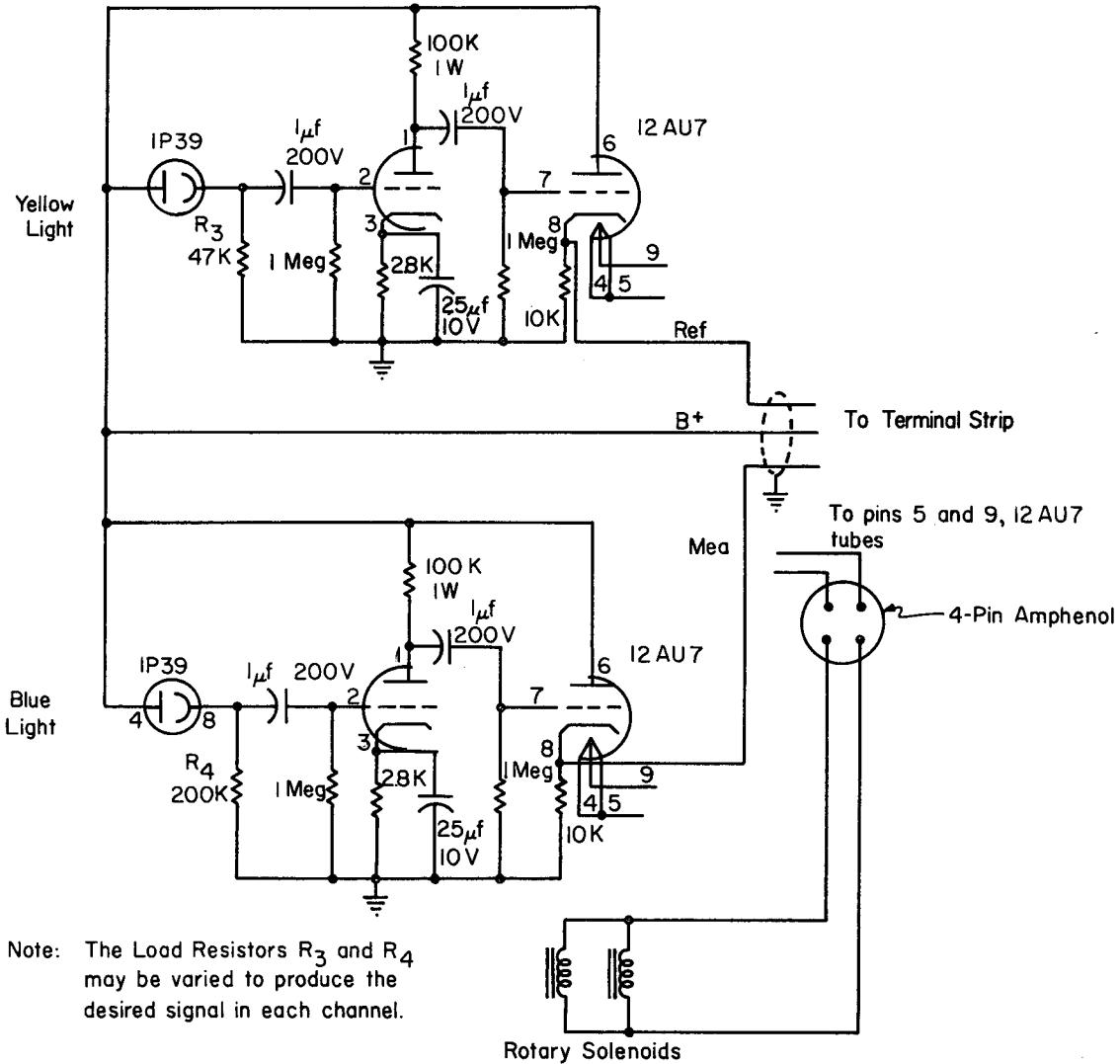
FIGURE 6 – PREAMPLIFIER CIRCUIT
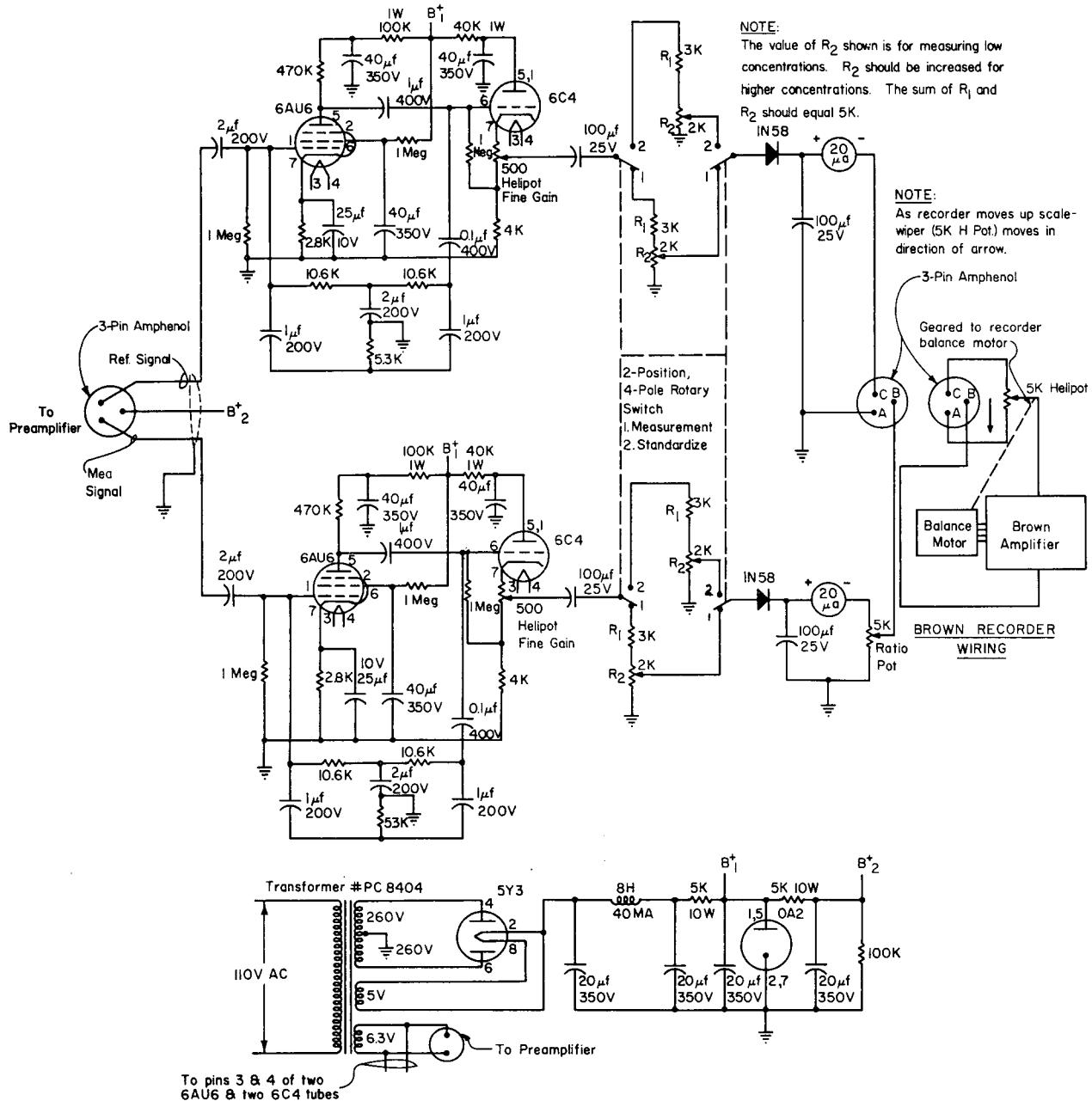
FIGURE 7 - AMPLIFIER CIRCUIT

