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Report

on

The Naval Research Laboratory Dissolved Oxygen Indicator

for

Continuous Analysis of Boiler Feedwaters

NAVAL RESEARCH LABORATORY
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ABSTRACT

This report gives the essential details in the design of a dependable instrument for the analysis of dissolved oxygen in boiler feedwaters by means of a spectrophotometric method. The operation of the indicator, results of a test period, and the experimental work involved in its design are given. Because of the rapidity of its indication, portability, ease of manipulation, overall compactness and accuracy, recommendations include its further development and use in routine and survey testing in the Naval Service.

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INTRODUCTION

Authorization

1. This problem was authorized by

(a) BuEng. letter S87 (3-13-Ds) of 20 March 1937.

Statement of Problem

2. The object of this problem was to develop an indicator which could be used on shipboard for the determination of the dissolved oxygen in boiler feedwater.

3. By the nature of the limitations of its use, compactness in size, speed and range of indication, ease of manipulation, portability, and accuracy are fundamental restrictions in its design.

Known Facts Bearing on the Problem

4. The deaeration of boiler feedwater has become a necessity due to the celerity of attack of dissolved oxygen on clean boiler metal at the high temperatures and pressures now used in the Naval Service. Obviously, the indication of the extent of deaeration is of prime importance, since this indicates the efficiency of operation of the deaeration system under any set of conditions.

5. Until the present time, there have been only two methods of analysis for dissolved oxygen applicable to any extended practical use. Only one of these, a method based on the difference in thermal conductivity of a pure gas from that of the gas when diluted with any oxygen displaced from the water under analysis, operates continuously. The other, the basic Winkler method, requires careful manipulation in sampling and intricate chemical analysis. The time factor involved in both of these methods is of a considerable magnitude. In the thermal conductivity apparatus, equilibrium of indication with actual oxygen content is only attained after repeated flushing of gas through the water under analysis, this process sometimes requiring upwards of twenty minutes to give a true analysis. The Winkler method requires a period of sampling of fifteen minutes or more, depending on the rate of flow of the water, length of sampling line, and other factors. The actual chemical analysis of the sample requires an additional 5 to 10 minutes depending on the skill of the operator and the type of indication of the titration endpoint in use. Also, it should be remembered that any result obtained with the Winkler test represents only an average of the oxygen concentration encountered during the period of sampling. This may be satisfactory in the case of a deaerator operating at an equilibrium condition, but sampling at two or more different intervals is necessary when the efficiency of the deaeration unit is changing.

6. These methods may be easily adapted to the space limitations of shipboard use. However, the glass equipment needed in the Winkler analysis is subject to the danger of breakage and subsequent loss of time and material.

7. Recently there has been developed to a limited extent a continuous flow analyzer which depends on the photometric measurement of light transmitted through a section of the water to be analyzed to which certain reagents have been added which generate a color, the depth of the color being dependent on the amount of oxygen present. This apparatus is in part based on U.S. Patent Nos. 1,919,858 and 2,019,871, and uses a gravity flow supply of a two solution reagent. Constructed largely from glass, its size and intricacy of operation require the services of trained and specialized personnel.

8. From what meager information available on this method, it does not appear at all adaptable to the Naval Service.

Theoretical Considerations

9. Bearing in mind the restrictions applicable to the design of the instrument, careful consideration of the methods available for this purpose resulted in the selection of a colorimetric principle combined with the photoelectric indication of spectral transmission. This principle gave promise of the best performance for use in the Naval Service.

10. The spectrophotometric type of analysis, with certain variations in arrangement, affords the analyst with an excellent tool in the quantitative determination of many different substances. This is accomplished with speed and accuracy.

11. The principle of operation of all such methods is based on the Lambert-Beer Law:

$$T = t^{c\ell}$$

where

T = Transmission factor of the solution

t = Transmission factor of the solution of unit concentration and thickness

c = Concentration of the solution

ℓ = Thickness of the solution (or depth)

12. Thus the concentration of any given substance in solution having a fixed depth will be directly proportional to the negative logarithm of the transmitted light through the solution.

13. However, as it will be shown later, this law is very seldom completely fulfilled in actual practice because of the practical difficulties in obtaining a "match" between the spectral absorption of the filter interposed in the light source and the spectral transmission of the colored solution under analysis.

14. Careful control of all possible variables is necessary in accurate spectrophotometry. Among these is the repeated compensation or setting of the output of the photoelectric cell at a point which represents true one hundred per cent absorption or transmission, thus allowing for any change in characteristics of the photoelectric cell or fluctuations in the optical condition of the solvent medium used in producing the color reaction.

15. The equivalence of light transmitting ability of any system of two or more absorption cells is also necessary, as is the constancy of addition of any solutions or reagents differing in density or light absorption from that of the solvent medium.

METHODS

Explanation of Report

16. An attempt has been made in the construction of this report to provide the reader with the information sought at a minimum expenditure of time and energy.

17. To that end, the arrangement of the material presented, is such that the main body of the report contains text, data and curves directly applicable to the oxygen indicator of the present model and design, with no thought or consideration to the earlier experimental work necessary to achieve these results. In this section will be found a detailed description of the indicator with its fundamental principles of operation, the results of a test period to which it was applied and a conclusion consisting of a critical summary of the advantages and disadvantages of the machine with appropriate recommendations for the future progress of the problem.

18. The appendix has been chosen to contain a rather detailed recapitulation of the experimental progress of the design of each component part of the finished apparatus. This treatment was undertaken because of a need of combining into a form readily available for future reference and record --- should the occasion arise --- the results of the stepwise evolution of this type of an instrument. The sequence of each topic in the appendix begins with the earliest form of the unit in question, proceeding through its experimental and developmental stages to the final form incorporated in the present model.

Description of Model IV N.R.L. Dissolved Oxygen Indicator

19. Principles of Operation and Features of Design. The operation of this indicator depends upon the color produced by the contact of water containing dissolved oxygen with a mixture of solutions of potassium hydroxide and pyrogallic acid containing a small amount of a sensitive orthoquinone compound. The color developed is a measure of the amount of dissolved oxygen present in the water and may be determined by comparing the light absorption of the water before and after the reagents have been added by means of a photoelectric cell connected to a suitable microammeter. The absorption cells containing the water and depth of color to be measured are mounted in a fixed position and in such a manner that the light source and photoelectric cell may be placed in line with either cell. With the light source and photoelectric cell in line with the absorption cell containing the water alone, an iris diaphragm is adjusted so as to give a full scale deflection on the microammeter. With the iris diaphragm at this setting, the light source and photoelectric cell are placed in line with the other absorption cell containing the water, reagents and color due to any oxygen present. The reading obtained on the microammeter is referred to a calibration curve for translation to milliliters oxygen per liter of water.

20. Provision is made for fluctuations in rate of flow of the water being analyzed by the use of a constant head device maintaining a flow of 100 cc. per minute and venting any occluded air bubbles in the water.

21. Turbidity of the water is automatically compensated for by the double absorption cell design.

22. The instrument is provided with a double range selector giving a good sensitivity throughout the ordinary range of dissolved oxygen concentration found in such waters.

23. Levels of solution in the reagent tanks are easily visible and may be equipped with electrical circuits automatically stopping the operation of the indicator in case of exhaustion of solution.

24. Inspection of the absorption cells for the presence of foreign matter is provided for by sight holes on one side of the case and a light aperture in front of the instrument for their illumination. The slight constant increment of absorption due to the reagents alone is cancelled by means of an off-scale zero setting.

25. Changes in line voltage from the 110 V., 60 cycle A.C. supplied to the instrument are without effect on its operation by the use of a constant-wattage transformer.

26. Replacement of the automobile headlamp type tungsten-bulb light source is made simple and quick and is without effect on the calibration of the instrument.

27. Should recalibration become necessary or advisable it may be easily accomplished if water of zero or known oxygen content is available. This is done by means of a small electrolysis cell inserted in the system which liberates any desired amount of oxygen premeasured by a milliammeter.

28. Should the absorption cell windows become dirty, making a zero balance impossible they may be easily removed and cleaned on both surfaces.

29. Rate of addition of reagents is controlled within the necessary limits by means of metering pumps, requiring no adjustment or attention.

30. Continuous or intermittent operation of the indicator is provided for and its only attention is that of replenishing reagents upon exhaustion, this length of time being about six hours with the present model.

31. The makeup of reagents is done with a minimum of manipulation and fragile glassware. Measured amounts of dry reagents are supplied, and sealed ampoules containing the sensitizer solution are made up with distilled water without contact with the operator, only one volume measurement being required with each solution prepared.

32. Details of Construction of the Indicator. An inspection of the flow sheet of the apparatus as sketched on Plate 1 will serve to clarify the following sequence of the water flow in the instrument:

The water to be analyzed is passed into a constant-head device which allows a part of it to overflow at all times. The main portion, however, enters the indicator through an emergency adjustment valve at (A) passing through the rotameter (B) which is graduated at one point, indicating a correct flow of water of 100 cc. per minute. By means of a copper tube the water then passes into the zero absorption cell (C). In passing into this cell the water is caused to flow through an orifice (D) which creates a turbulence, forcing any suspended particles in the water away from the surface of the glass window in the end of the cell. In this cell the zero absorption of the water is obtained by the transmission of the light beam originating at (E) and controlled by the lens and iris diaphragm (F). The spectrum of this light beam is rendered selective by the filter (G) before it impinges on the photoelectric cell (H) giving rise to a minute current registered on the microammeter (I). The water then is passed into a glass unit containing the inlet for the basic reagent, potassium hydroxide, at (J). This is mixed thoroughly with the water by the zig-zag convolutions (K) of the glass tubing, and flows into the calibrating electrolysis cell (L) where oxygen may be added to it in measured amounts if recalibration of the

instrument should be necessary.

Following this step the other reagent, pyrogallic acid and sensitizer solution, is added at (M) and mixed by means of another zig-zag portion of tubing in connection with a final mixer (N) which serves as a ballast, preventing too rapid a fluctuation in light absorption when the colored water reaches the color cell at (O).

In this cell its absorption is compared with that obtained from the water alone by shifting the light source and photoelectric cell in a position indicated by the dotted lines.

If the transmission of the light in this color cell is lower than a basic value (indicated on the calibration curve) a shift of filters at (P) may be accomplished giving a range better suited for analysis at this concentration.

Translation of meter readings to milliliters oxygen per liter water is accomplished by means of a calibration curve similar to that on Curve 17.

The water flows to waste from this cell through a water trap (not shown) which prevents draining of the system when not operating.

33. The arrangement of the component parts of the indicator is best seen by the photographs on Plates 2, 3, 4, 5, 6, 7 and 8 which are self-explanatory. Plate 9 shows the equipment for makeup of reagents including volumetric flasks, special funnels, reagents and sensitizer solution ampoules adequately marked A and B, the latter markings being in red as an additional safety factor.

DATA OBTAINED

Tests of the Preliminary Model Indicator at the Naval Engineering Experiment Station

34. Due to the large proportion of experimental work on this problem before it was possible to perform any large scale tests on a deaerator setup, only one opportunity has existed to apply the indicator to conditions similar to those found aboard ship.

35. The occasion of this test was in connection with the deaerator experimentation being conducted at the Naval Engineering Experiment Station.

36. During February and March of 1939 a preliminary model of the Indicator was set up at the E.E.S. by Laboratory personnel and

connected to a sampling line from the Booster Pump Discharge. The water being used in the deaerator at this time had been in use for a long period and results in the Indicator showed the calibration curve to be not applicable to the conditions encountered. A recalibration of the instrument was performed in about twenty minutes by means of the electrolytic calibrator and using as a base line the results of Winkler analysis of the water by the staff of the E.E.S.

37. Using the resulting calibration curve oxygen analysis of the water was made at one-minute intervals and plotted as a continuous curve. Results of these tests are shown by Curves 1, 2, 3, 4, and 5. Curve 1 shows the oxygen content after the deaerator had reached an equilibrium value and the rise in oxygen content when the steam was turned off. Curve 2 gives the oxygen content as the deaerator was started up. Curve 3 gives the results of a run on the station deaerator as it was started up and during the time of a valve test and after it had settled down to regular operation. Curves 4 and 5 show the results of experimental changes in deaerator conditions.

38. The following correlation is given of Winkler analysis results (both the average of a 500 ml. and 250 ml. sample and the Schwartz and Gurney difference are given) at intervals during the tests covered by the above curves:

Date	Winkler Analysis ml. per Liter		Analysis by the Indicator
	Average	S.& G.Difference	
2/15/39	.021	.038	.027
2/15/39	.015	.033	.019
2/15/39	.017	.028	.019
2/15/39	.016	.025	.019
2/16/39	.113	.122	.126
2/16/39	.110	.106	.120
2/16/39	.061	.062	.065
2/16/39	.046	.041	.047
2/16/39	.214	--	.218
2/16/39	.025	.025	.025

Discussion of Results of the Annapolis Test

39. Unfortunately this one and only test of the oxygen indicator was carried out with a very rudimentary model of the indicator so that any results of its mechanical operation are not necessarily applicable to the present model due to the many changes made in its construction and operation.

40. However, the speed of response of the indicator is evident by the time - oxygen content curves. This is strikingly illustrated by Curve 5 where the time lag varied from one minute to a three minute

maximum for any change in steam or water flow. The time lag of any such instrument would, of course, be influenced by the length of the sampling line tapped from the supply of water. All of the above tests were made with a sampling line length of about thirty feet. The advantage of a continuous analysis in an experimental set-up such as this made possible the changing of many variables within the space of an eight-hour run to ascertain their effect on the deaeration without the necessity of waiting for equilibrium conditions to maintain after each change before sampling for Winkler analysis. Any Winkler analysis results obtained when an equilibrium condition does not exist really represent an average value over the length of time of sampling. The recalibration of the instrument, performed twice while conducting these tests, provides a simple quick check on the entire curve at any desired time. It gives the Indicator a flexibility of use which could be of considerable advantage when changing from one installation or water supply to another, or when highly questionable results are obtained during an analysis.

CONCLUSIONS AND RECOMMENDATIONS

Facts Established

41. The use of a spectrophotometric principle employing organic reducing agents for the analysis of the dissolved oxygen in water has been shown to be an entirely practical method and readily applicable within the Naval Service.

42. The apparatus for accomplishing this has been designed to meet the following restrictive conditions:

(a) Size and Portability: The outside dimensions of the present model instrument are 13 inches x 17-1/2 inches x 12 inches deep. Weighing about 45 lbs., it is easily transported by means of two handles on each side of the case. Hook-up ready for operation requires only the insertion of an electrical plug and a rubber or copper tubing connection to the source of water to be analyzed.

(b) Ease and Simplicity of Operation: A total number of three individual steps are necessary for obtaining a reading during the running operation of the present indicator. The starting operation is likewise very simple and easily performed. In fact, the principles of the analysis are quite evident to an operator after a thorough inspection of the instrument.

(c) Accuracy of Indication: Repeated efforts during the development of the indicator have led to an increased accuracy. Unfortunately, the period of actual testing under comparable Service conditions has been too short to base any claims upon

as to its overall accuracy. However, laboratory results show an agreement with Winkler analyses of about .005 ml. per liter in ranges up to .15 ml. per liter oxygen and about .02 ml. per liter in ranges up to .5 ml. per liter. The great variability of the Winkler analysis results is also a point of issue when considering it as a standard for such an instrument.

(d) Speed of Indication: Here also a comparative value must be agreed upon, but tests show an immediate response of the indicator to change in oxygen concentration with a three minute maximum lag in time which could be very easily changed depending on the method of sampling used.

(e) Continuous Operation Without Attention: The present model indicator is designed for continuous running with these limitations: For an accurate analysis, rebalance of the zero of the photoelectric cell circuit is necessary at about ten minute intervals. This is necessary because of a minute drift in sensitivity of the photocell with time exposed and also by the possibility of inclusion of any suspended matter in the water during analysis. The reagent tanks must not be allowed to run dry as this would cause pumping of air into the system.

(f) Mechanical Stability: The optical system has been designed to consist of a one-piece casting supporting the photocell and light source integrally in one unit. Distortion is thus impossible. The pumping mechanism is enclosed from any possibility of dirt or corrosive liquids entering the gear or cam chambers. The indicator is completely enclosed in an aluminum box so that any tampering of the more accurate permanent adjustments cannot occur. Two units of glass fabrication were found necessary in this model. One of these, the reagent tanks, are protected by paper cradles in which the tanks rest. The other, the reagent mixing unit is well protected by being sunken into a wooden block which both supports and shields the glass tubing.

(g) Chemical Stability: If the operation of the indicator is carried out as recommended, no interference will be found from the oxidation of the reagents. Interference due to any large amounts of foreign salts dissolved in the sample water has not been substantiated as yet due to the limited testing period undergone by the indicator. It is to be expected, however, that only considerable concentrations of materials will cause any effect on the accuracy of the calibration curve.

(h) Manipulation of Reagents: The make-up of individual reagents has been simplified to such an extent that no skill other than the routine following of a sequence of instructions should be necessary. The pre-weighing of solid materials and transfer of the sensitizer solution to the final reagent is as foolproof as any chemical analysis procedure can be made. The use of glassware for these operations is

necessary only as far as the volumizing of the solutions is concerned. It is hoped that materials will be procured in the future to eliminate all other glass equipment.

(i) Provision for Adjustment and Recalibration of the Indicator: In spite of the compactness of the arrangement of the component parts of the indicator, accessibility for adjustment is provided for by the "unitized" method of assembly. Removal of the top and front of the indicator case makes possible the adjustment of all units of the apparatus and their disconnection and removal if this should be necessary. If the analysis results should be questioned at any time during its operation, or inspection and checking of the functioning of the indicator be necessary, the external calibration unit makes recalibration simple and conclusive.

Recommendations

43. The success of the tests on the Annapolis deaerator set-up indicate the many possibilities of this Indicator for boiler feedwater oxygen analysis.

44. While the present model of the apparatus is a satisfactory one for current testing purposes, work should be initiated immediately on an improved model fabricated by the Laboratory machine shop with a view toward mechanical perfection not possible with the equipment used to construct the present model. This would lead to a greater ease of manipulation of the instrument.

45. Many small problems inherent to the present model need further attention for their ultimate solution. Among these, the possibility of increased stability of the reagent requires study, as does the use of corrosion-proof metals in lieu of parts now constructed of glass.

46. Redesign of parts of the indicator in order to provide a continuous recording of oxygen analyses should also be undertaken.

47. However, the most important objective for the near future is an increased opportunity for testing the Indicator, concomitant with shipboard conditions of use.

48. It would seem possible that the type of results produced by this instrument would be of inestimable value in the present program of Naval ship construction, where the factor of decreasing of time necessary to place additional vessels in the fleets with complete records of the performance of their vital units of operation is of great importance and even a tactical advantage.

APPENDIX

EXPERIMENTAL WORK INVOLVED IN THE DESIGN OF THE COMPONENT PARTS OF THE INDICATOR

Selection of Reagents and Experimentation Leading to Their Stabilization

In the early stages of the research on this problem it was concluded that, in order to escape the difficulties inherent in existing practical methods of dissolved oxygen analysis, namely, the lack of compactness, durability, speed and accuracy and variabilities in sampling, the spectrophotometric method of analysis was the most promising at this time for adaptation to the Naval Service.

The question then remained as to what chemical reactions resulting in the production of color due to oxidation would be sensitive enough and usable in the range desired. Necessarily the reaction would require a two or more component reagent producing a color of sufficient intensity to be measurable by photoelectric or visual methods.

An attempt to use the standard Winkler reagents to produce a depth of color of iodine set free in proportion to the amount of dissolved oxygen, the entire reaction occurring under oxygen-free conditions in a closed mixing chamber as illustrated in Plate 10, resulted in the conclusion that oxygen present in amounts less than .1 ml. per liter would require too long an absorption cell for practical use.

Binder and Wieland (2) recommend the use of an alkaline solution of catechol with traces of $FeSO_4$ present for the detection of small amounts of dissolved oxygen. This was tried using two solutions, one slightly acidic, containing the $FeSO_4$, catechol and dilute H_2SO_4, and the other a dilute solution of KOH. Mixing of these solutions in contact with oxygen-free water was unsuccessful in obtaining a colorless solution, due to the very small amounts of oxygen dissolved in the reagents. The red color produced became very dense upon even the slightest exposure to air.

The method described by Frankforter, Walker and Wilhoit (3) using the blue color of the complex ion, $[Cu(NH_3)_4]^{++}$, that is formed when Cu_2Cl_2 is oxidized by oxygen to $CuCl_2$ in the presence of NH_4OH was also found to be insensitive to small amounts of oxygen.

A two solution reagent consisting of a saturated solution of pyrogallic acid in acidulated water and a 50% solution of KOH was added to oxygen-free water confined under nitrogen and a color-free solution resulted which was remarkably sensitive to very small amounts of oxygen. Because of several promising results with this type of reducing agent many tests were made with compounds of the same class in combination with solutions of varying concentration of the following bases: KOH, K_2CO_3, NaOH, Na_2CO_3, LiOH, triethanolamine, monoethanolamine, ethylenediamine,

and NH_4OH. The following reducing agents were tested: hydroquinone, chlorohydroquinone, bromohydroquinone, paramidophenol hydrochloride (Kodelon), m-methoxy-p-hydroxy aniline sulfate (Edinol), monomethyl para amido phenol sulfate (Elon), and 2, 4, diaminophenol hydrochloride (Amidol). The leuco bases of Indigo carmine and methylene blue were tested also but these showed such a poor stability when kept in two-solution form that they were considered out of the question.

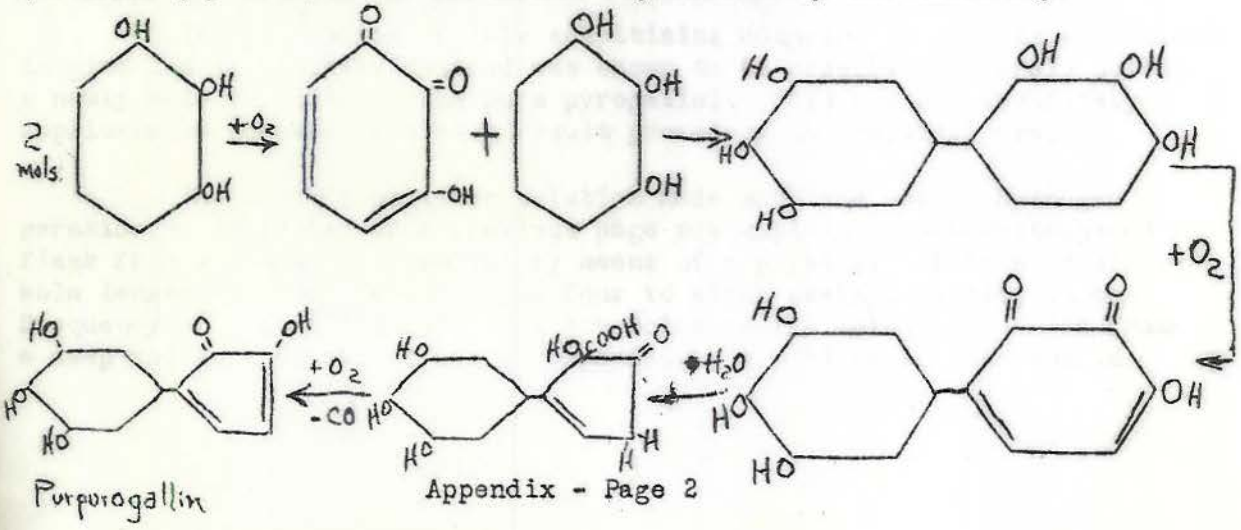
The reactions of these materials all showed possibilities for their use as oxygen indicators in certain ranges but the pyrogallol-KOH mixture was selected from point of view of obtainability and sensitivity to the range of concentrations necessary for the widest scope of the instrument.

Subsequent to the early use of pyrogallol comparative tests indicated that a solution of pyrogallol became exceedingly sensitive after a short period of aging. The displacement of the calibration curve was very marked even after 24 hours elapsed time since making up the reagent. Concurrent with this production of sensitivity was a pronounced deepening of the color of the solution from water-white to a brownish-black with small particles of suspended matter. This occurred in acidic solution and it was concluded that a partial oxidation was occurring which produced a compound even more desirable in the production of color than the original pyrogallol.

An effort was made to stabilize the solution with a weak reducing agent such as oxalic acid. This was only successful after the oxidation had proceeded to a certain stage as may be seen by a comparison of Curves 6, 7, and 8. Curve 6 also illustrates the increase in sensitivity of the curve when partial oxidation of the reagent occurs.

A search of the literature revealed the existence of purpurogallin, the end-product of the oxidation of pyrogallol in acid solution. This material was synthesized but proved to be inferior to the effect noted above and it was finally established that some intermediate quinone compound of pyrogallol was responsible for the tremendous sensitivity to oxygen when in a basic medium.

The oxidation of pyrogallol has been postulated by Willstatter and Heiss (1) to occur in the manner represented by the following:



Thus the probable mechanism of oxidation in acid solution is the oxidation of pyrogallol to an orthoquinone which then condenses with pyrogallol to form a bi-pyrogallol which oxidizes further to an orthoquinone-pyrogallol. This undergoes a rearrangement and addition, forming a pyrogallol-cyclopentane which further oxidizes to an orange colored substance, purpurogallin, difficultly soluble in water, and which only is susceptible to further oxidation in basic solution, in which medium a deep brown colored material is produced, to which the name purpurogallone is affixed. If the above oxidation is interrupted at a point before its completion in acid solution, a pinkish crystalline material is obtained, very soluble in water and somewhat unstable on exposure to air.

By purely empirical methods this partial oxidation product of pyrogallol was produced in solution using hydrogen peroxide solutions and timing the reaction, stopping it at the desired point by the addition of oxalic acid. The following is a typical oxidation which gave very satisfactory results:

240 cc. dist. H_2O)
130 g. CP, Pyrogallol) @ 98° - 100°C.
.5 cc. conc. H_2SO_4) (water bath)

To this mixture 10 cc. 10% H_2O_2 was added and the solution was held at 100°C. After a reaction time of exactly 10 minutes 26 g. oxalic acid was added and the solution cooled immediately.

The above resulted in a fairly concentrated solution of the quinone compound which was measured out with a pipette and diluted for use.

This compound when added in varying amounts to fresh solutions of pyrogallol showed very interesting effects on the slope of the calibration curve. Reference to Curve 9 illustrates the increase in sensitivity obtained with increase in amount of compound present. The approach to linearity of the curve with increase in pyrogallol is also apparent. The use of the quinone compound only (which we will hereinafter call "sensitizer solution") with no pyrogallol present, resulted in a curve of very erratic appearance and no explanation of its fluctuations could be advanced.

The production of this sensitizing compound in amounts sufficient to give the sensitivity desired was shown to be possible by merely boiling a newly made solution of the pure pyrogallol. This was not accurately duplicatable however, and as a result proved of no practical use.

The stock sensitizer solution made with the use of hydrogen peroxide as described on a previous page was kept in a rubber-stoppered flask from which it was removed by means of a pipette. After a considerable length of time, varying from four to eight weeks, depending on the frequency of use of the solution, the color of the solution changed from a deep red to a black and was accompanied by a noticeable increase in

sensitivity of the calibration curve. This same increase in sensitivity was noticed with the final solutions of pyrogallol made up ready for use in the instrument, the effect appearing in much less time, being in the order of 3 to 5 days.

For this reason the more powerful inorganic sulfite reducing agents were tried as possible antioxidants, it being established by a previous test that this type of reducing agent did not affect the reaction of the production of color in the presence of oxygen.

Sodium sulfite, bisulfite and hydrosulfite present in proportions ranging from 0.5% of the total amount of pyrogallol to 8.% of the pyrogallol was tried. These salts of course liberated sulfur dioxide from the acid media in which the pyrogallol was made up. Preservation of color and appearance of the solutions was marked with the use of any of these but another effect occurred which obviated their incorporation in solutions necessary to be protected for any length of time. This effect was that of reduction of the orthoquinone compound which was present as a sensitizer. After a period of 9-10 days the reduction in sensitivity was quite noticeable in its effect on the calibration curve.

With the failure of these antioxidants the remaining method of preservation of the sensitizer solution was that of sealing immediately after synthesis in an ampoule which was opened and exposed to oxygen only at the time of use. This was done by the use of glass ampoules with a thin glass diaphragm in the lower end protected against breakage by being countersunk into the width of the tube. Tips of thin glass on the ampoules with a file mark placed thereon for easy breakage and also a specially constructed funnel with a piercer mounted within it is provided so that by merely dropping the ampoule into the funnel the glass diaphragm is punctured and the contents allowed to flow into a volumetric flask. These details are more clearly defined by an inspection of Plate 9. An elapsed time test of almost eight months has shown this method of protection to be very satisfactory.

The oxidation of the ready-to-use pyrogallol reagent, however, is not as easily prevented. The inclusion of .2% Na_2SO_3 of the total amount of pyrogallol present has lengthened the time of reliability of the solution from 24 hours to 120 hours, but results obtained with solutions older than this are not dependable.

Absorption Cells and Comparator Mounting

The spectrophotometric method of analysis requires the use of a double absorption cell comparison scheme in any continuous flow system. This gives, for a basic reading, a zero, automatically compensated for any change in absorption of the medium used, which is in this case, water. Turbidity and initial color is thus cancelled from any effect of the results obtained. However, this leads to complications involved in the matching of the light absorption of the two cells. This must be exactly the same for both cells or a constant error will be present. The possibility of deposition of a cloud, or film of foreign matter on the window

of one cell and not the other must be carefully guarded against or obviated. With these restrictions in mind the design of absorption cells was changed from an all glass fabrication to one of brass with removable glass windows very early in this research. This was then urgent because of the formation of deposits of silica present in the boiler water on the inside of the cell window. The design of the cell is apparent by the sketch on Plate 11.

This cell, as first designed, was without any provision for decreasing the possibility of deposits of foreign matter on the windows. By the insertion of the nozzle in the inlet tube as in the sketch, a turbulence is created that sweeps any suspended particles down the length of the tube away from the window where they will either drop down in the comparatively slower moving water or will be swept out of the tube, thus keeping the windows free from foreign matter.

The use of a fixed mounting containing the light source and photoelectric cell makes it unnecessary to employ two matched photoelectric cells but yet corrects for any variation in the light source or changes in the light-sensitive surface of the cell. Being absolutely rigid it may be rotated from one position to another with continuously duplicating results.

Light Source, Spectral Filters and Photoelectric Cell Circuit

Tests made early in the experimentation on this problem substantiated the necessity of an adequate length of absorption cell so that sufficient sensitivity be obtained in the lower concentrations of oxygen. It was also found necessary to employ a spectral filter in the light beam to increase the effective range and selectivity of the instrument. To cope with these restrictions the light source of the system must be very intense and of a small area. The most satisfactory and practical of the many incandescent sources tried was that incorporated in the final model, a 50 c.p. automobile headlamp-type bulb. This bulb is supplied with a current source consisting of a constant wattage transformer, operating from 110 volts A.C., designed for the bulb and giving constant output, trouble-free operation.

The intensity and size of the beam of light is fixed by the focal lengths of the double-convex lenses placed in front of the light source and this was found to be the most satisfactory when an image of the filament after passing through the absorption cells was focused on the photoelectric cell.

A trial was made using a mercury-arc light source, with and without the filter. The resulting curves were widely dissimilar, and, although the curve resulting from the combination of mercury-arc source and green filter showed a noticeable improvement over that obtained when a tungsten filament was used, complications of a mechanical nature rendered its inclusion in the instrument impractical.

The "matching" of the spectral absorption of the pyrogallic acid-KOH-oxygen color with that of a filter in order to provide the greatest extent in selectivity and range was found to be practically impossible. A rough spectrographic analysis was made of the color developed in the absorption tube when dissolved oxygen was present. On the basis of this knowledge the following filters were tried in an attempt to cause a more close agreement of the absorption curve with that predictable by Beer's Law:

Wrattan	gelatine	filter	No. 63
"	"	"	" 66
"	"	"	" 67
"	"	"	" 68
"	"	"	" 69
"	"	"	" 75

Corning	Signal	Green
"	"	Red

Cenco	glass	filter	No. 1 -- Blue
"	"	"	" 2 -- Green
"	"	"	" 4 -- Orange

The Cenco #2 glass filter (green) was found to give the closest match possible within the limits of the available illumination and the departure from monochromaticity of the color produced in the reaction. This filter absorbs strongly in the violet and the red orange (See Curve 10) and although not being monochromatic causes the calibration curve to approach linearity to a fair extent as may be seen by a comparison of the curves with and without a filter (See Curve 11). In order to provide for an increase in range of the indicator a lift knob is mounted on the top of the cabinet whereby the Cenco #2 filter may be removed from the path of the light beam traversing the color cell and replaced with a filter of similar spectral characteristics but absorbing less total light. Thus the range is extended by the difference in transmission of the two filters, which is about a factor of 3.8 in the present model.

The choice of a photoelectric cell was the subject of much preliminary testing until a combination of cell and low-internal resistance microammeter was found which responded accurately to a percentage change in illumination within the levels in use in the instrument. The sensitivity of the photoelectric cell selected, the G. E. Blocking Layer Type, Cat. #88x565 is given in Curve 12. It also possesses the advantage of being easily mounted and adjusted.

This cell was used in conjunction with a 15 microampere Weston meter model 440 with an internal resistance of only 175 ohms. This meter is protected from undamped oscillations of the pointer during transit by a shorting switch.

In order to adjust the beam of light for a deflection of 100 divisions or a zero which compensates for the initial color of the reagents it was necessary to place an iris diaphragm in the parallel beam which could be easily adjusted by a rotating knob. This diaphragm does not affect the size of the pencil of light falling on the photocell but rather its intensity.

In the early stages of development of this instrument, the compensation for the color of the reagents alone was proceeded with by the use of an absorption wedge placed in the path of the light traversing the zero cell but this was later discarded in favor of an off-scale zero marking on the microammeter accurately placed to obviate this constant error.

The use of a comparison method and alternation in position of photocell and light source from one absorption cell to another possessed many advantages as has been pointed out before. The electrical circuit could obviously be of only the one type. By the inclusion of two photocells of matched characteristics many possible circuits may be used. Some of these arrangements are shown on Plate 12.

Trials of these different circuits were made and it was found that in the type of balancing hook-up desirable for the apparatus only #1, #4, and #5 were usable. Calibration curves were made using these three circuits and were found to closely agree with the curve taken by the single photocell method. (See Curve 13.) However, Circuit #5 was discovered to be a very flexible one and possessed the advantage of being preset to any desired oxygen concentration level by means of the control resistances and suitably placed diaphragms. Thus it would be possible to select any range of oxygen concentration for obtaining a curve of 0 to 100 division readings and an initial calibration would be all that is necessary. This method is clarified by an inspection of Curve 14.

Reagent Pumps

One of the most fundamental difficulties of an instrument of this type using a two-solution reagent of concentrated chemicals is that of delivering these corrosive liquids at a constant rate within a minimum of space and equipment. This was early realized by the testing of a set-up using the gravity flow of reagents metered by a capillary to give the correct rate of addition of each reagent as experimentally established for the maximum production of color. The method was very unsatisfactory, being subject to changes in temperature and head.

Then the use of a gas displacement method of injecting reagents was tried by employing small electrolysis cells to produce gases to be led into the closed reagent tanks, thus displacing a volume of liquid equal to the volume of gas generated. This was very sensitive to changes in temperature on the outside walls of the reagent tanks and was in addition subject to any small variation in the water flow of the system.

Several types of commercial pumps were tested during the course of this experimentation but all were found to be subject to corrosion. One model, the Zenith pump, was very satisfactory from the mechanical point of view, however, and it is possible that, were this pump made from corrosion resistant materials, it would be perfectly acceptable to our use. This is a gear pump, valveless and accurately machined to be closely fitting and leakproof. As testimony of the latter, the Zenith pump was tested at 1.02 r.p.m. and gave a constant flow of .587 cc/min with changes in head up to 12 inches.

The decision to fabricate a twin injection pump in our own shop and from corrosion-proof materials came after the successful trial of a small pump designed by Mr. E. L. Luke of the Laboratory personnel. This design is very suitable to our restricting needs. It requires no valves or ball check ports, but operates on the principle of a rotating notched piston which displaces a volume of the reagent solution by a reciprocating motion, the notch acting as the valve, rotating into a position opening the inlet part on the start of the intake stroke and then into a position opening the exhaust port on the closed stroke of the piston. Details of the design necessary to produce this action are evident from an inspection of Plate 13. It will be noted that the piston and cylinder in contact with the reagent solutions is easily interchangeable. This design facilitated the testing of materials for corrosion and abrasion resistance. The initial pistons and cylinders were constructed from stainless steel, giving a life of only about 40 hours before leakage and pitting occurred. This was followed by a tightly fitting pyrex glass fabrication which proved to be too delicate. Since the major amount of difficulty was due to a corrosion of the metal in contact with the reagent solution an immersion test was devised for corrosion resistance of any materials available for inclusion in the pump. The tabulated results of this test follow:

Material	Reagent in Contact	Time of Exposure	Results
Coin Silver	12% Pyrogallol	4 days	Blackened after 1 day.
Illium Alloy	" "	20 days	Slight blackening at air interface & surface etched.
Koroseal comp.	" "	3 days	No action.
Hard Rubber	" "	3 days	No action.
Ni-Resist Alloy	" "	2 days	Blackened in 2 hours.
Monel Metal	" "	2 days	Blackened in 2 hours.
Durimet Alloy	" "	22 days	No action.
18-8 Moly.Steel	" "	20 days	No action.
Monel Metal	25% KOH	30 days	No action.
Hard Rubber	" "	3 days	No action.
Coin Silver	" "	2 days	Greenish discolor.

A piston and cylinder machined from the Monel Metal was placed in the KOH pump and one machined from Durimet Alloy was used in the pyrogallol side of the pumps. No corrosion was evident in these even after a total of 160 hours' running time and a 50-day length of exposure period. Slight wear, however, occurred with the Durimet piston causing a very slow leakage past the pump. The 18-8 Moly. Steel piston and cylinder also give excellent protection against corrosion in contact with the 12% pyrogallol and are at present in use in the indicator.

Mixing Unit

The complete mixing of the reagents with the water flow before entry into the color cell is a definite necessity and at first this was accomplished entirely by the closed magnetic-mechanical mixer as illustrated in Plate 10. Requiring too much space this was displaced by a mixing unit which depended on the turbulence created within a small diameter tube when water and comparatively heavy reagent were forced through it. By forming the tube in the shape of a zig-zag curve with sharp turns, the reagents and the water were very efficiently mixed in a small space. The design of this mixer is evident by inspection of the sketch on Plate 14. Three fabrications of this mixing unit in nickel, copper and Monel metal were unsuccessful because of a minute corrosion effect which displaced the calibration curve erratically. Glass is at this time the only material which does not affect the reaction which takes place when the reagents come in contact with dissolved oxygen.

Deaerator Unit

The supply of oxygen-free water for testing earlier models of the indicator was obtained by the batch method of boiling vigorously 12 liters of tap water for 15 minutes, then allowing a portion for testing to flow through a cooler to the apparatus while keeping the temperature of the residual water in the boiler at the boiling point. Winkler analysis of this water on several different occasions gave fairly consistent results varying between .004 m . O_2 per liter and .008 m . O_2 per liter.

It soon became necessary, however, to expand this deaerator into one giving a continuous flow of oxygen-free water for use in calibrations. This was done by the use of two 10 gallon Westinghouse domestic hot-water heaters as boilers. The design of the set-up including the water-cooler is explained in more detail on Plate 15 and the photograph of the unit on Plate 16. This unit has operated with no difficulty for about 12 months, the only care it has required is that of occasionally cleaning the spray jet in Stage 2 and draining the entire system once each week. Winkler analysis of the water shows a maximum of .006 m . O_2 per liter under extreme conditions of rapid flow, and continuous analysis over eight hour periods by means of the indicator show an extremely minute variation in residual oxygen content.

Calibrating Unit and Winkler Tests

Early in the testing procedure it was found necessary to obtain water of differing concentrations of dissolved oxygen. This was accomplished by the insertion in the known rate of water flow of a supply of water kept saturated by bubbling air through it, this saturated water being measured on its addition to the oxygen free water by the use of a precalibrated dropping tube controlled by a pinchcock. Knowing the accurate volume per drop of saturated water and its temperature it was then only necessary to time the rate of addition of saturated water and rate of oxygen free water and, using a curve similar to Curve 15 giving the solubility of oxygen in water at various temperatures, the final concentration could be easily determined and varied by changing the rate of flow of saturated water, the other factors remaining the same. The following data illustrate the agreement of results of this method of producing differing oxygen concentrations when correlated with the actual Winkler analysis of the mixtures of saturated and oxygen-free waters:

Winkler Analysis (average of 2 determinations) m . O_2/L.	Calculated Oxygen Conc. (Using Curve II and rates of flow of water) m . O_2/ L
.054	.049
.175	.160
.259	.290
.281	.282

The basic Winkler method of analysis was adapted to our use by various improvements and time-saving changes in the procedure. It was found that the method of reagent addition to the sample was a source of frequent entrainment of minute air bubbles. This was obviated by attaching to the sampling flask a short length of glass tubing graduated in milliliters as sketched on Plate 17. Thus the reagent is in direct liquid contact from the beginning of its addition to the sample until the proper amount has been added and the stopcock closed. Obviously, careful rinsing of this graduated tube was necessary following the use of each reagent. The Schwartz and Gurney method (4) of compensating for the blank due to the reagents by the use of two different sized samples was employed with a change in the method of discerning the end-point of the titration with thiosulfate. The method used was that advocated by Foulk and Bawden (5) and more recently, Hewson and Rees (6) where a galvanometer is used to indicate the presence of any excess thiosulfate in the titration by means of the polarization of the cathode of two bright platinum electrodes immersed in the solution across which a small potential is applied. The details of the circuit are apparent in the sketch on Plate 18 and the photograph on Plate 19. Back titration was resorted to, as in the method

of Hewson and Rees, and this was found to be exceedingly simple and useful.

Electrochemical means for the production of oxygen was tried and found to be very successful, displacing the saturated water method of adding oxygen. This consisted of an electrolysis cell in the form of a double walled glass tube with platinum electrodes in contact with the flowing water. The details of its design are made evident by the sketch on Plate 20. Difficulties of reduction due to the hydrogen evolved were only apparent when the cell was placed in the flow at such a point that the mixed reagents came into direct contact with the electrodes themselves. When the generation of oxygen and hydrogen took place at a point where only the water and the KOH reagent were present the gases dissolved immediately and by the use of suitable resistances and a milliammeter in the current supply to the cell, control and measurement of the oxygen concentration (at constant, known rates of water flow through the instrument) becomes simple, immediate and precise. By the utilization of Faraday's Law in an apparatus such as this, with a water flow of 100 ml. per minute, one milliampere will liberate oxygen sufficient to cause a final concentration of .035 ml. dissolved O_2 per liter at standard conditions of temperature and pressure. The calibrator unit which is used on the present model is illustrated by Plate 8, applicable to two ranges of oxygen concentration.

A comparison of the two methods of addition of oxygen for calibration may be seen by Curve 16, one curve being taken by the use of the saturated water method, the other by the electrolytic cell calibrator.

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(2) Binder and Wieland-Berichte 46, 255

(3) Frankforter, Walker and Wilhot - J.A.C.S. 31, 35 (1909)

(4) Schwartz and Gurney - Proc. Am. Soc. Testing Materials, 34, part II (1934)

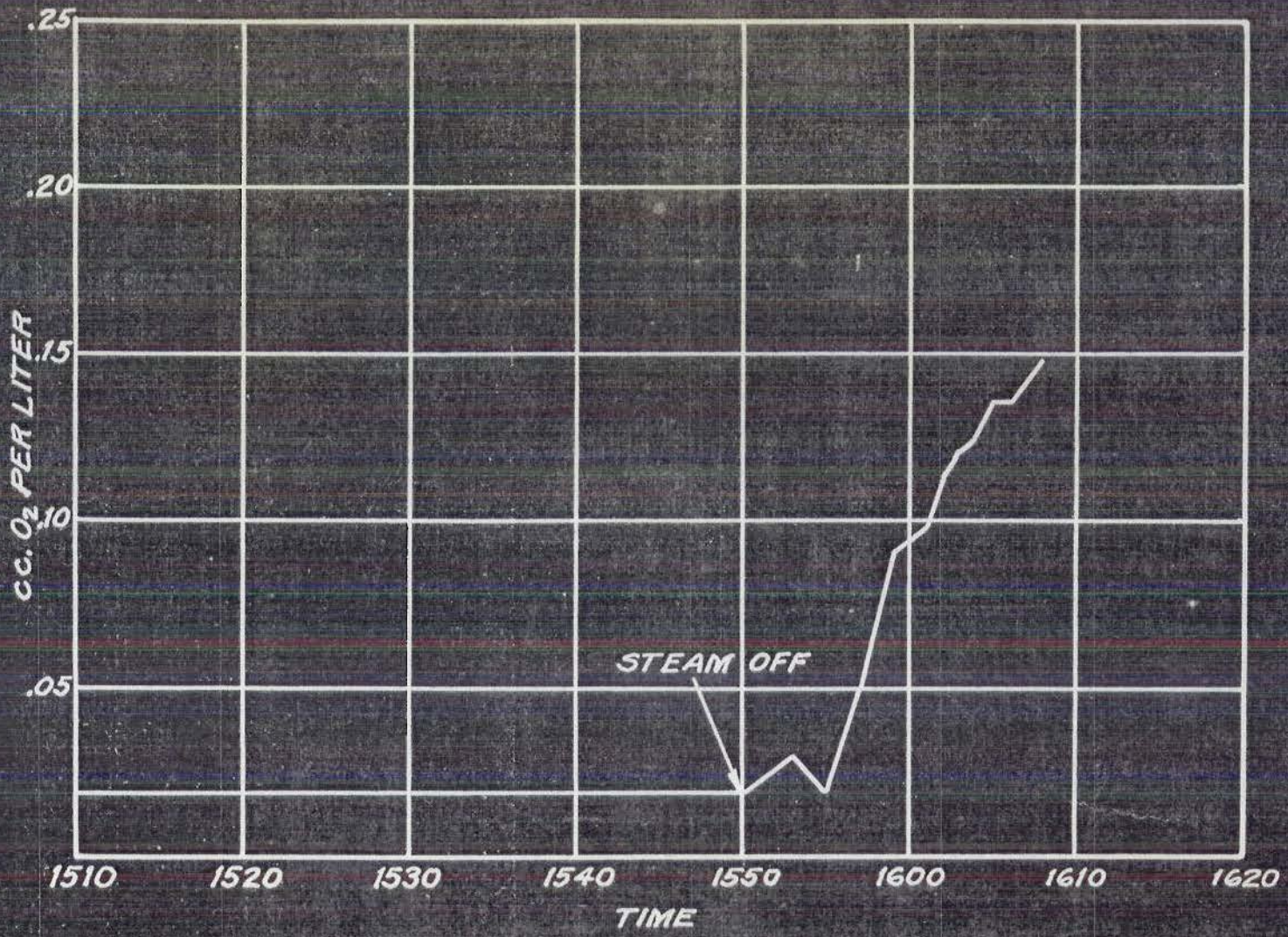
(5) Foulk and Bawden - Jour. Amer. Chem. Soc. 48, 2045 (1926)