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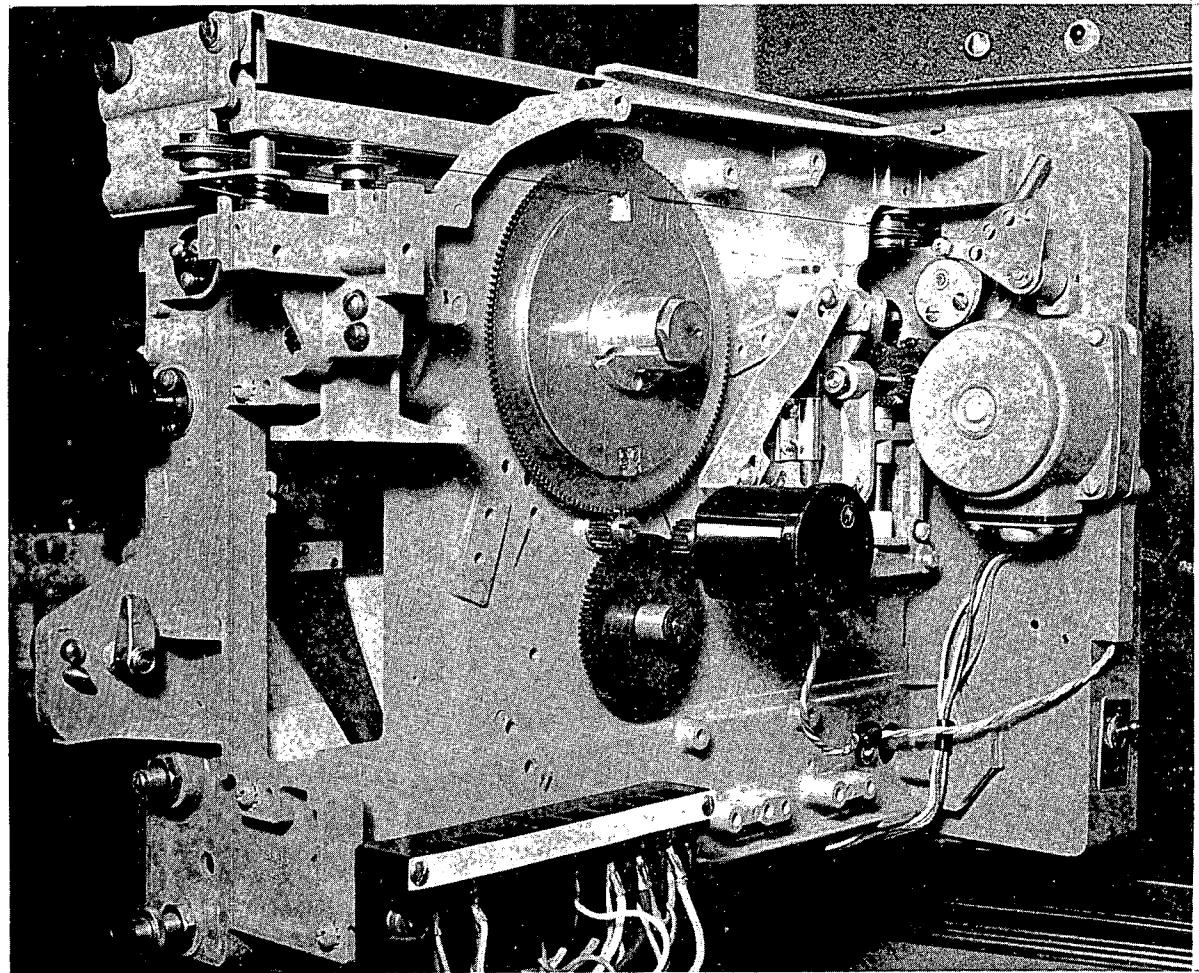
FIGURE 8 — MODIFICATION OF BROWN RECORDER
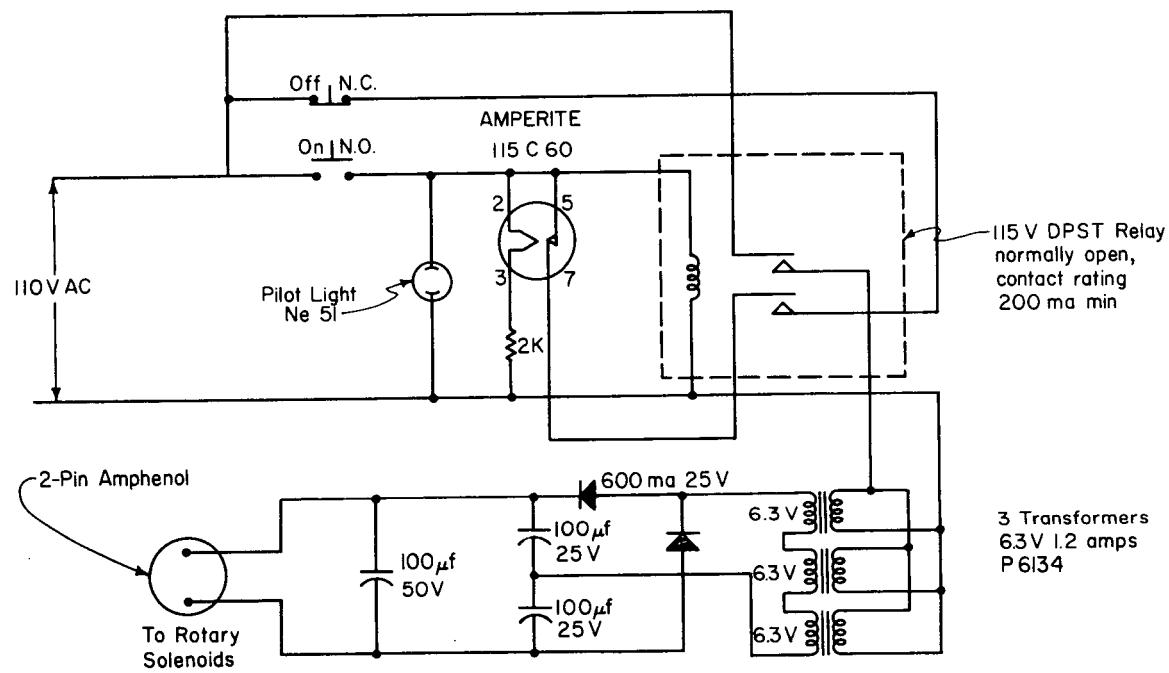