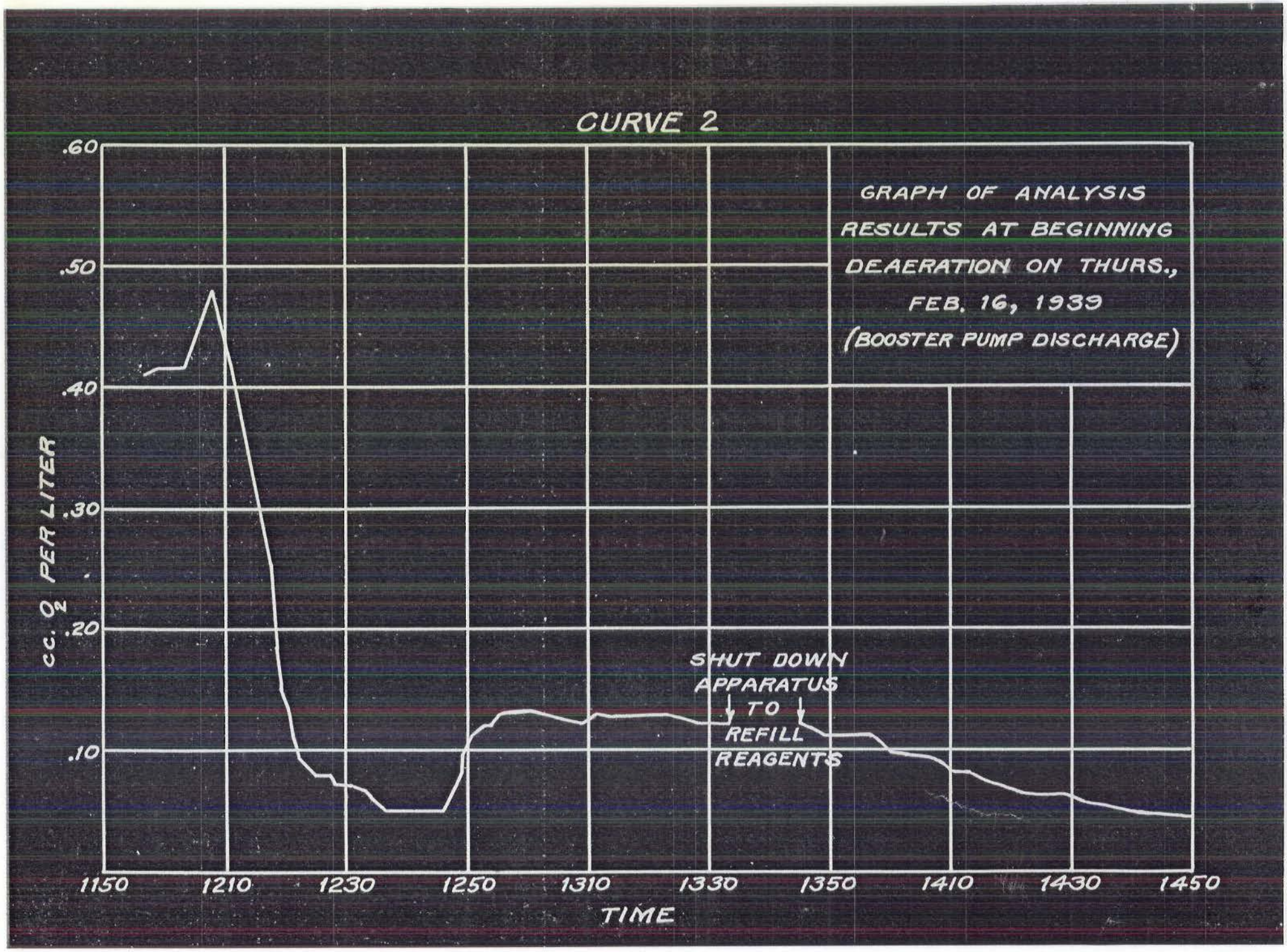
(6) Hewson and Rees - Jour. Chem. & Ind., 54, No. 30 (1935)

CURVE 1

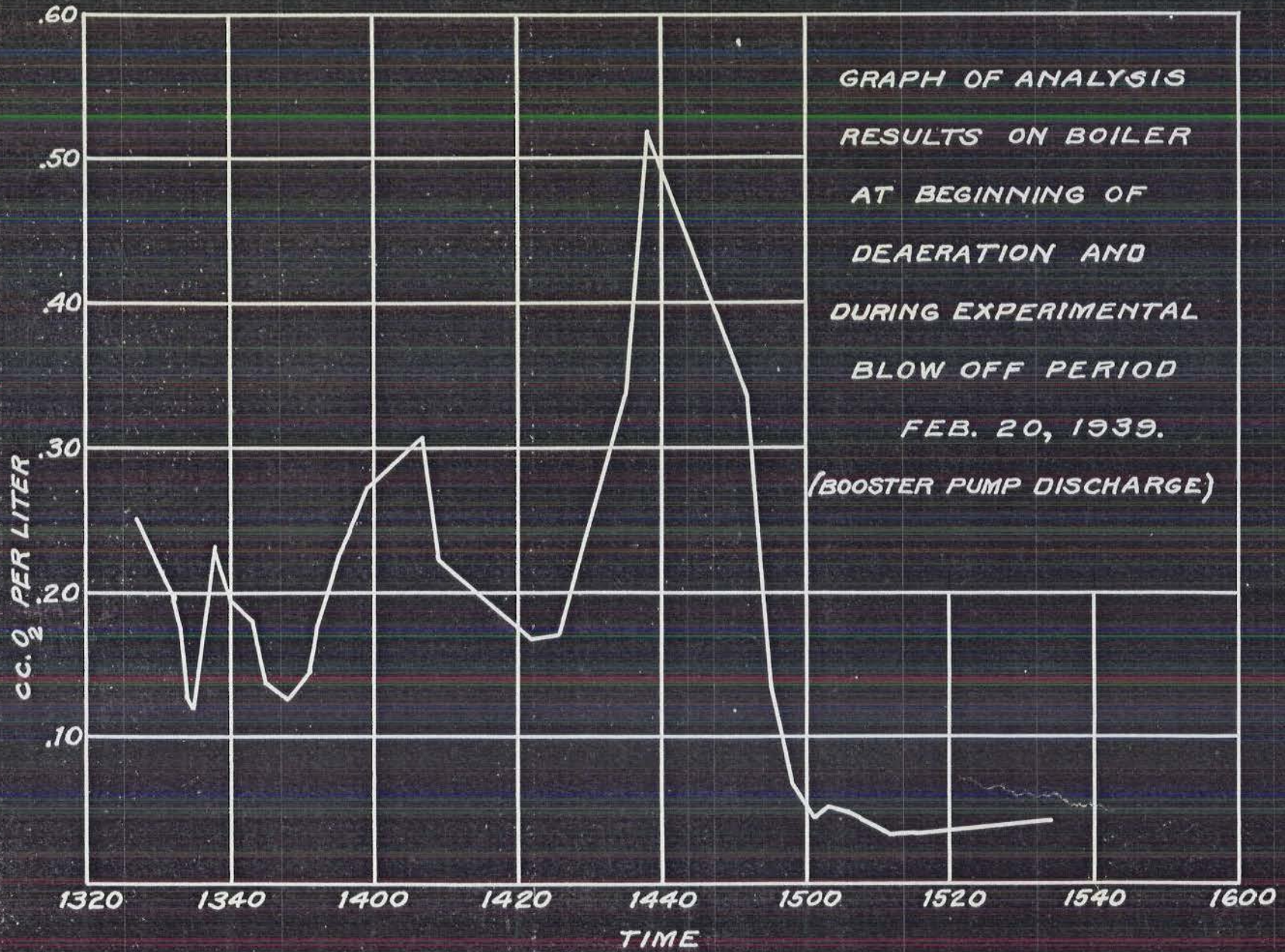
GRAPH OF ANALYSIS RESULTS OF SHUTDOWN ON WED., FEB. 15, 1939.

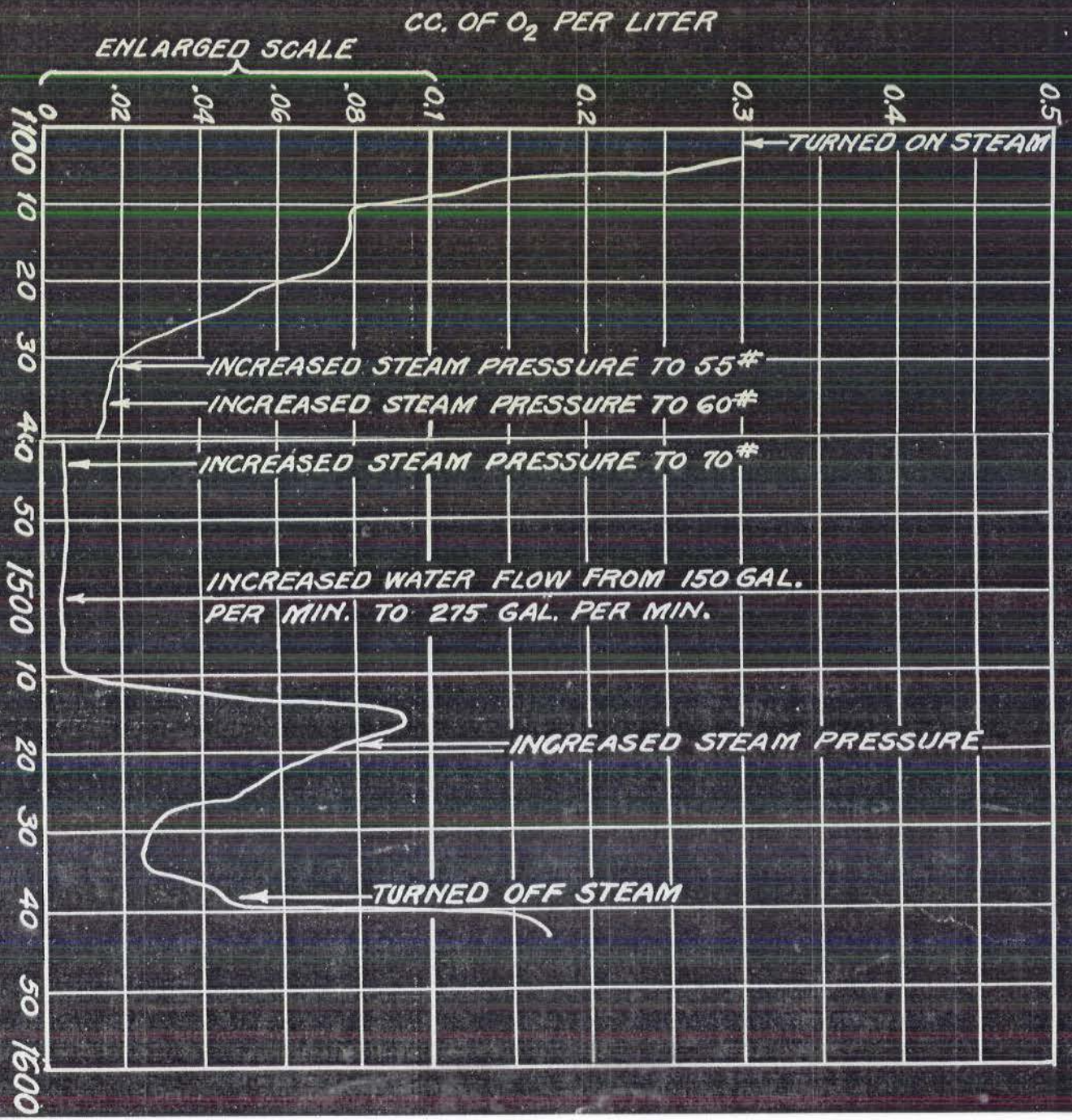
(BOOSTER PUMP DISCHARGE)

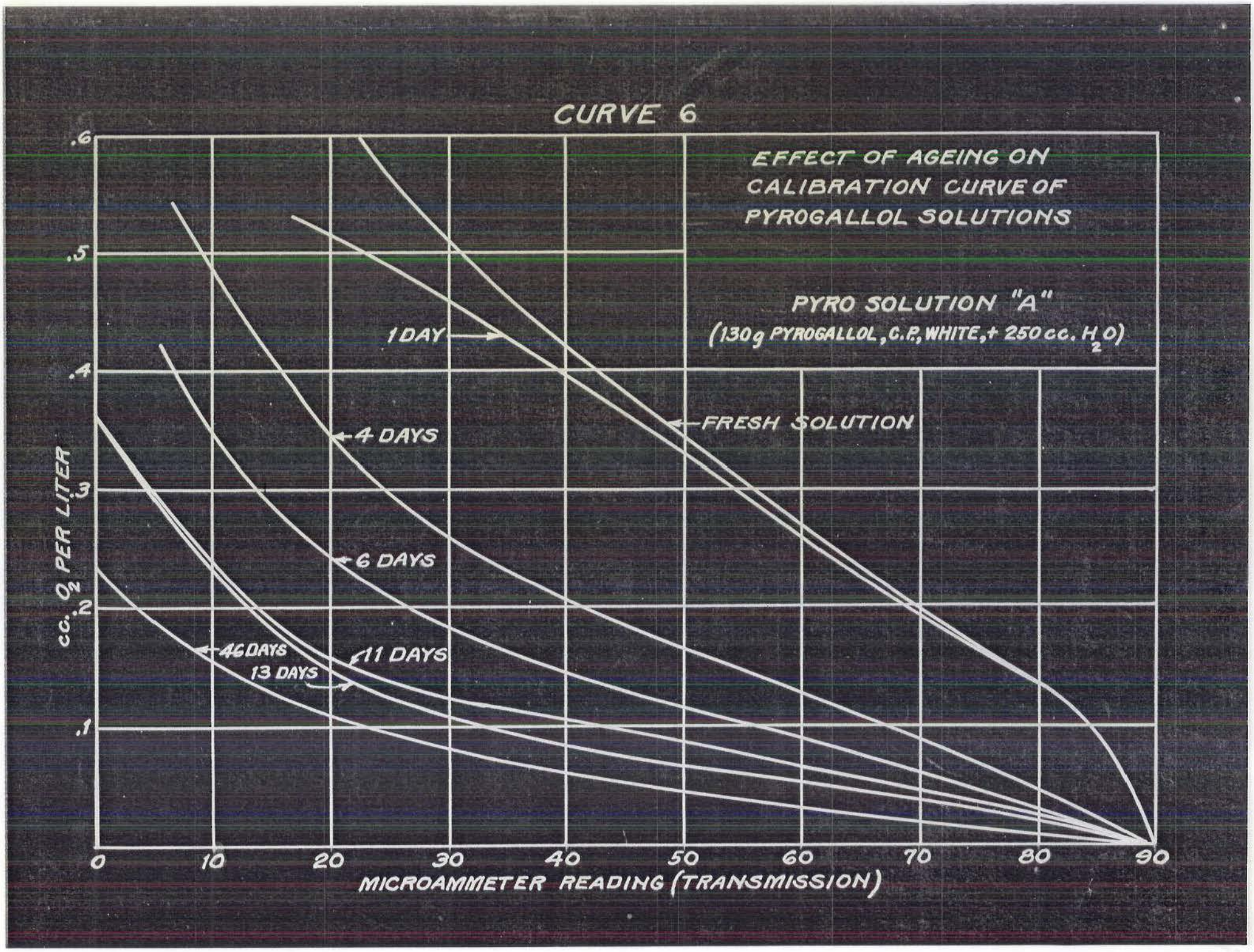


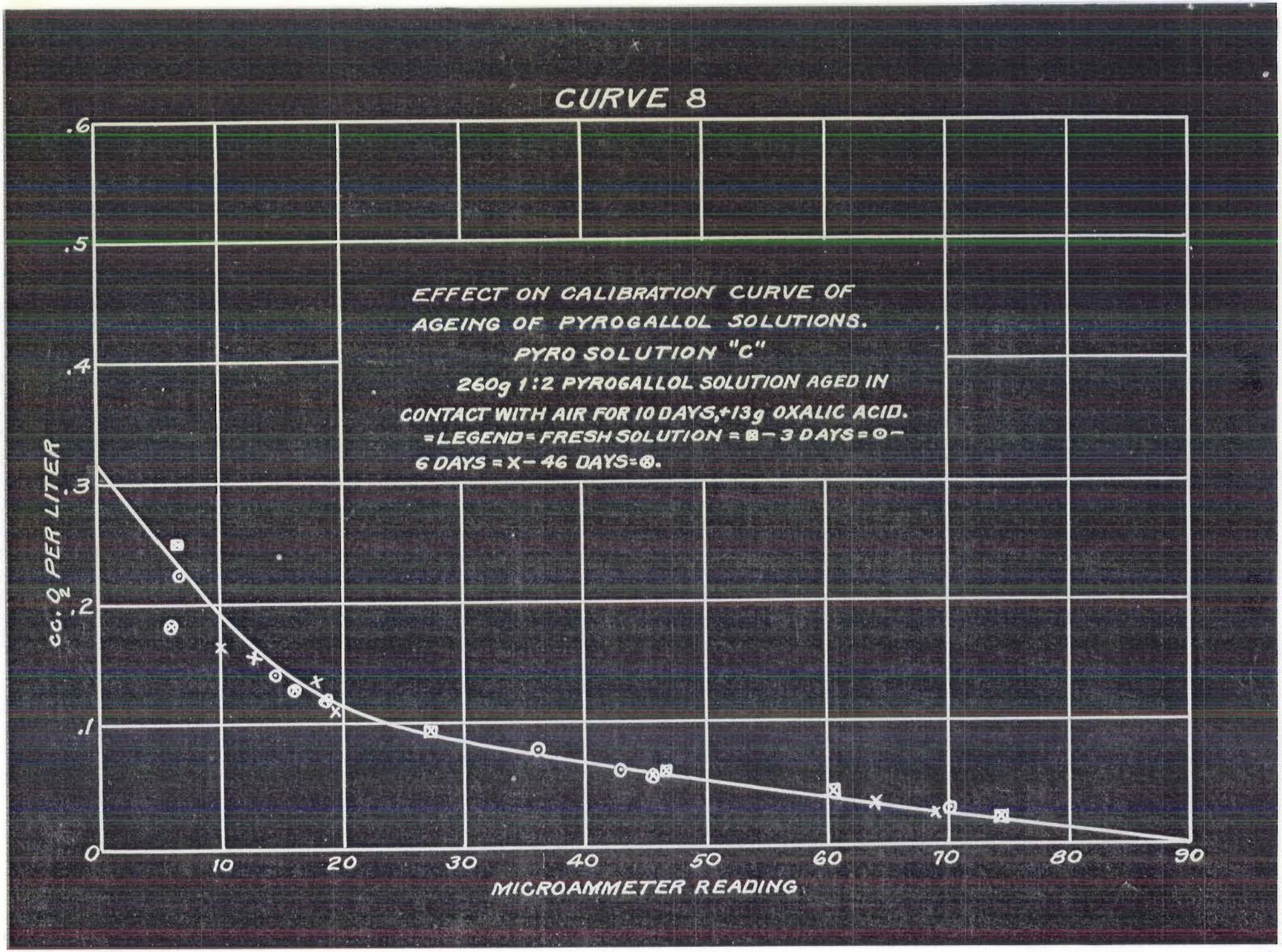

CURVE 2
GRAPH OF ANALYSIS RESULTS AT BEGINNING DEAERATION ON THURS., FEB. 16, 1939 (BOOSTER PUMP DISCHARGE)
SHUT DOWN APPARATUS TO REFILL REAGENTS
.60
.50
.40
.30
.20
.10
CC. O2 PER LITER
1150
1210
1230
1250
1310
1330
1350
1410
1430
1450
TIME

CURVE 3


GRAPH OF ANALYSIS
RESULTS ON BOILER
AT BEGINNING OF
DEAERATION AND
DURING EXPERIMENTAL
BLOW OFF PERIOD
FEB. 20, 1939.
(BOOSTER PUMP DISCHARGE)
.60
.50
.40
.30
.20
.10
cc. O_2 PER LITER
1320
1340
1400
1420
1440
1500
1520
1540
1600
TIME

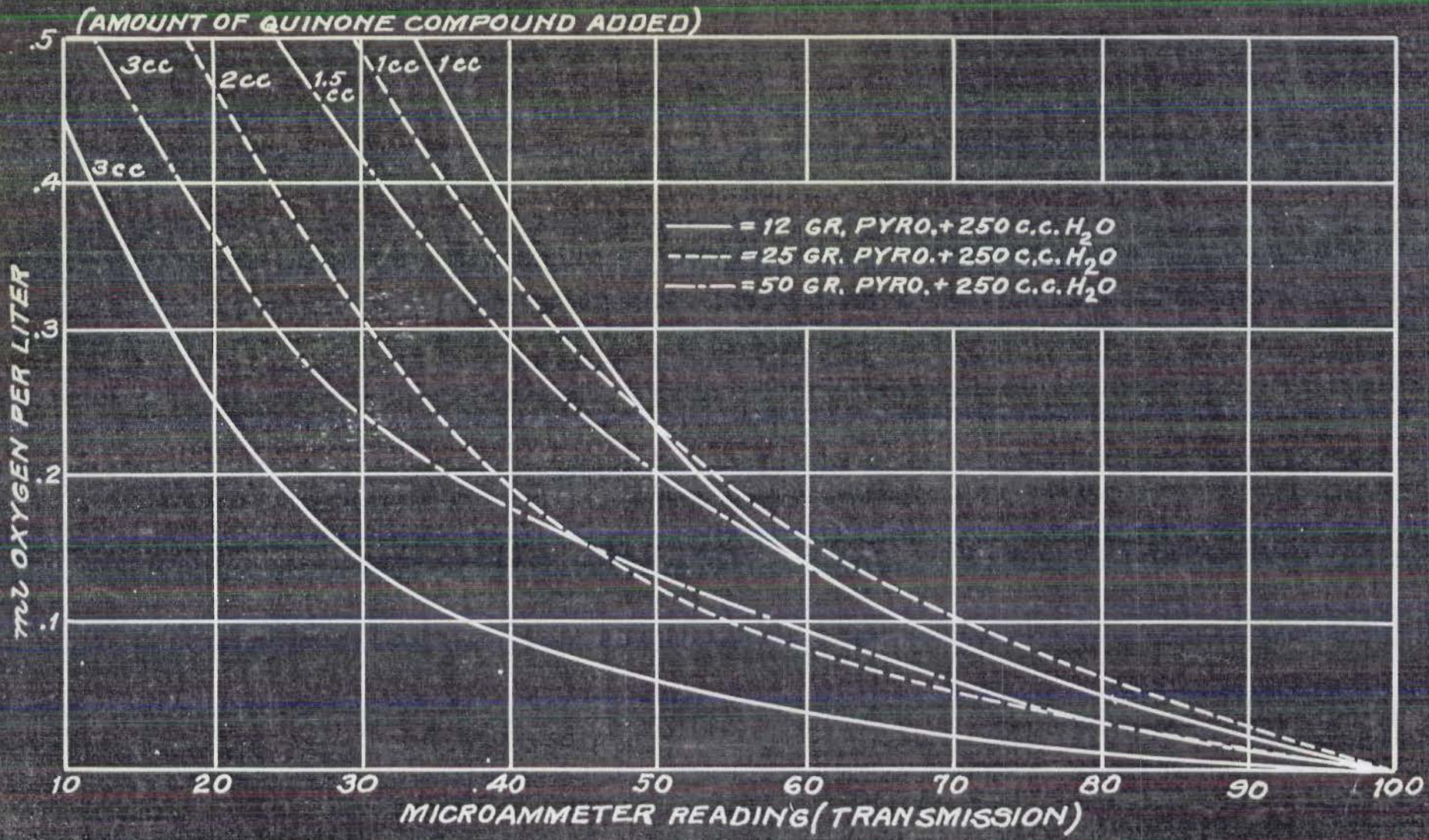

CC. OF O_2 PER LITER
ENLARGED SCALE
0
.02
.04
.06
.08
0.1
0.2
0.3
0.4
0.5
1100
10
20
30
40
50
1500
10
20
30
40
50
1600
TURNED ON STEAM
INCREASED STEAM PRESSURE TO 55#
INCREASED STEAM PRESSURE TO 60#
INCREASED STEAM PRESSURE TO 70#
INCREASED WATER FLOW FROM 150 GAL. PER MIN. TO 275 GAL. PER MIN.
INCREASED STEAM PRESSURE
TURNED OFF STEAM


CURVE 6
EFFECT OF AGEING ON CALIBRATION CURVE OF PYROGALLOL SOLUTIONS
PYRO SOLUTION "A"
(130g PYROGALLOL, C.P., WHITE, + 250 cc. H_2O)
1 DAY
4 DAYS
6 DAYS
46 DAYS
13 DAYS
11 DAYS
FRESH SOLUTION
cc. O_2 PER LITER
.6
.5
.4
.3
.2
.1
0
10
20
30
40
50
60
70
80
90
MICROAMMETER READING (TRANSMISSION)


CURVE 8
EFFECT ON CALIBRATION CURVE OF
AGEING OF PYROGALLOL SOLUTIONS.
PYRO SOLUTION "C"
260g 1:2 PYROGALLOL SOLUTION AGED IN
CONTACT WITH AIR FOR 10 DAYS,+13g OXALIC ACID.
=LEGEND= FRESH SOLUTION = ⊠ – 3 DAYS = ⊙ –
6 DAYS = X – 46 DAYS = ⊗.
cc. O_2 PER LITER
.6
.5
.4
.3
.2
.1
0
10
20
30
40
50
60
70
80
90
MICROAMMETER READING

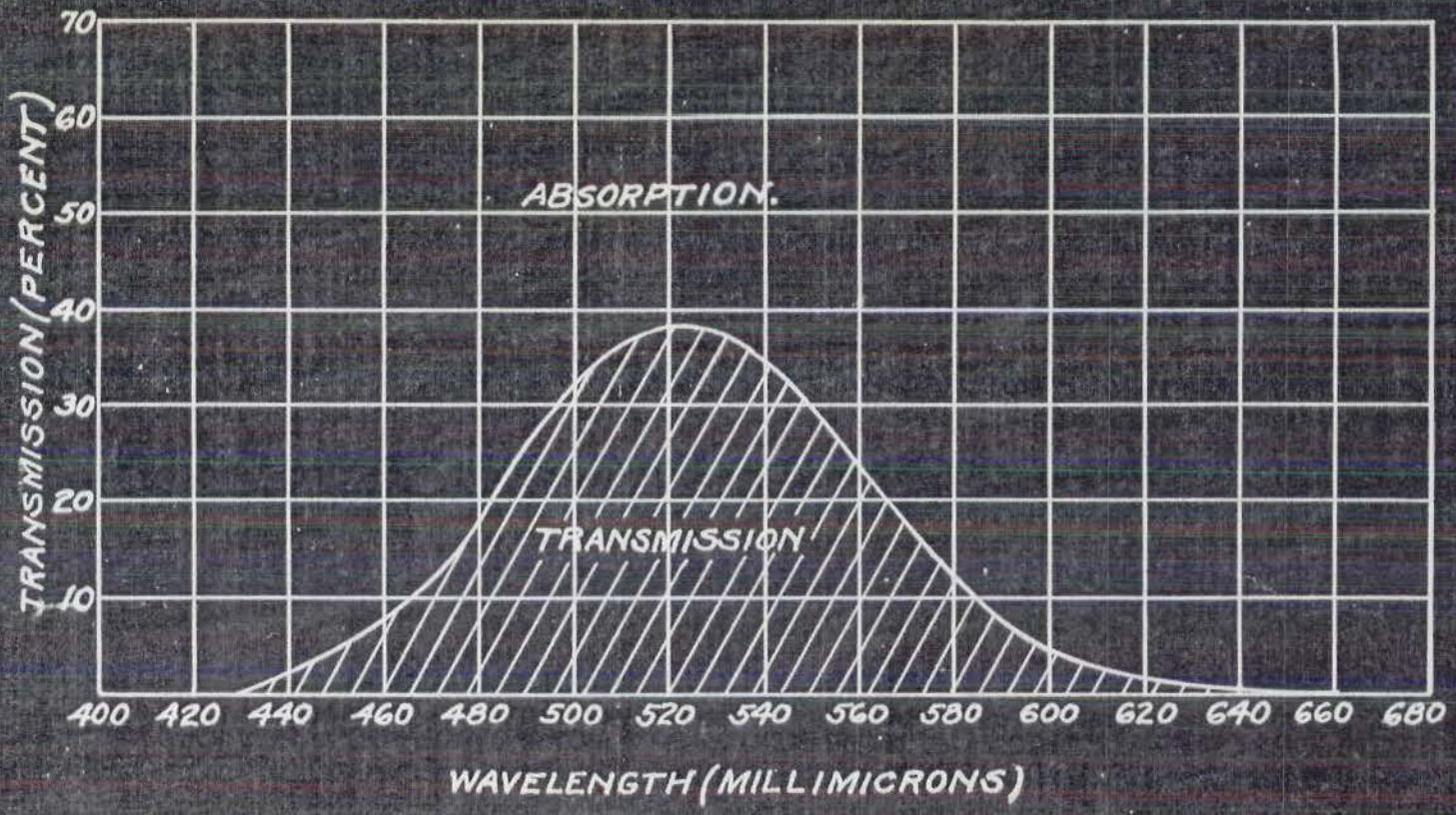
CURVE 9

EFFECT OF CHANGE IN RATIO OF C.P. PYROGALLOL TO QUINONE COMPOUND ON CALIBRATION CURVE.



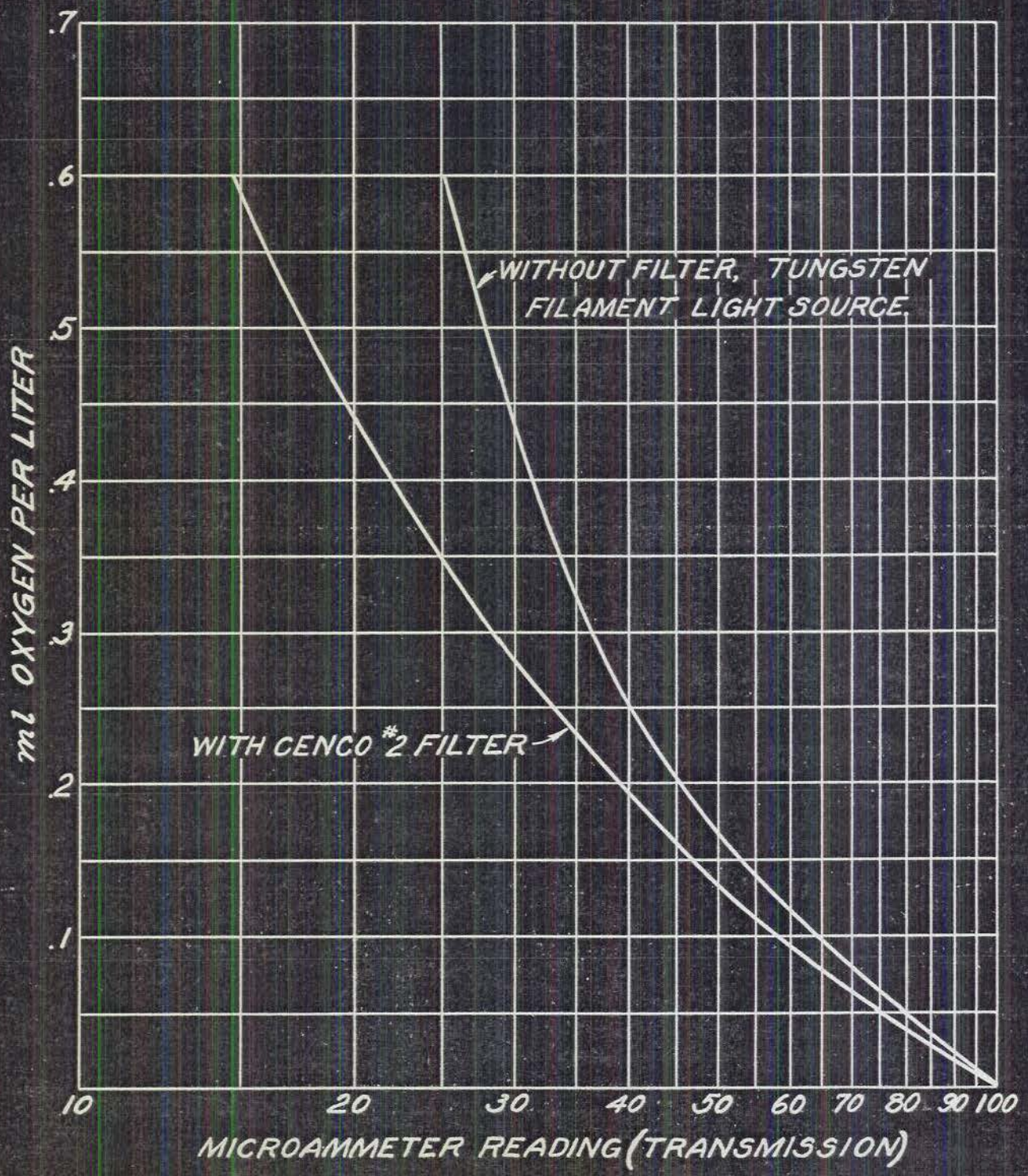
CURVE 10

TRANSMISSION CURVE OF #2 GREEN SPECTRAL FILTER



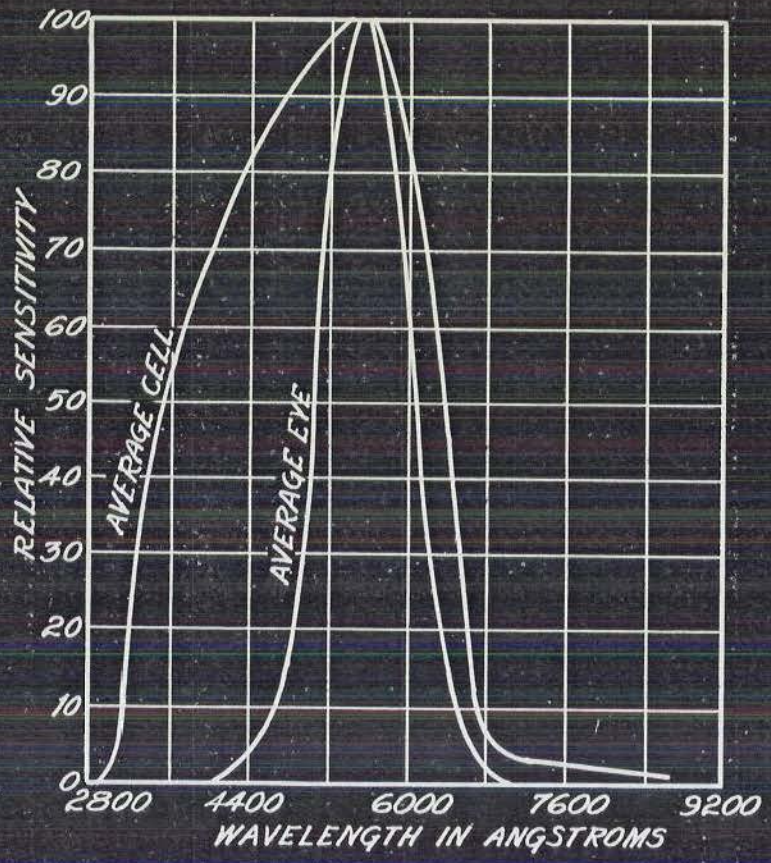
CURVE II

COMPARISON OF CALIBRATION CURVES
WITH AND WITHOUT SPECTRAL FILTER

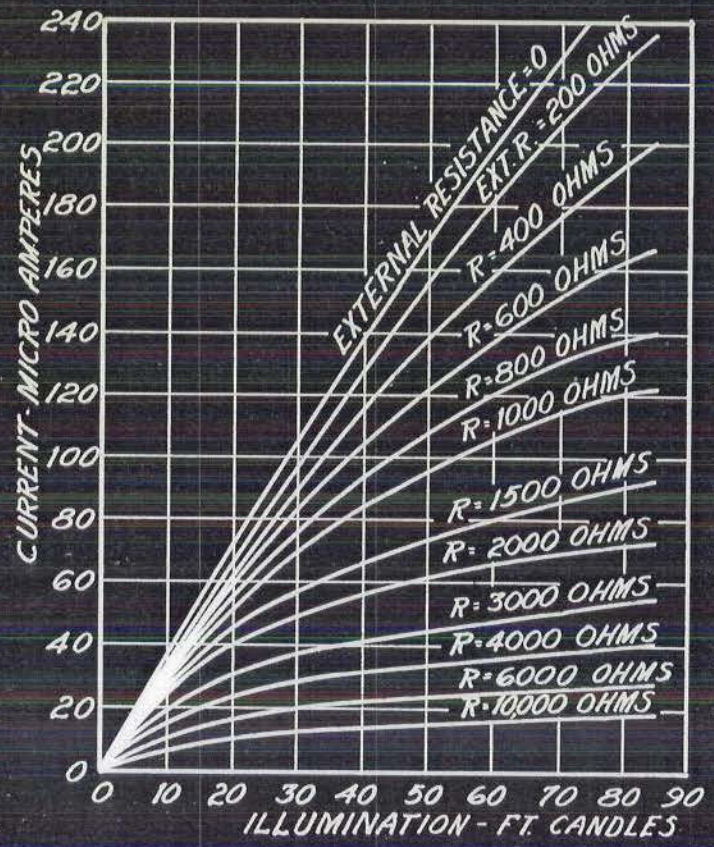


CURVE 12

SENSITIVITY AND CURRENT ILLUMINATION CURVE
OF G.E. BLOCKING-LAYER TYPE PHOTOELECTRIC CELL



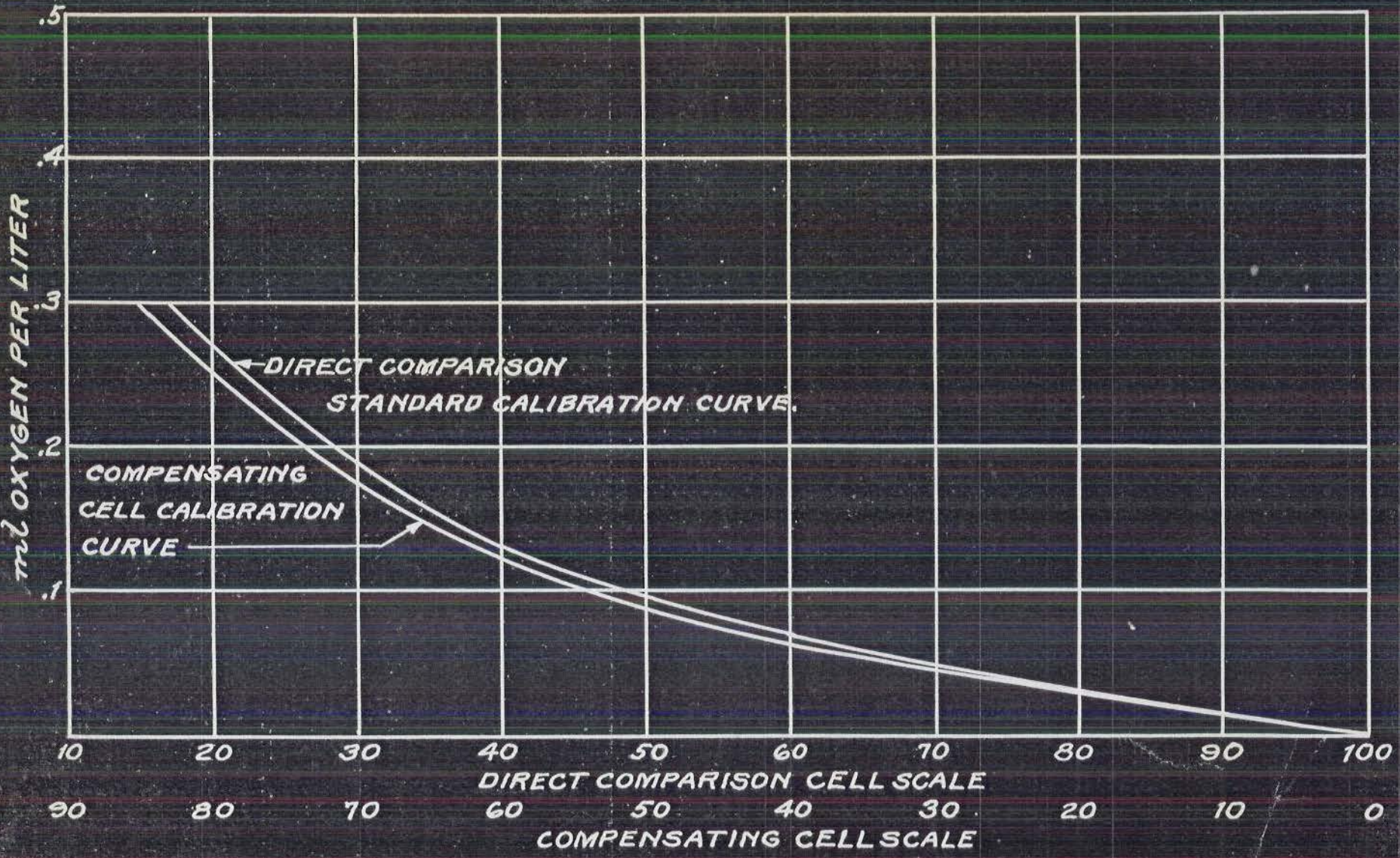
SPECTRAL SENSITIVITY OF CELL COMPARED
WITH RESPONSE OF AVERAGE EYE.



CURRENT-ILLUMINATION CHARACTERISTICS
OF CELL

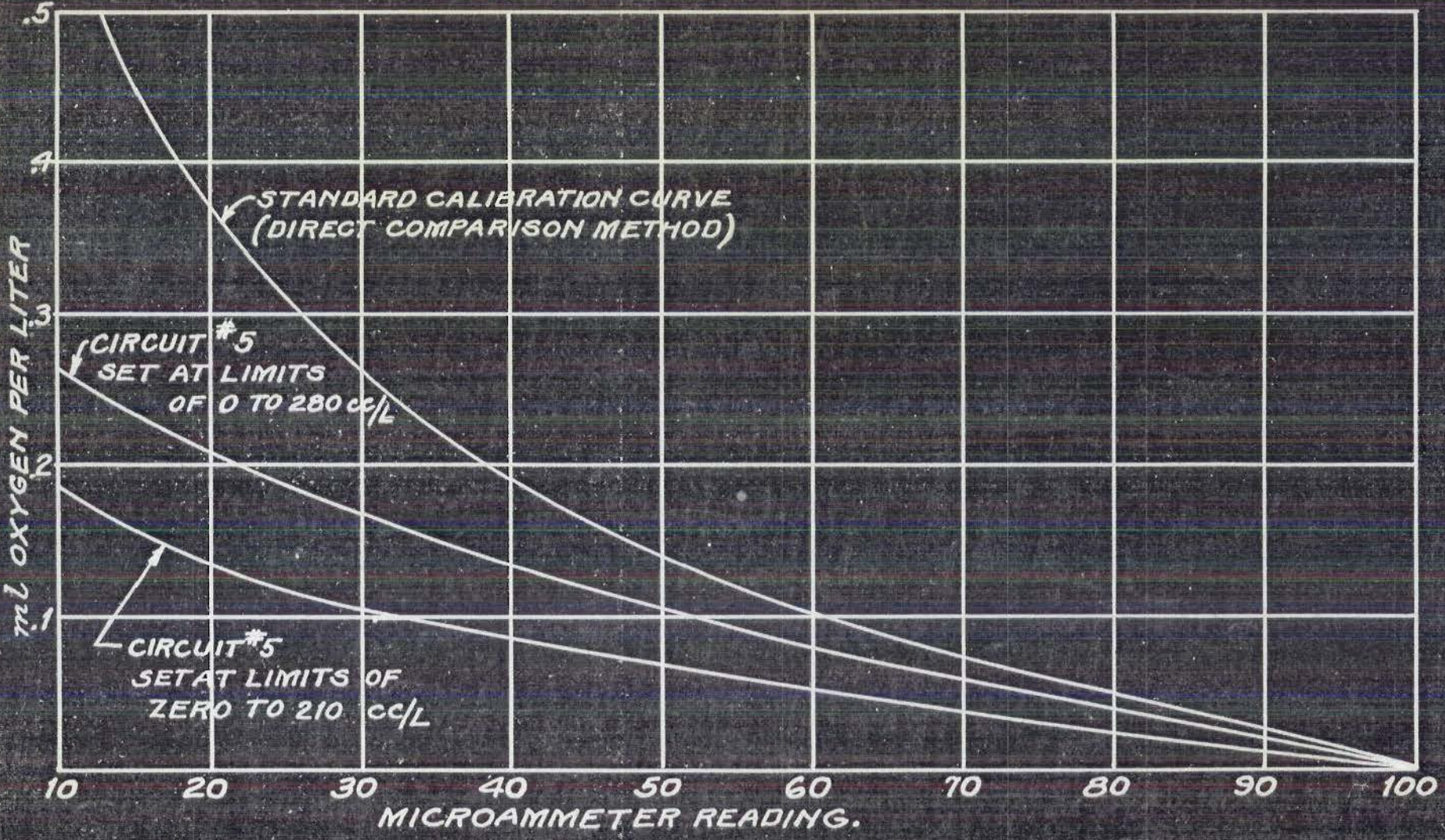
CURVE 13

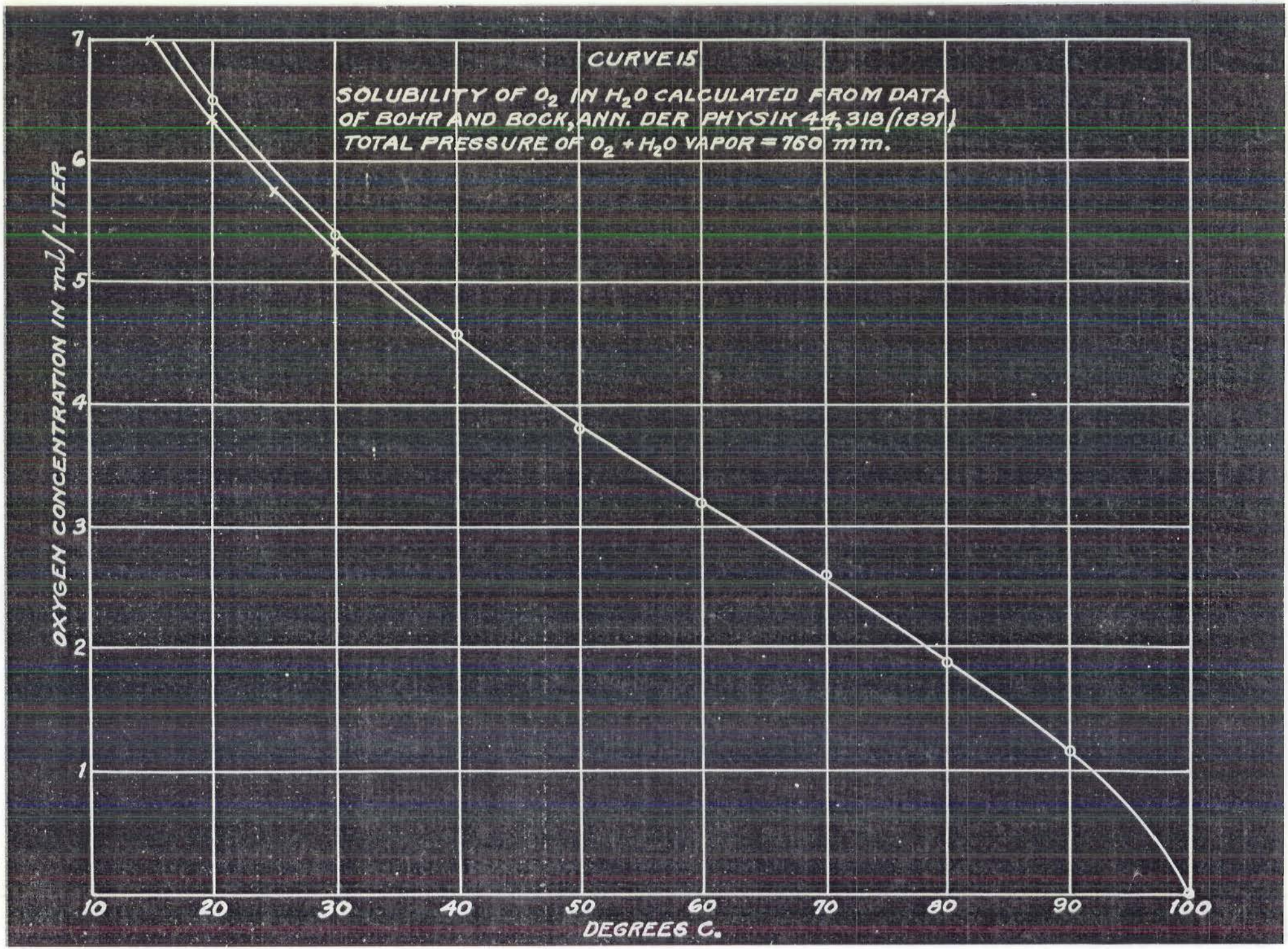
DIRECT COMPARISON OF CALIBRATION CURVES.
SINGLE PHOTOCELL ARRANGEMENT AND
COMPENSATING 2 PHOTOCELL CIRCUIT.