FIGURE 9 - SOLENOID POWER SUPPLY
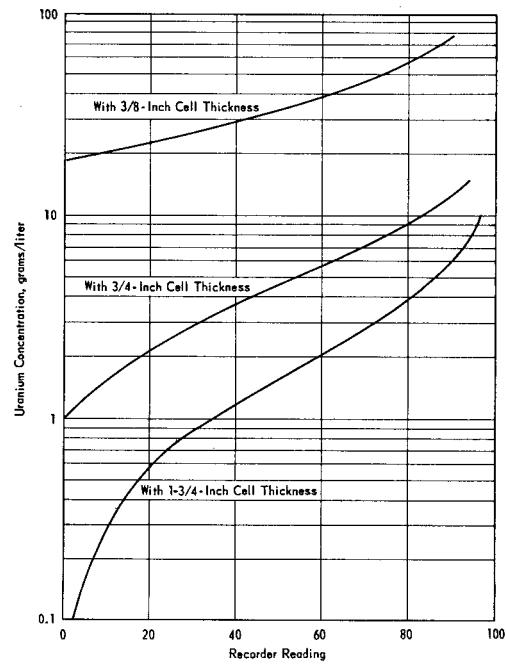
FIGURE 10 — CALIBRATION CURVES FOR URANYL NITRATE
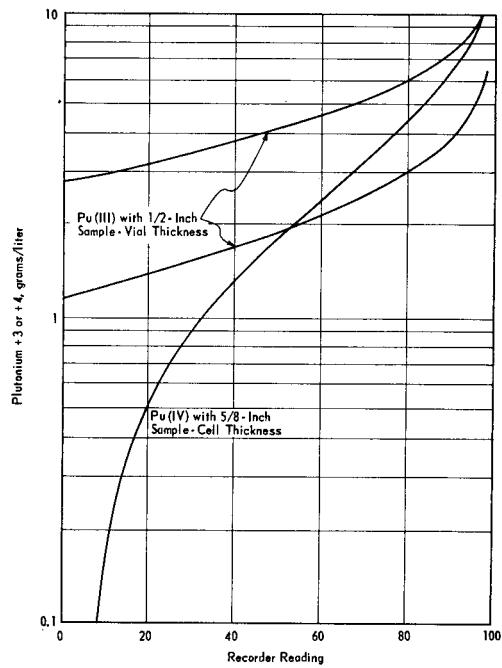