CURVE 14X

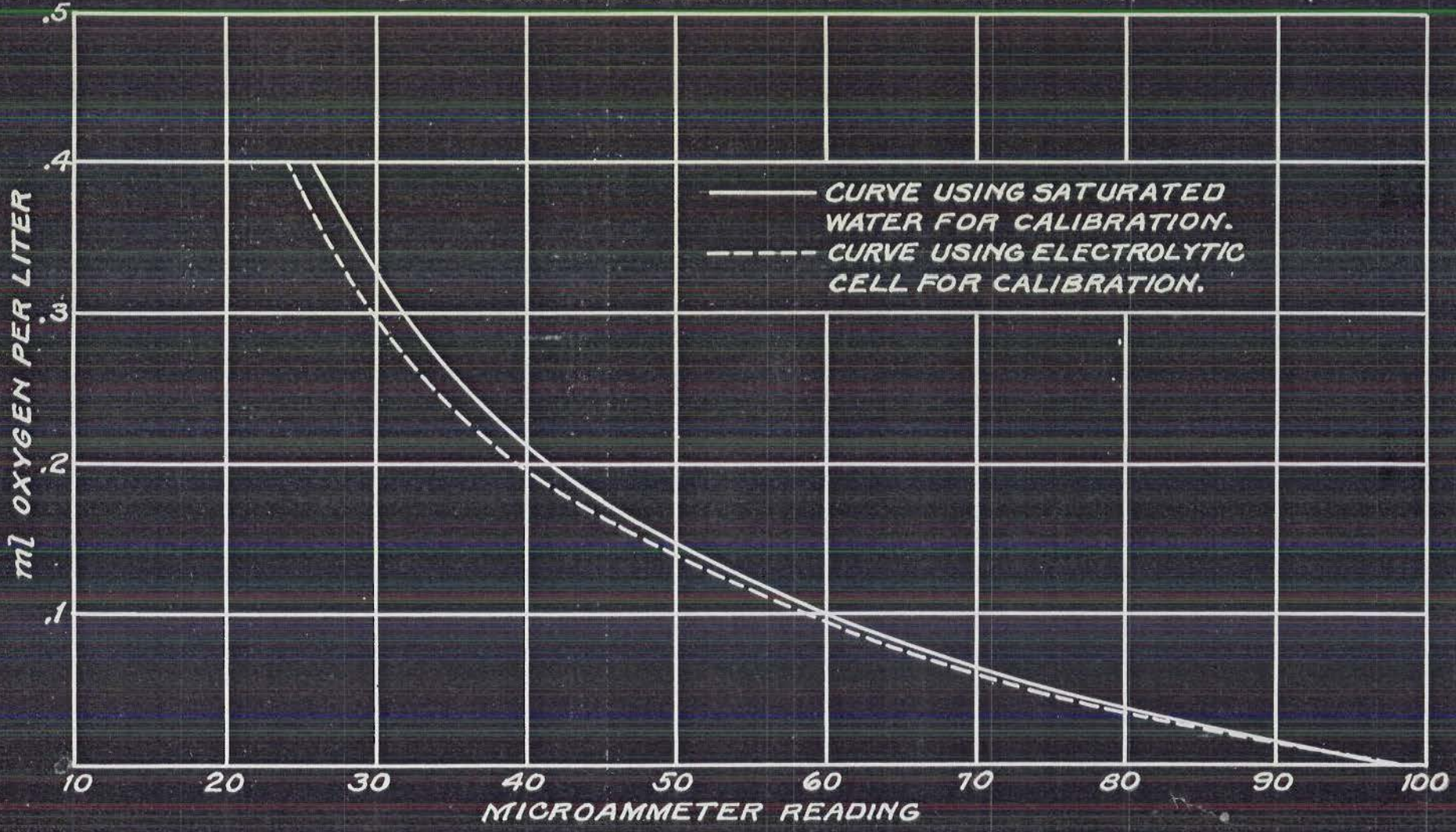
CALIBRATION CURVE TAKEN WITH 2-PHOTOCELL CIRCUIT #5, ADJUSTING FOR 0 TO 100 SCALE READING AT PREDETERMINED OXYGEN CONCENTRATION LIMITS




CURVE 15
SOLUBILITY OF O_2 IN H_2O CALCULATED FROM DATA OF BOHR AND BOCK, ANN. DER PHYSIK 44, 318 (1891)
TOTAL PRESSURE OF O_2 + H_2O VAPOR = 760 mm.
OXYGEN CONCENTRATION IN ml/LITER
DEGREES C.
1
2
3
4
5
6
7
10
20
30
40
50
60
70
80
90
100

CURVE 16

COMPARISON OF SATURATED WATER
VS
ELECTROLYTIC CELL METHOD OF CALIBRATION.

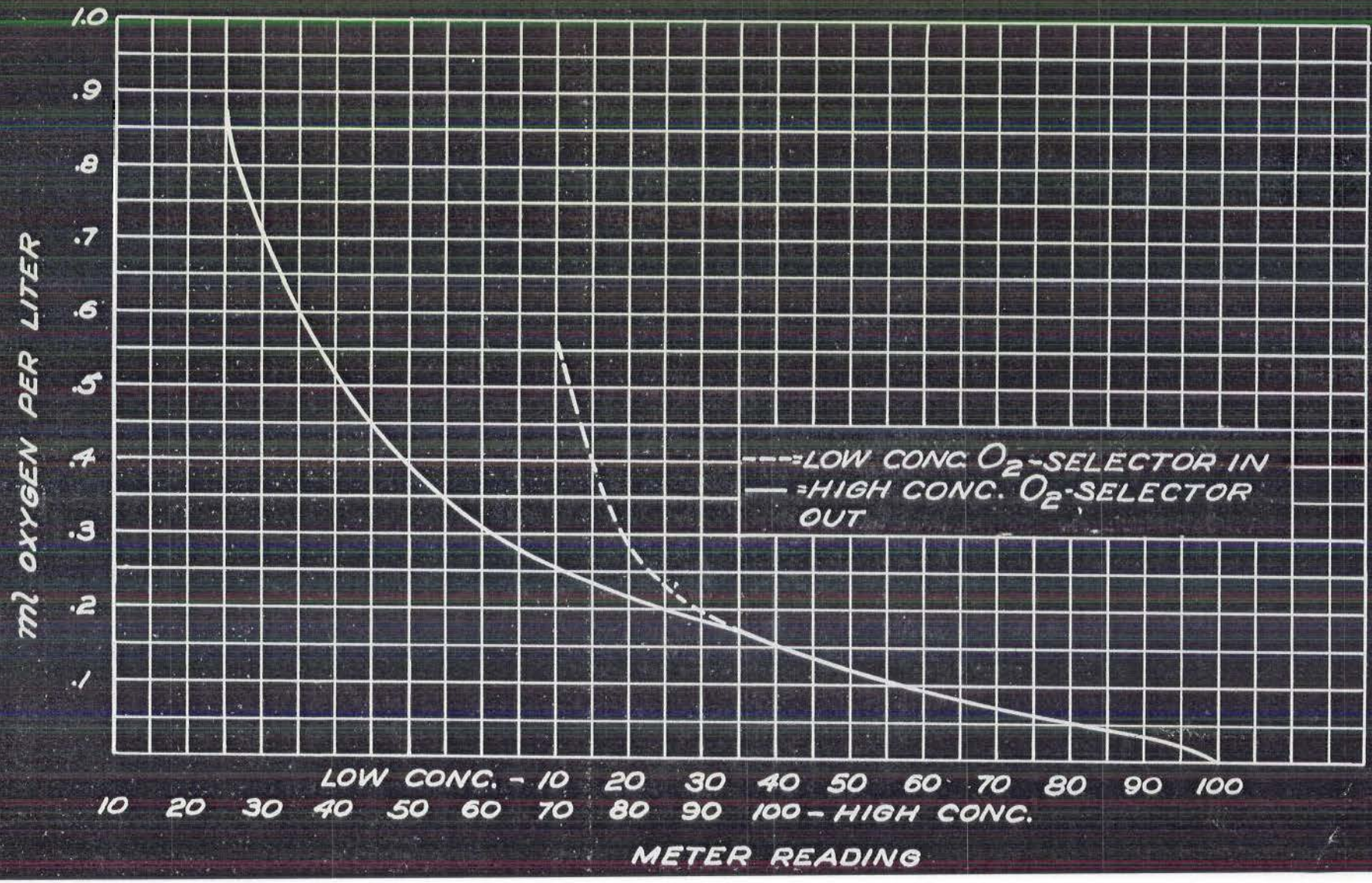


CURVE 17

CALIBRATION CURVE FOR

N.R.L. DISSOLVED OXYGEN INDICATOR

(EXPERIMENTAL MODEL)



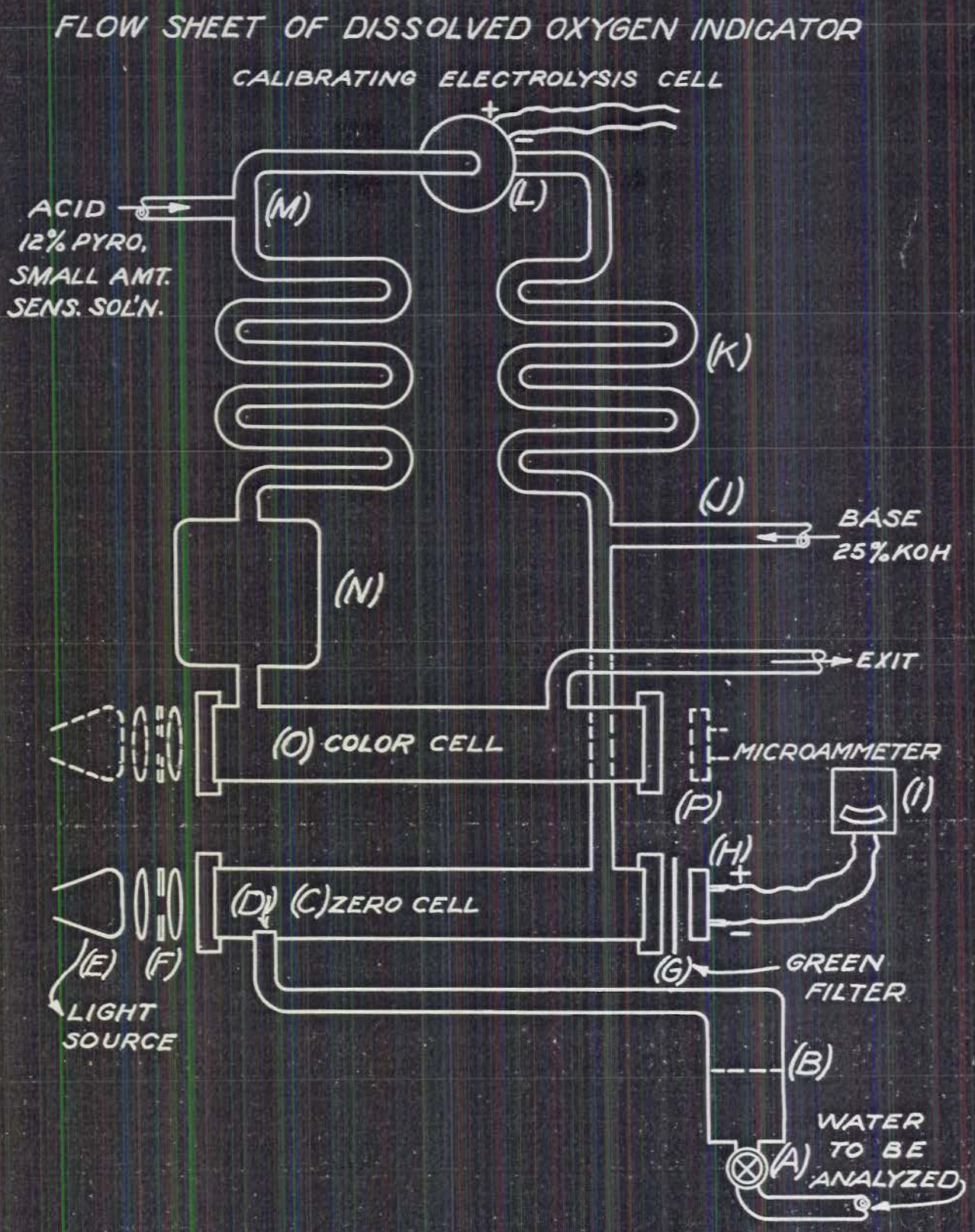

FLOW SHEET OF DISSOLVED OXYGEN INDICATOR
CALIBRATING ELECTROLYSIS CELL
+
−
(L)
(M)
ACID
12% PYRO.
SMALL AMT.
SENS. SOL'N.
(K)
(J)
BASE
25% KOH
(N)
EXIT
(O) COLOR CELL
MICROAMMETER
(P)
(I)
(H)
+
−
(D) (C) ZERO CELL
(E) (F)
LIGHT
SOURCE
(G)
GREEN
FILTER
(B)
WATER
TO BE
ANALYZED
(A)

PLATE 1

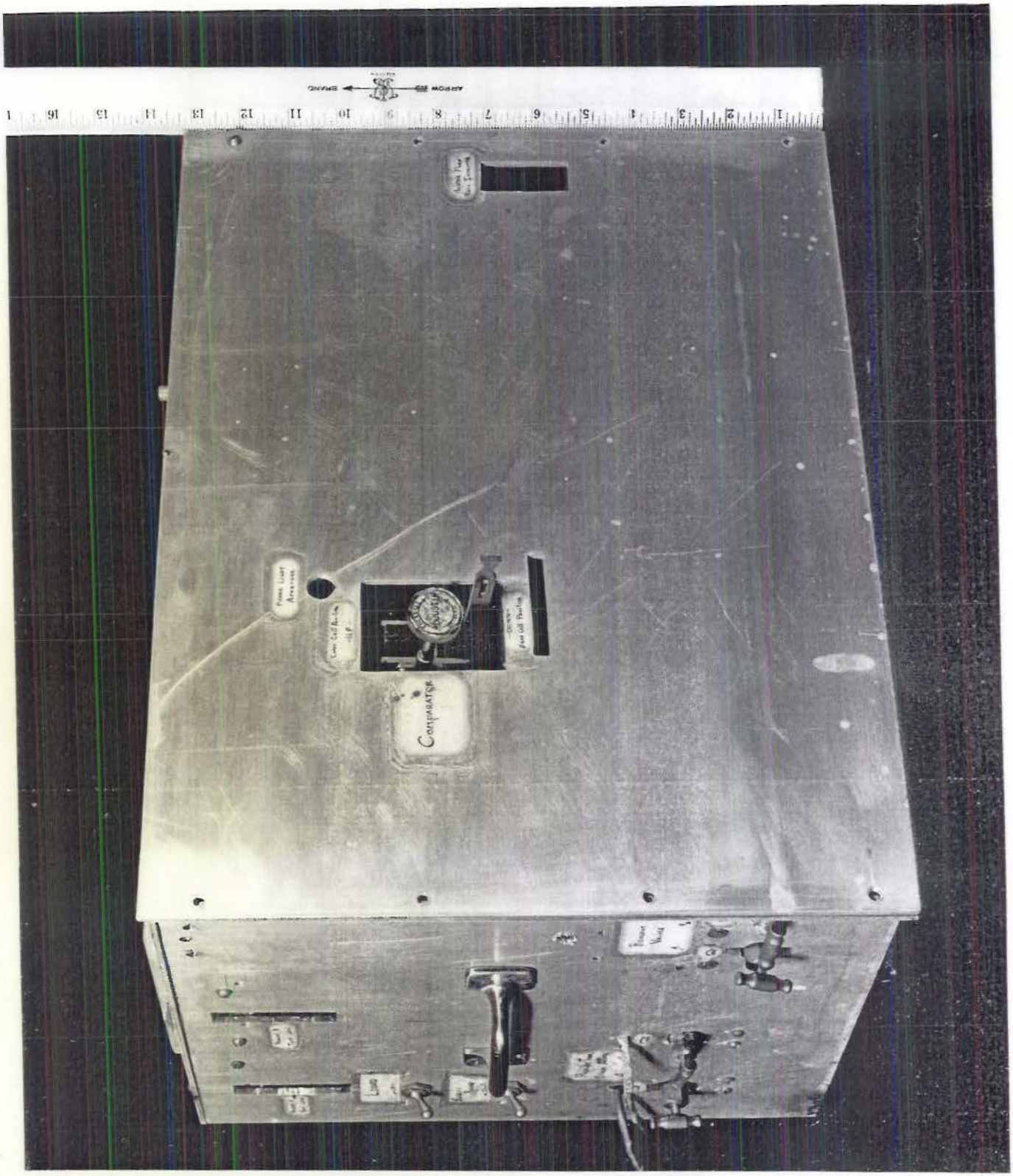


PLATE 2

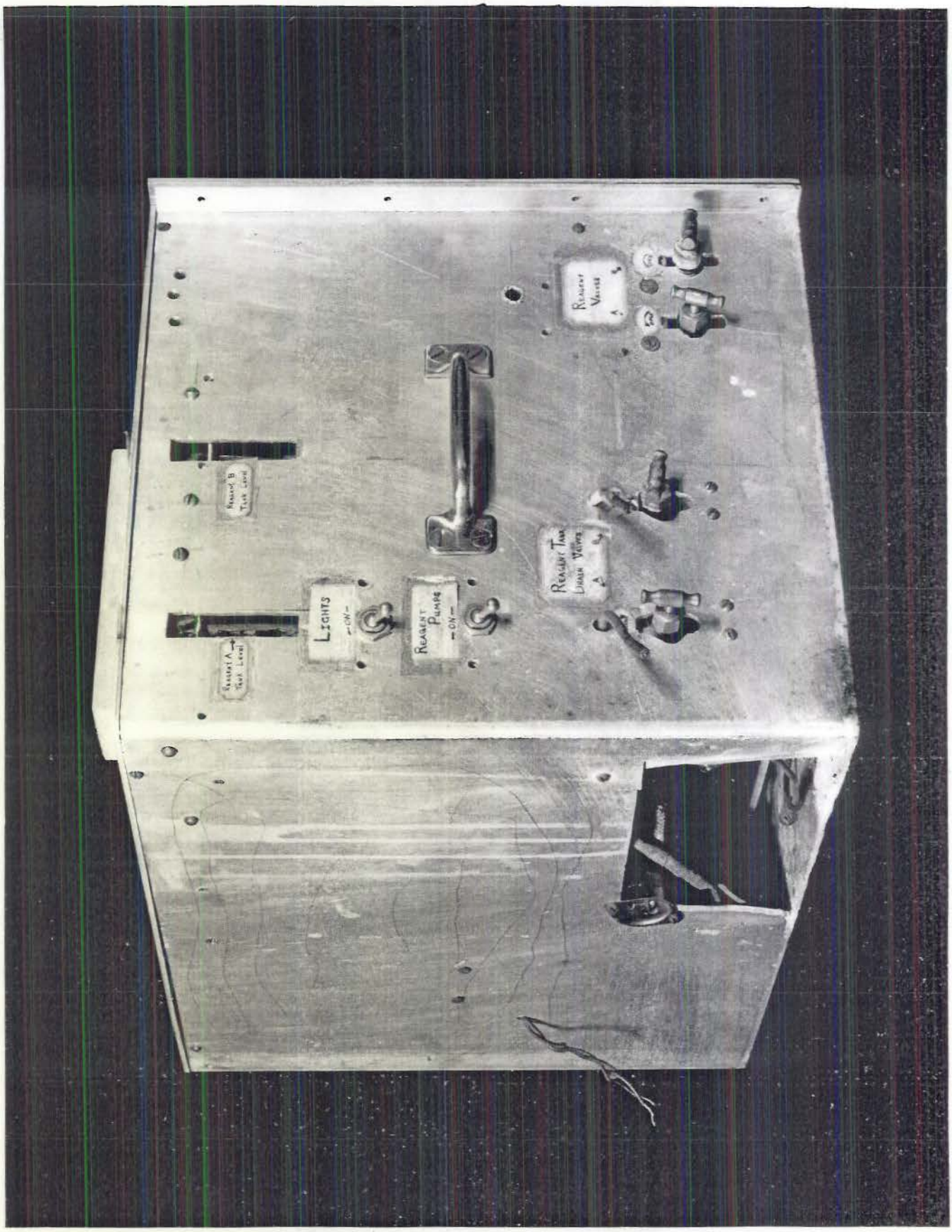

Reagent B Tank Level
Reagent A Tank Level
Lights
-ON-
Reagent Pumps
-ON-
Reagent Tank Drain Valves
A
Reagent Valves
A

PLATE 3

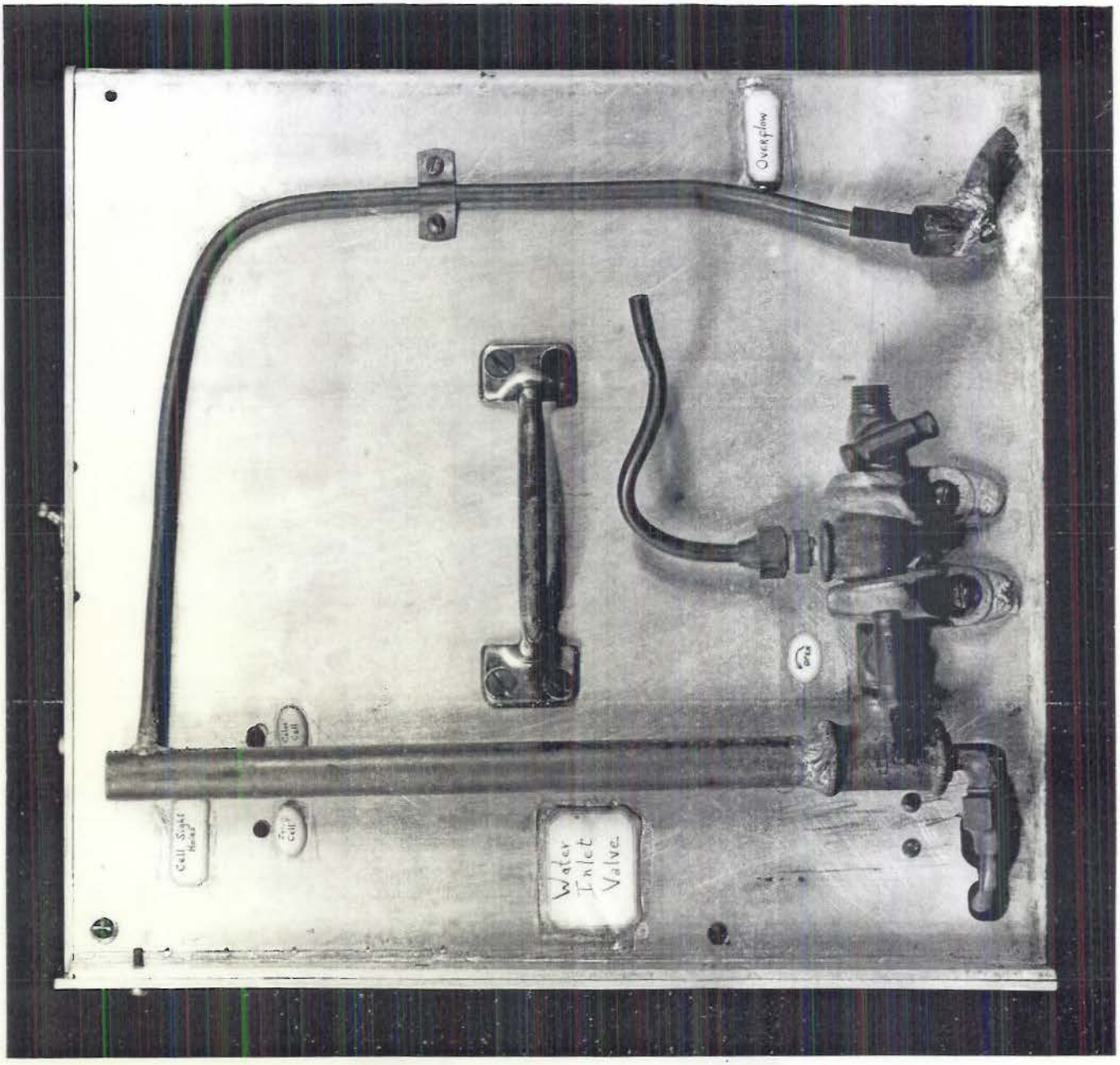

Cell Sight Head
Zinc Cell
Glass Cell
Water Inlet Valve
Overflow

PLATE 4

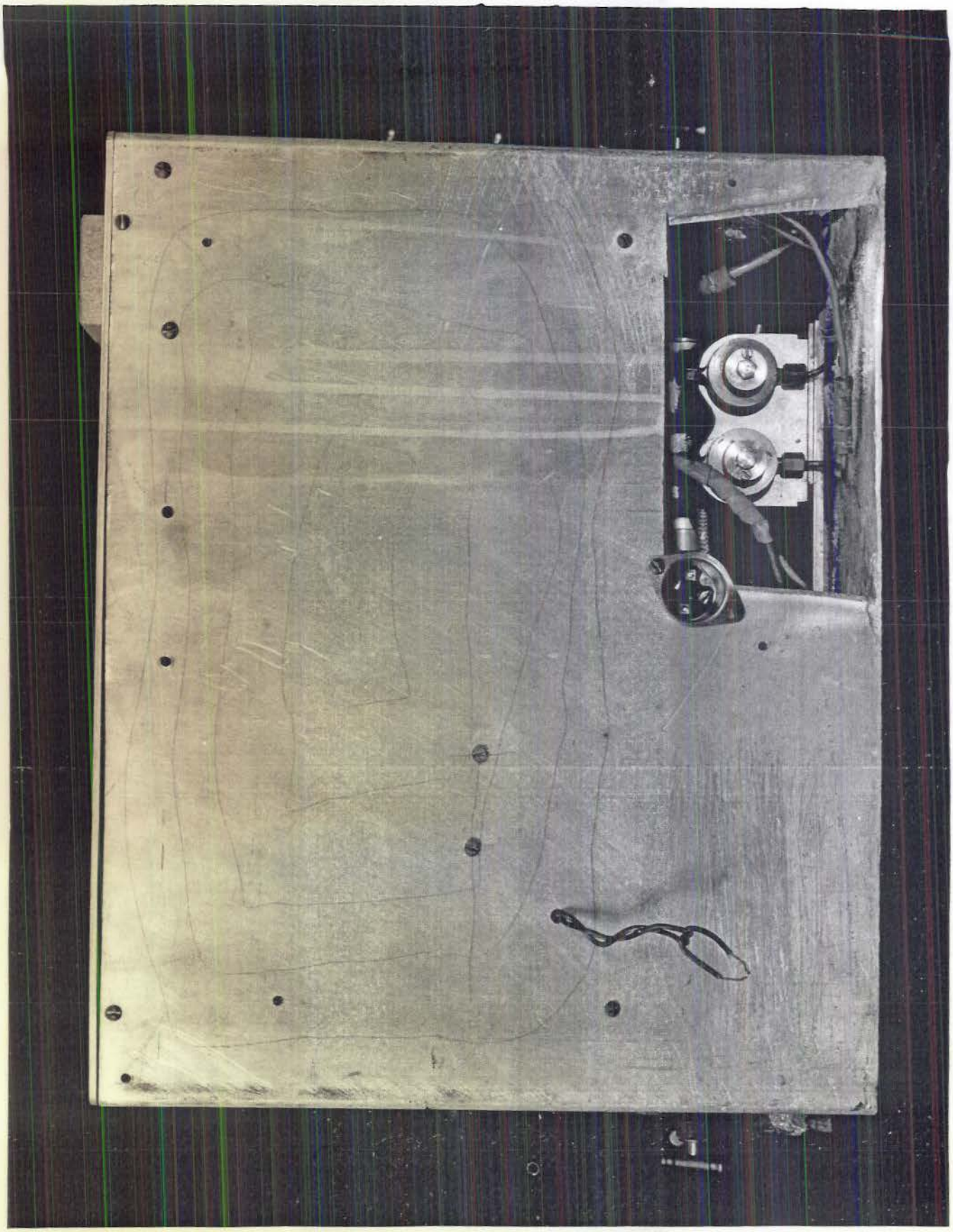


PLATE 5

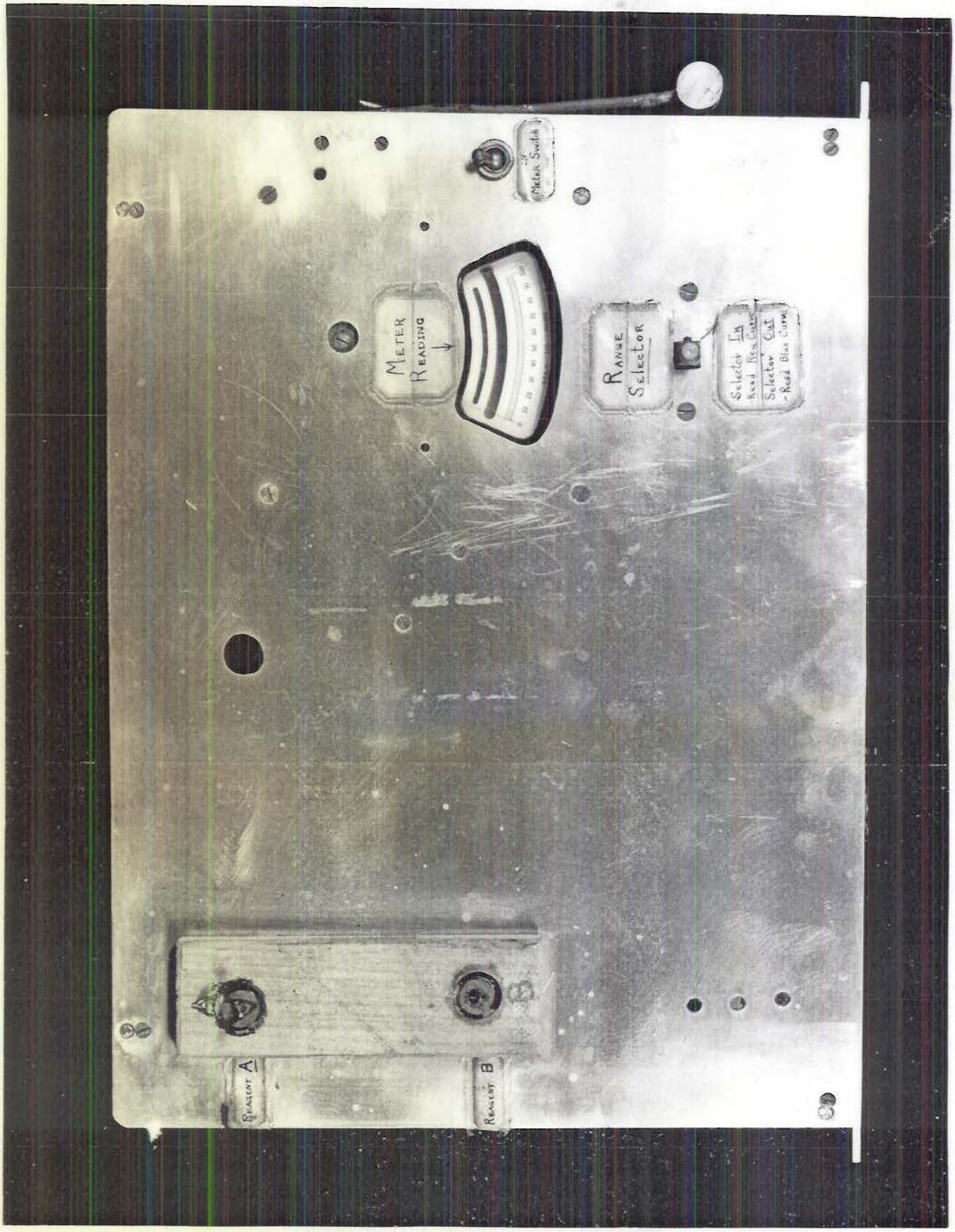

Reagent A
Reagent B
Meter Reading
Range Selector
Selector In
Read Red Curve
Selector Out
Read Blue Curve
Meter Switch

PLATE 6

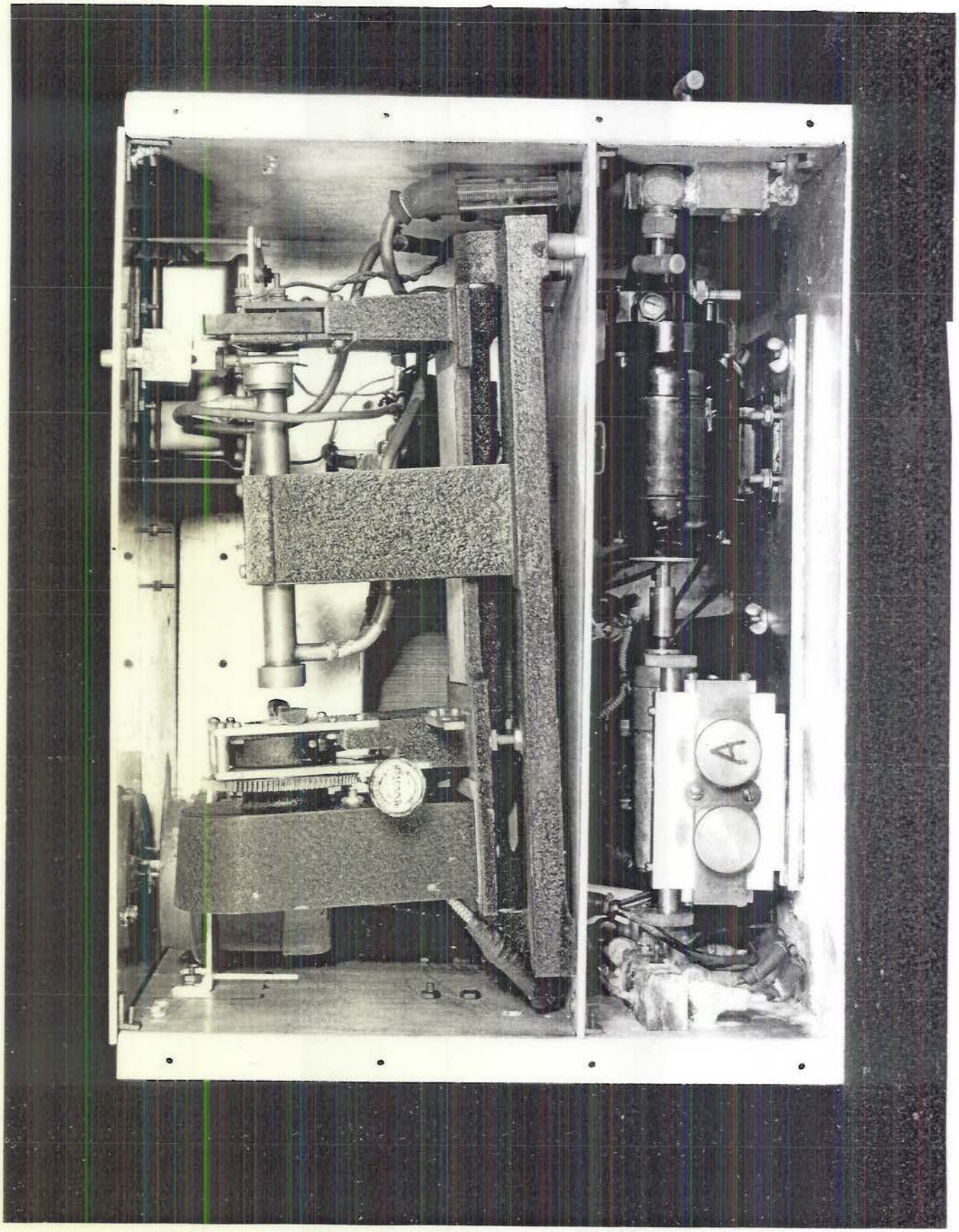


PLATE 7

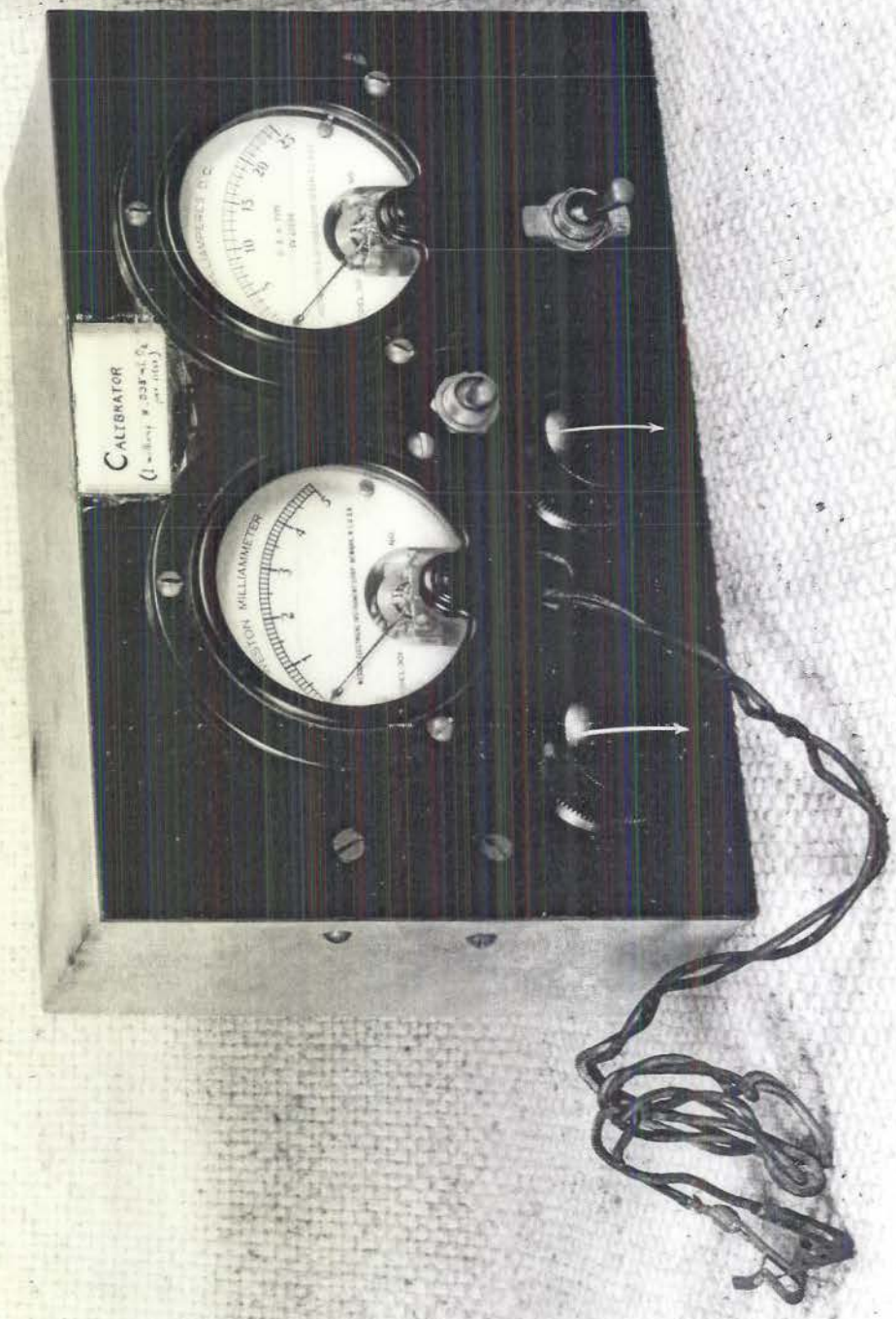


PLATE 8

PLATE 9

SEALED REACTION AND AGITATING CHAMBER FOR THE REACTION OF WINKLER REAGENTS WITH WATER UNDER ANALYSIS.

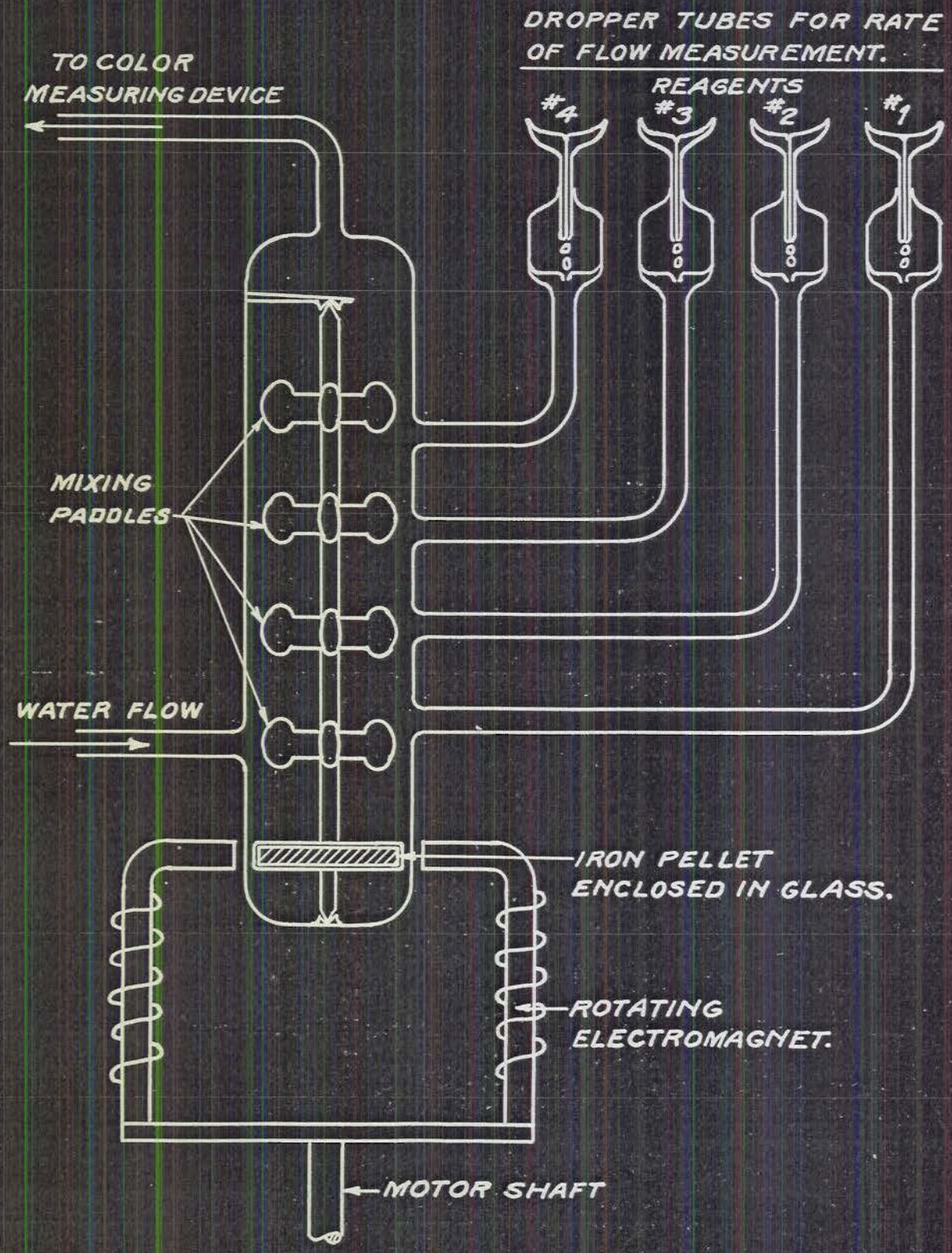


PLATE 10

Plate 11

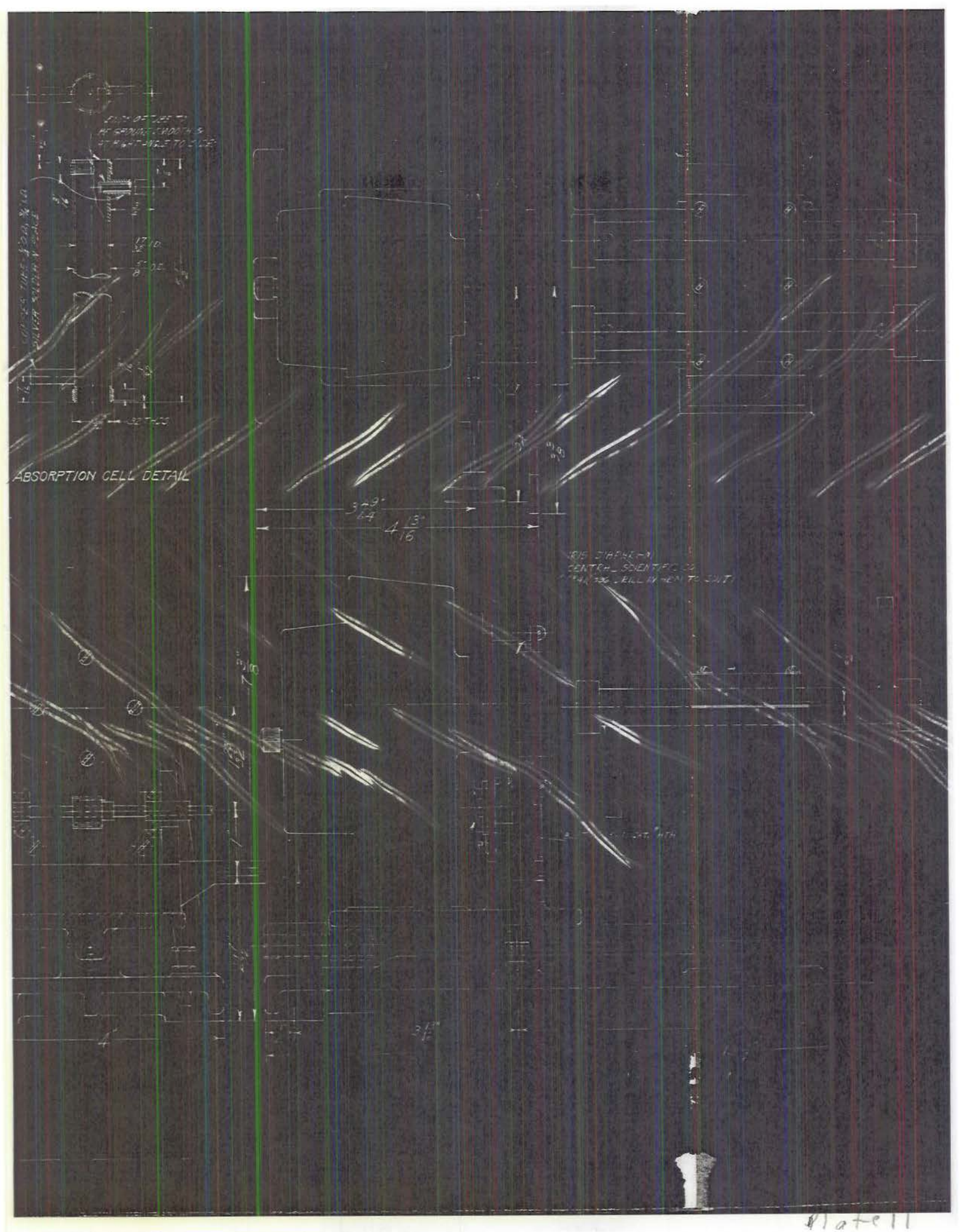
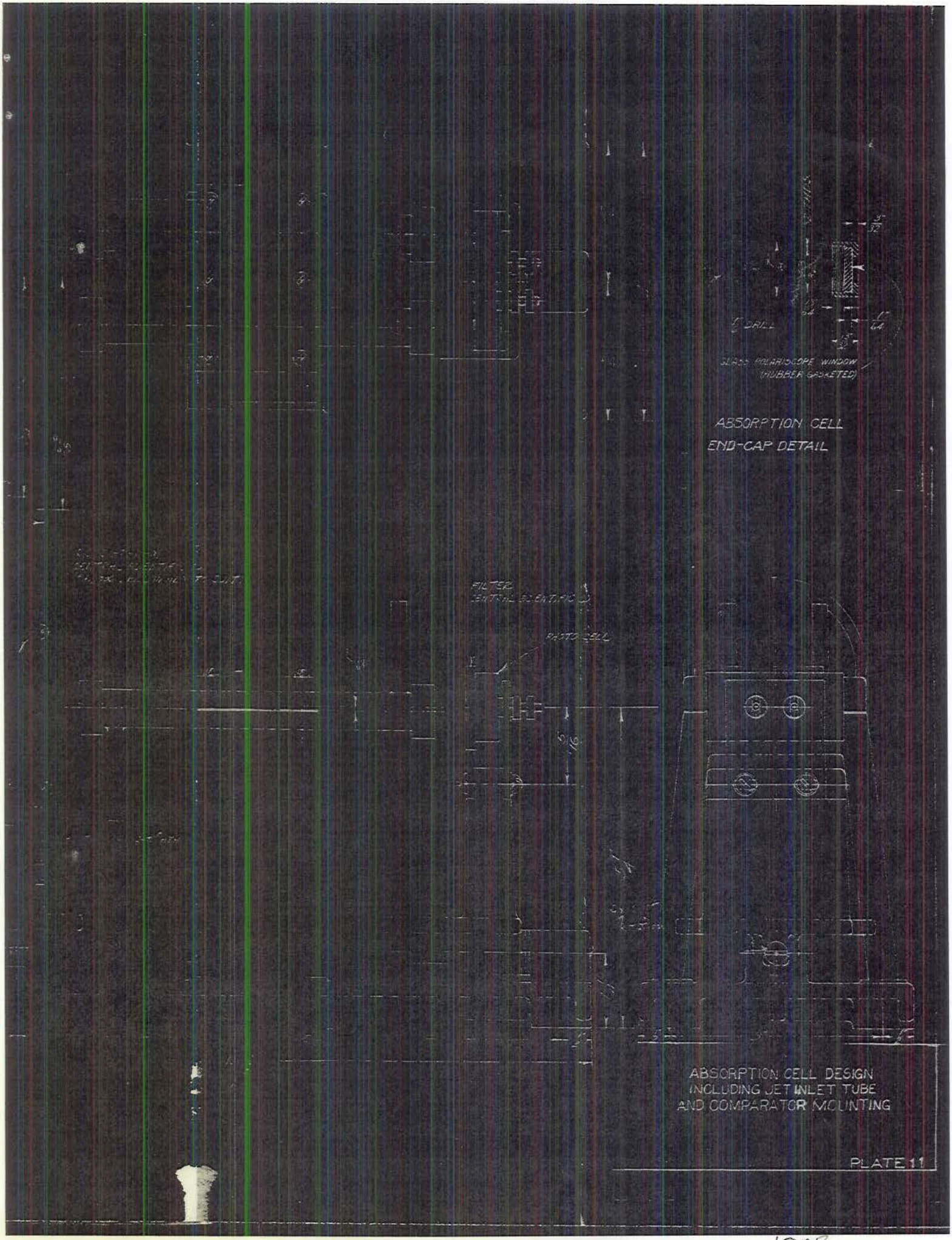