FIGURE 11 — CALIBRATION CURVES FOR PLUTONIUM NITRATE
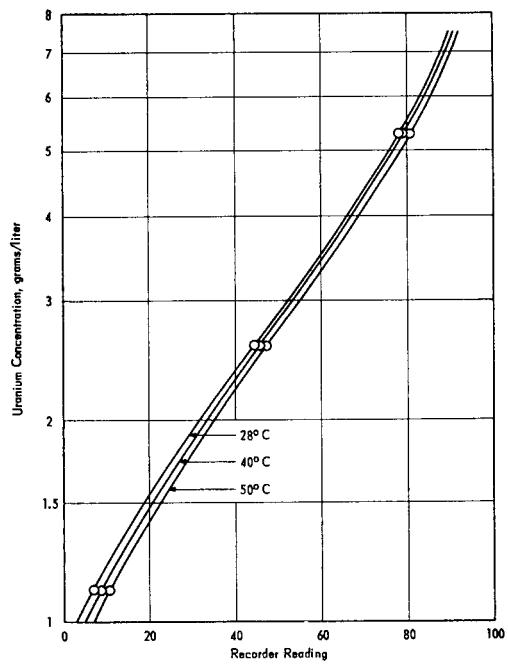
FIGURE 12 – EFFECT OF TEMPERATURE ON COLORIMETER MEASUREMENT
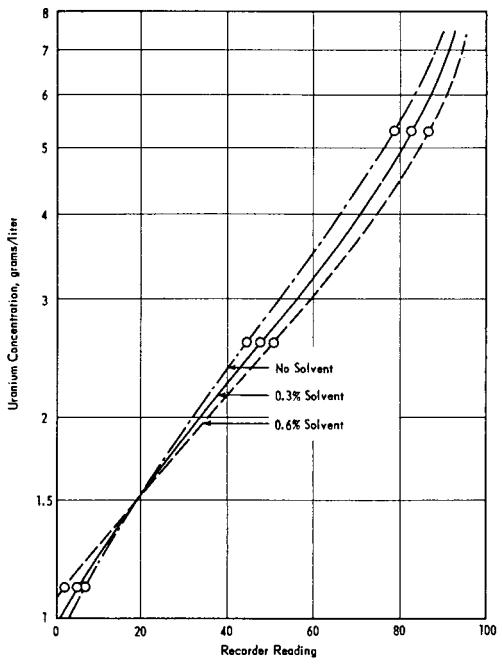