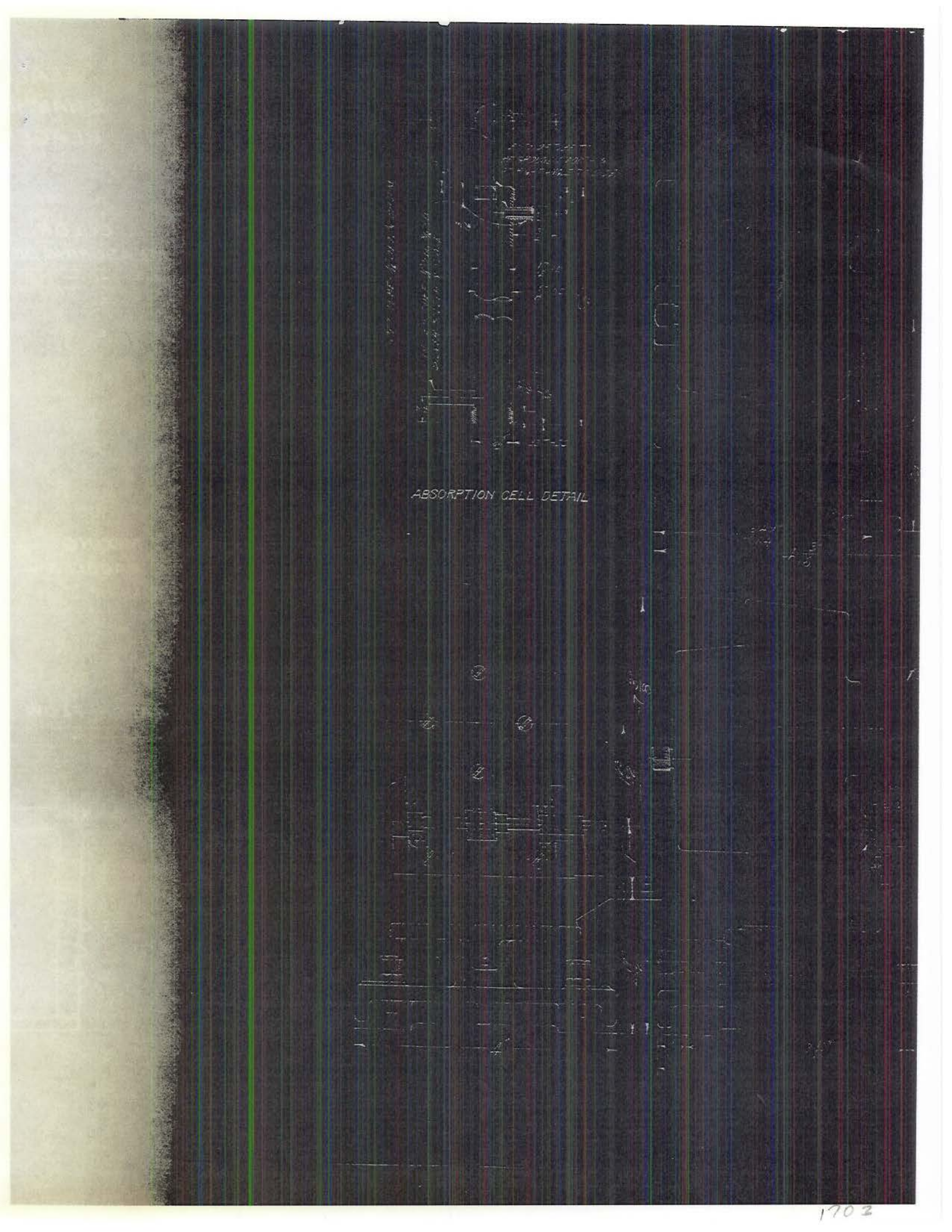
Plate 11



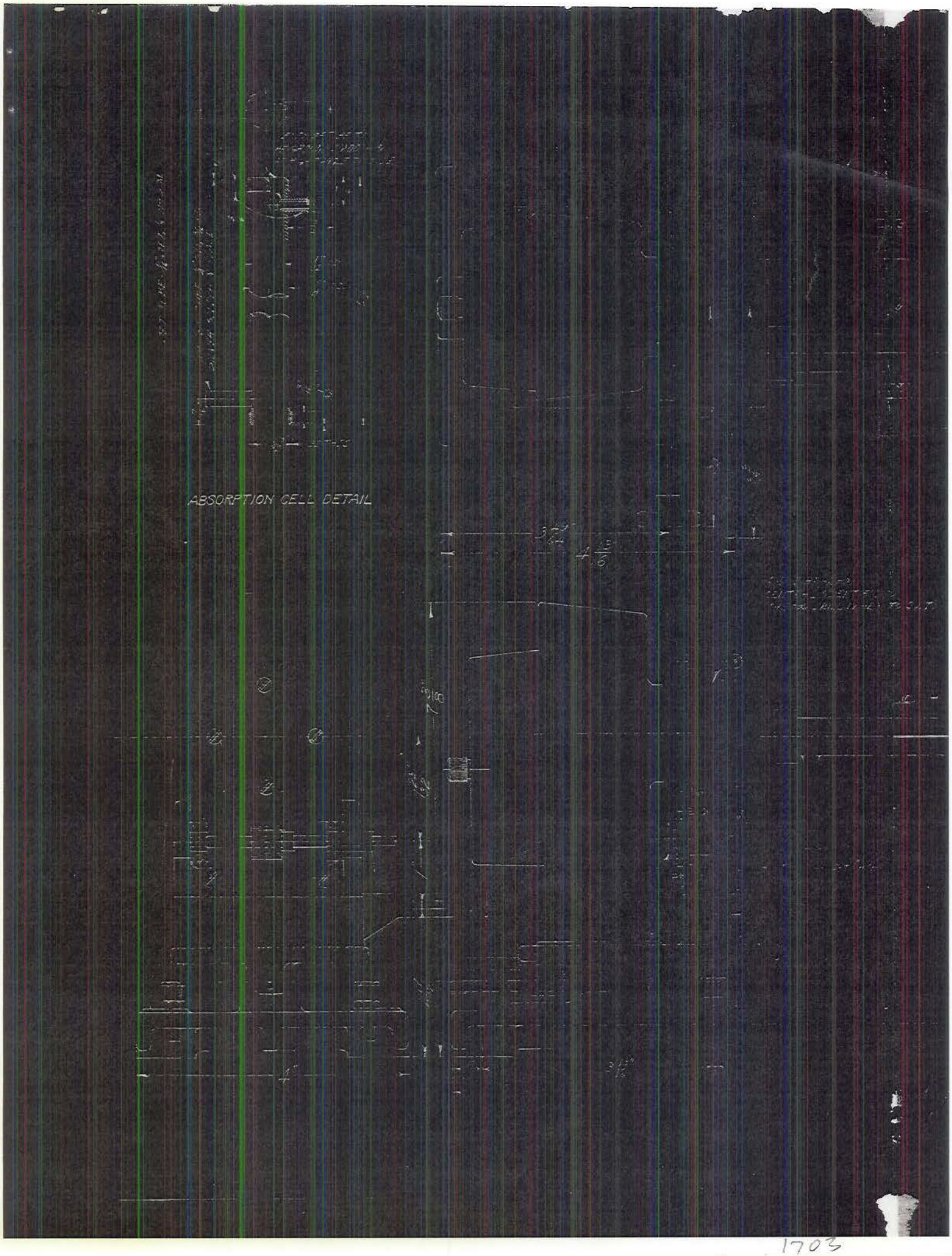
ABSORPTION CELL DESIGN
INCLUDING JET INLET TUBE
AND COMPARATOR MOUNTING

PLATE 11

1703



1703



1703

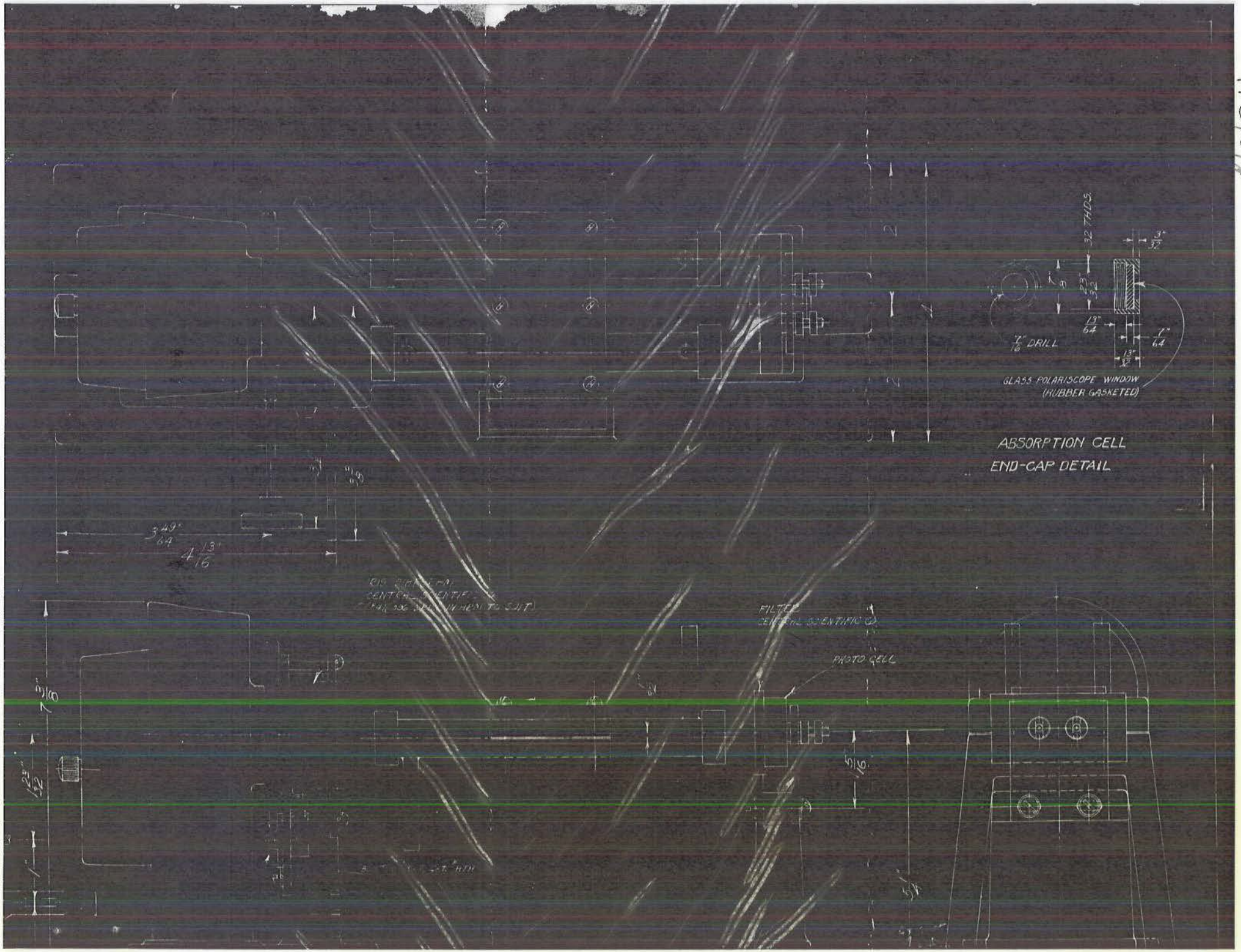
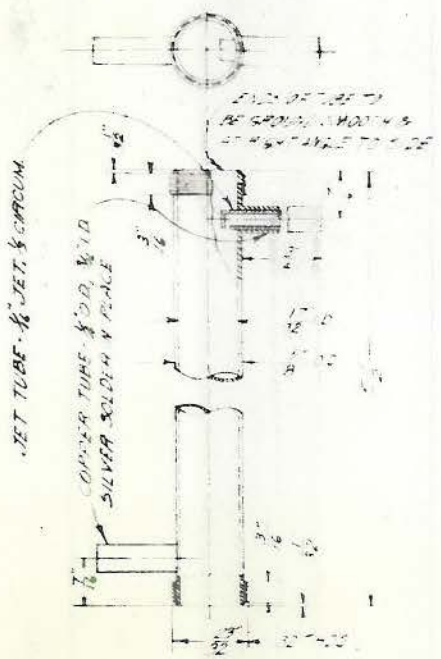
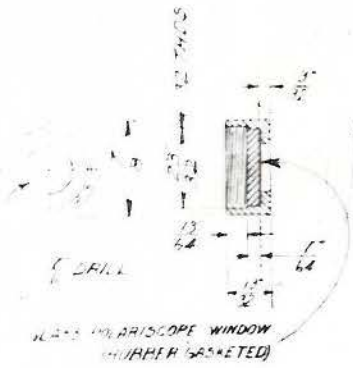

32 THDS.
7/8" DRILL
GLASS POLARISCOPE WINDOW
(RUBBER GASKETED)
ABSORPTION CELL
END-CAP DETAIL
FILTER
PHOTO CELL

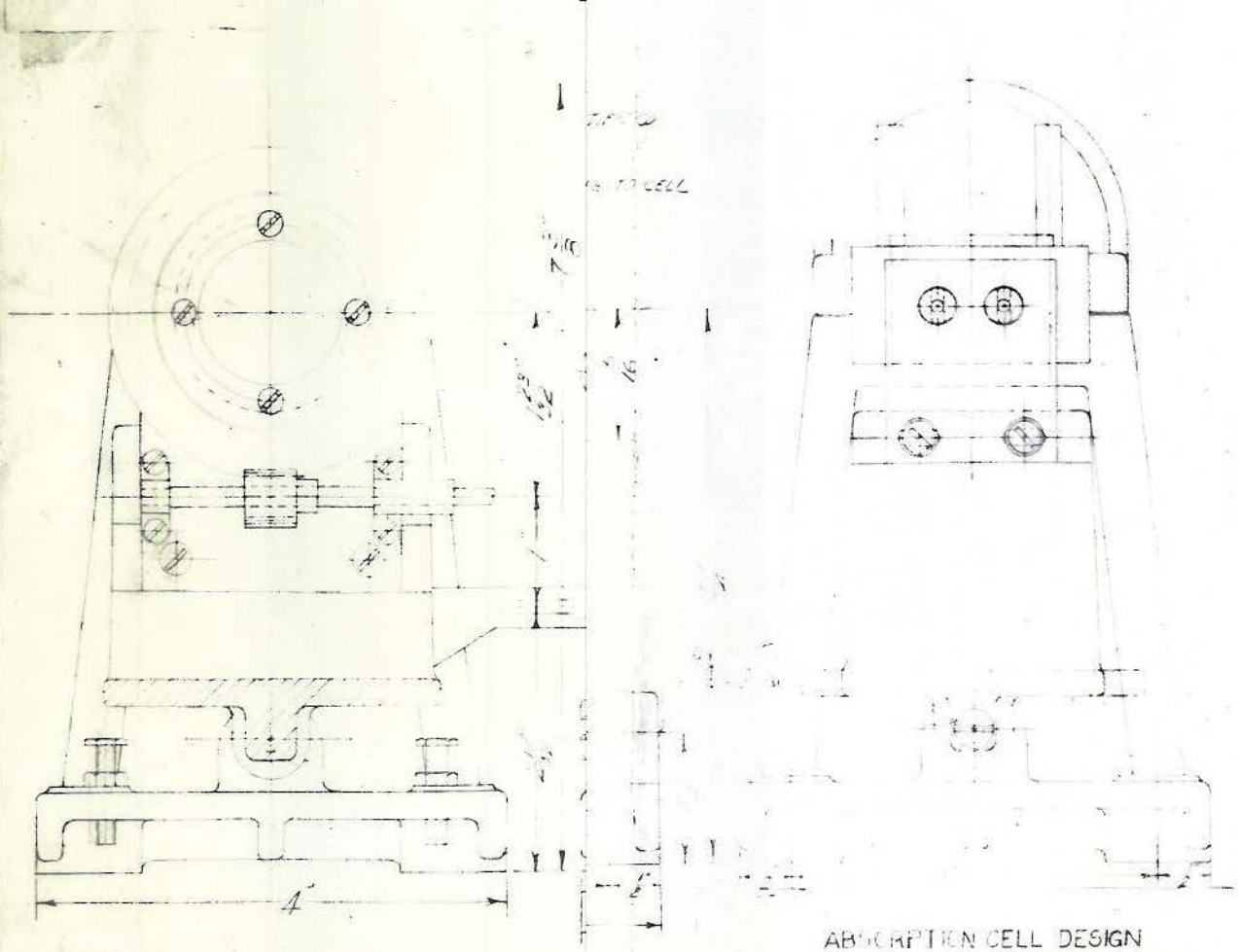
Plate 11



ABSORPTION CELL DETAIL



ABSORPTION CELL
END-CAP DETAIL

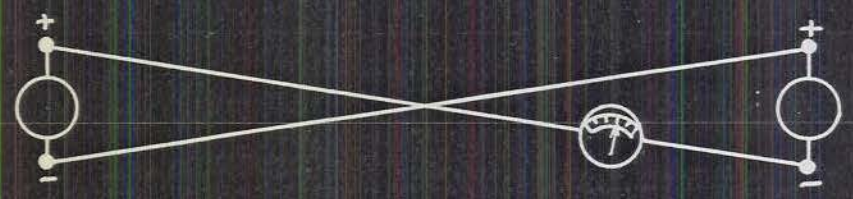


ABSORPTION CELL DESIGN
INCLUDING JET INLET TUBE
AND COMPARATOR MOUNTING

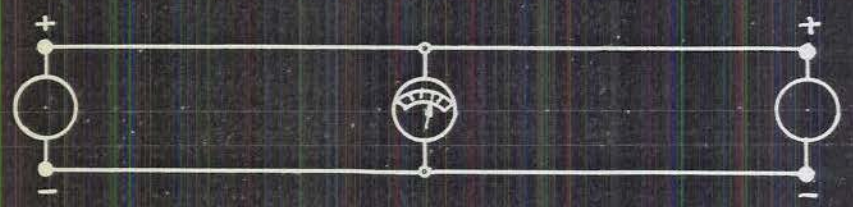
CIRCUIT DIAGRAMS EMPLOYING TWO PHOTOCELLS AND ONE LIGHT SOURCE.

CIRCUIT #1 - PHOTOCELLS IN PARALLEL - METER IN SERIES.

CIRCUIT #2 - PHOTOCELLS IN SERIES - METER IN SERIES.



CIRCUIT #3 - PHOTOCELLS IN PARALLEL - METER IN PARALLEL.



CIRCUIT #4 - PHOTOCELLS IN SERIES - METER IN PARALLEL.

CIRCUIT #5 - SAME AS #4 BUT WITH CONTROL RESISTANCES INSERTED.

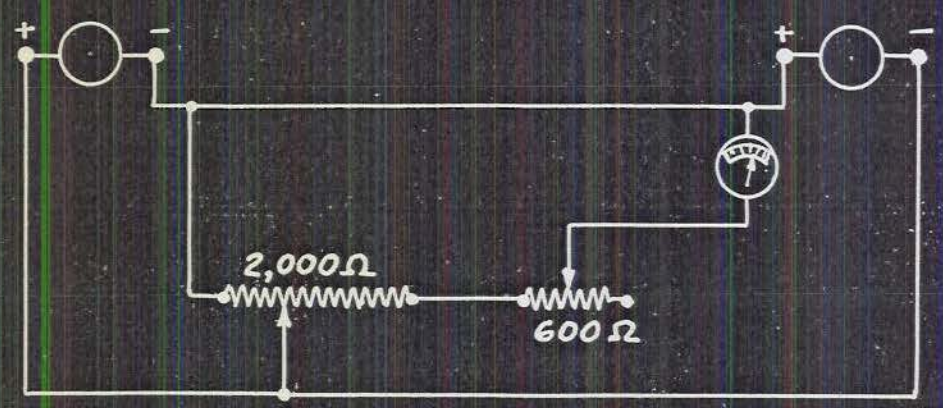
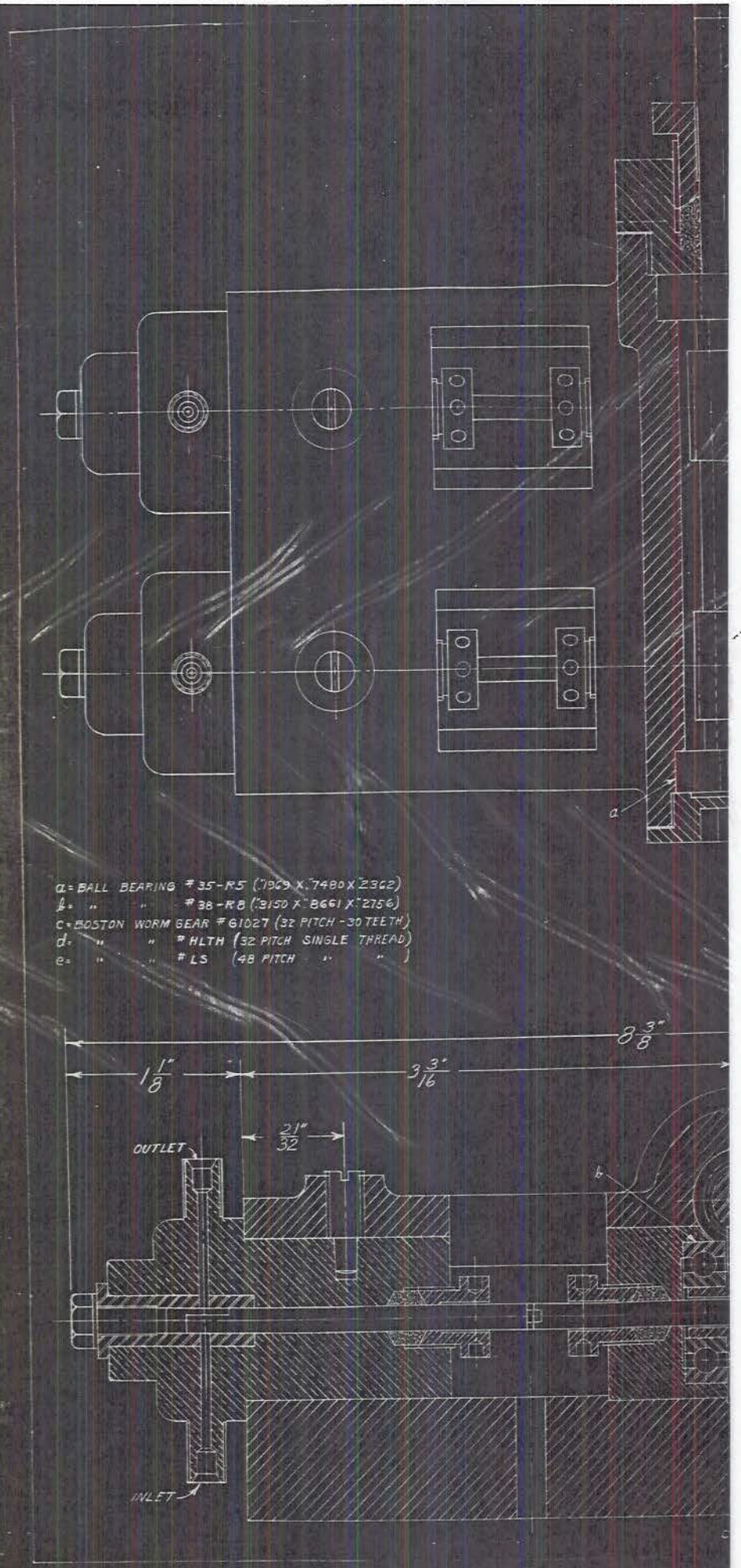
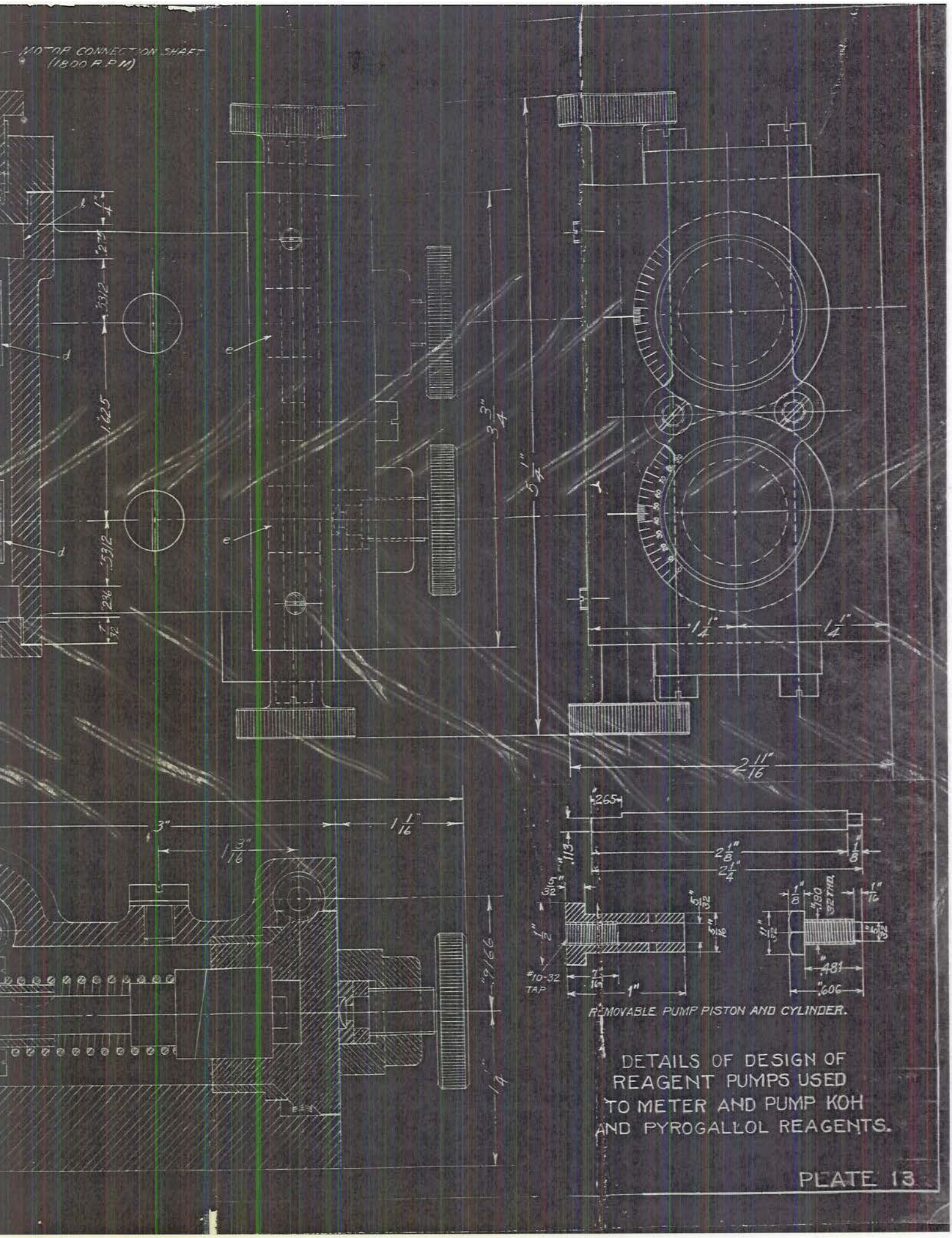