FIGURE 13 – EFFECT OF TURBIDITY ON COLORIMETER MEASUREMENT
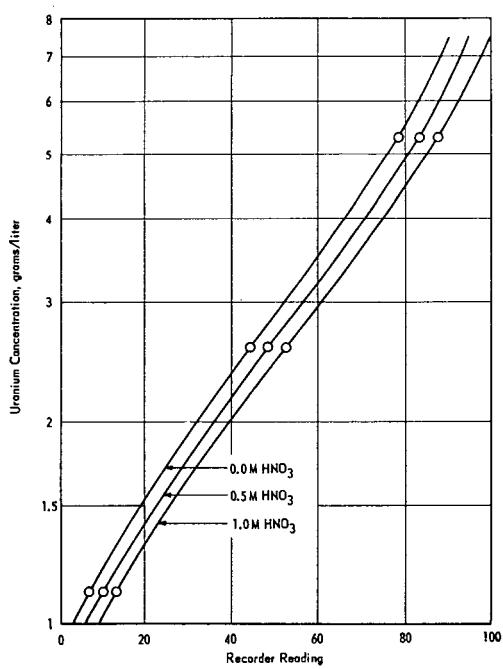
FIGURE 14 – EFFECT OF NITRIC ACID ON COLORIMETER MEASUREMENT