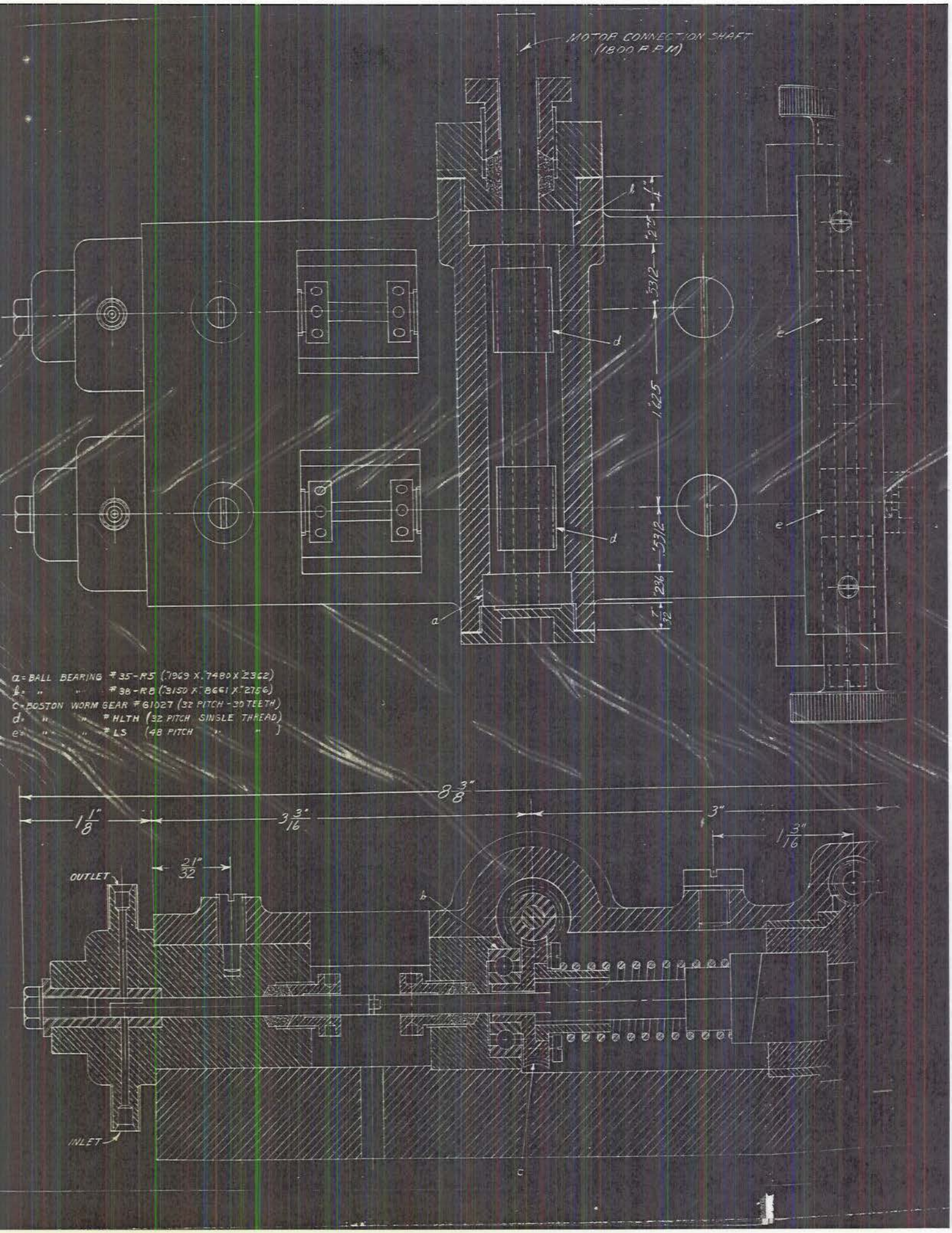
PLATE 12

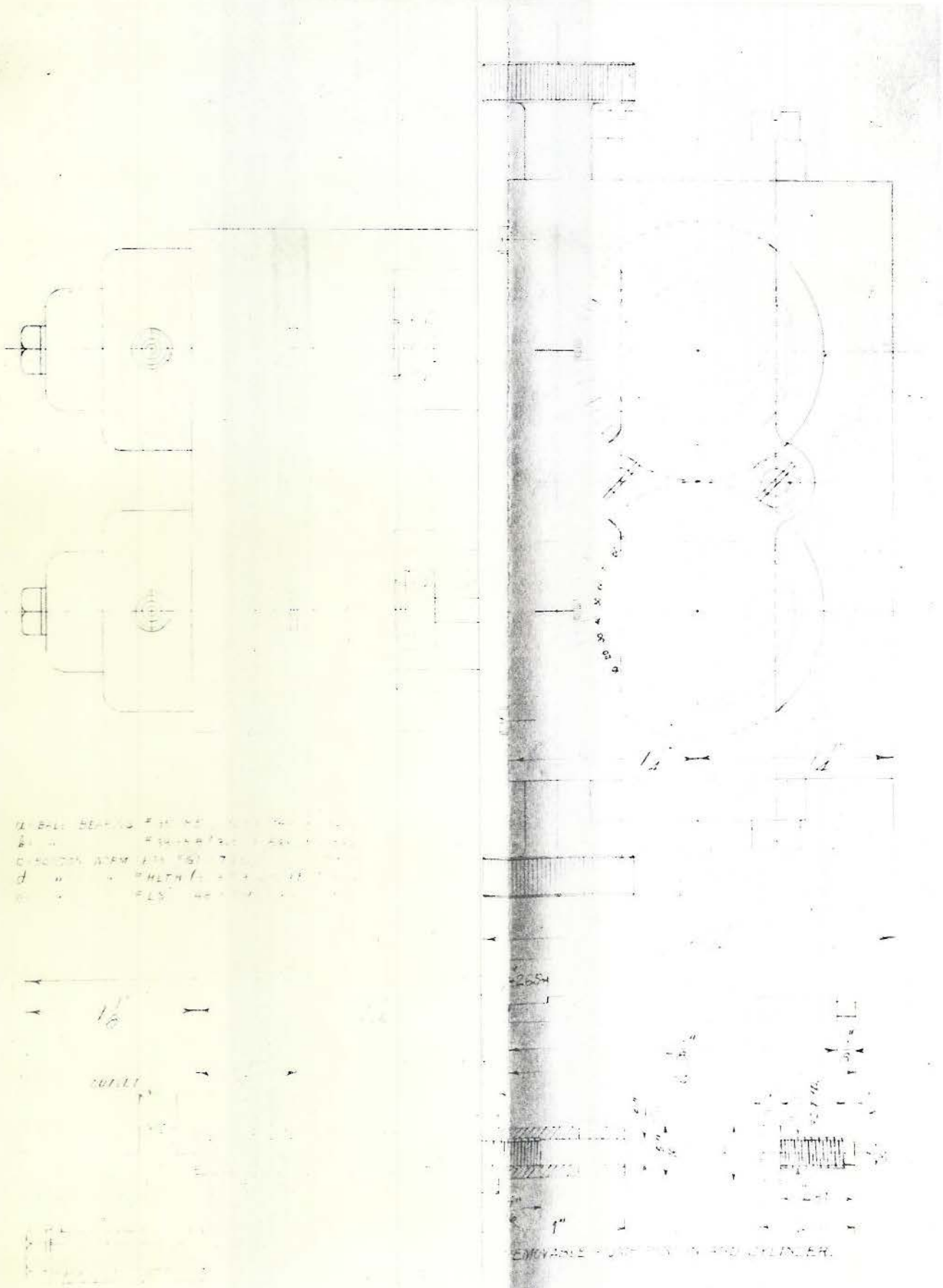

a
a = BALL BEARING # 35-R5 (.1969 X .7480 X .2362)
b = " " # 38-R8 (.3150 X .8661 X .2756)
c = BOSTON WORM GEAR # 61027 (32 PITCH - 30 TEETH)
d = " " # HLTH (32 PITCH SINGLE THREAD)
e = " " # LS (48 PITCH " ")
8 3/8"
1 1/8"
3 3/16"
21/32"
OUTLET
b
INLET



DETAILS OF DESIGN OF REAGENT PUMPS USED TO METER AND PUMP KOH AND PYROGALLOL REAGENTS.

PLATE 13


MOTOR CONNECTION SHAFT
(1800 R.P.M)
a = BALL BEARING #35-R5 (.1969 X .7480 X .2362)
b = " " #38-R8 (.3150 X .8661 X .2756)
c = BOSTON WORM GEAR #61027 (32 PITCH - 30 TEETH)
d = " " #HLTH (32 PITCH SINGLE THREAD)
e = " " #LS (48 PITCH " ")
OUTLET
INLET


DETAILS OF DESIGN OF
REAGENT PUMPS USED
TO METER AND PUMP ROH
AND PYRO-GALLOL REAGENTS.

SKETCH OF MIXING UNIT SHOWING DETAILS OF BALLAST TANK AND ZIGZAG MIXER TUBES.

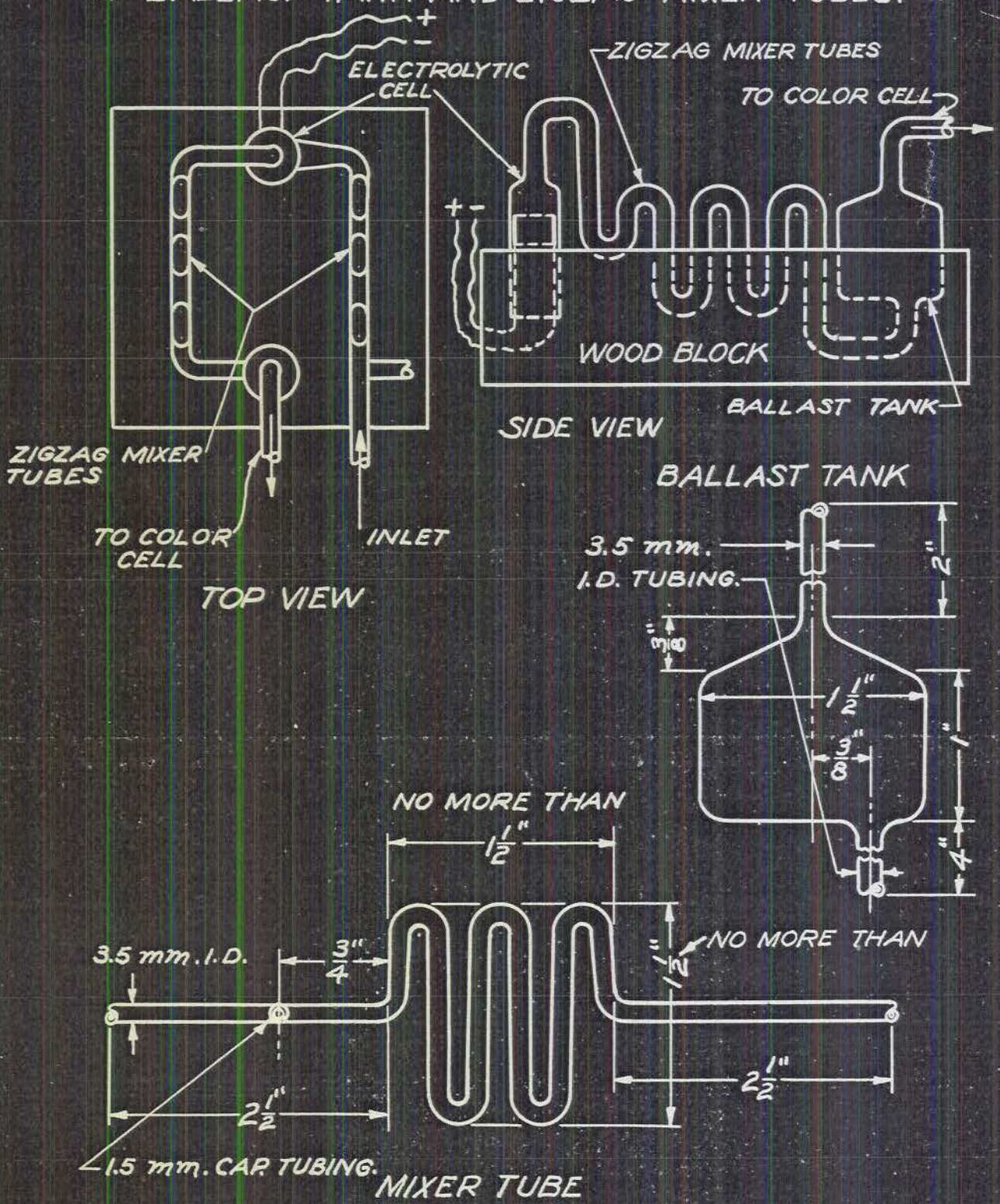


PLATE 14

SKETCH SHOWING DESIGN
DETAILS OF DEAERATOR UNIT.

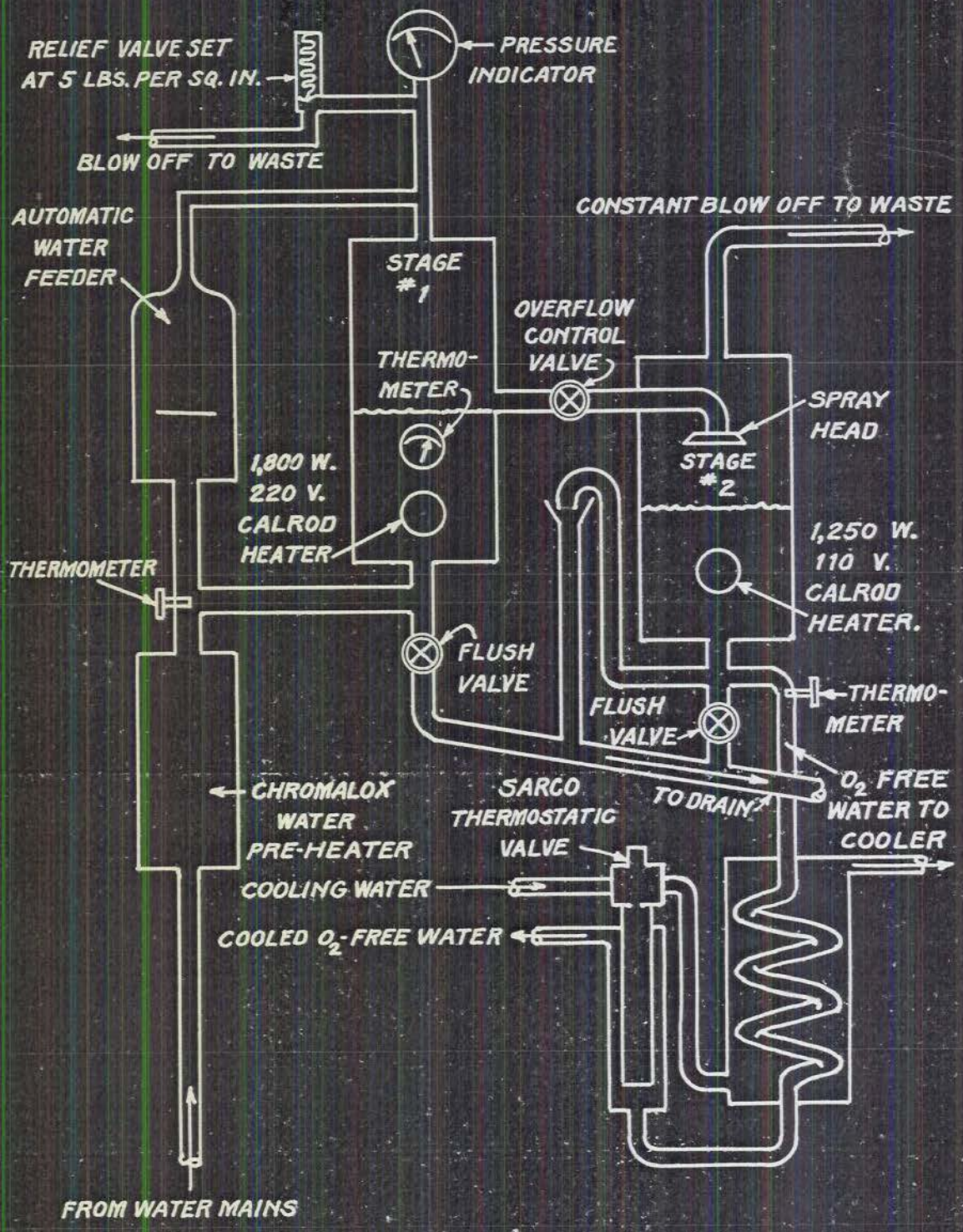


PLATE 15

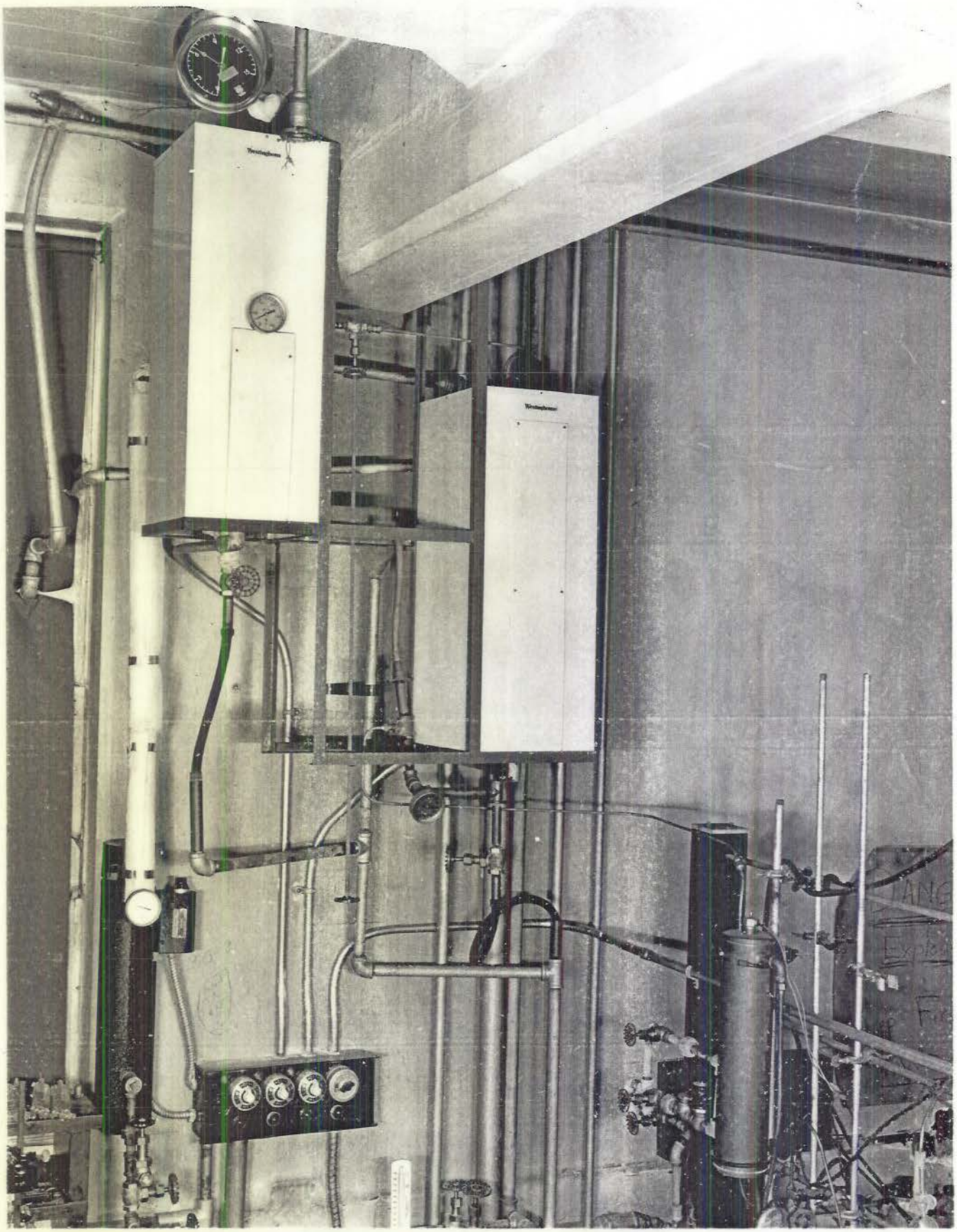


PLATE 16

SAMPLING FLASKS USED IN WINKLER ANALYSIS

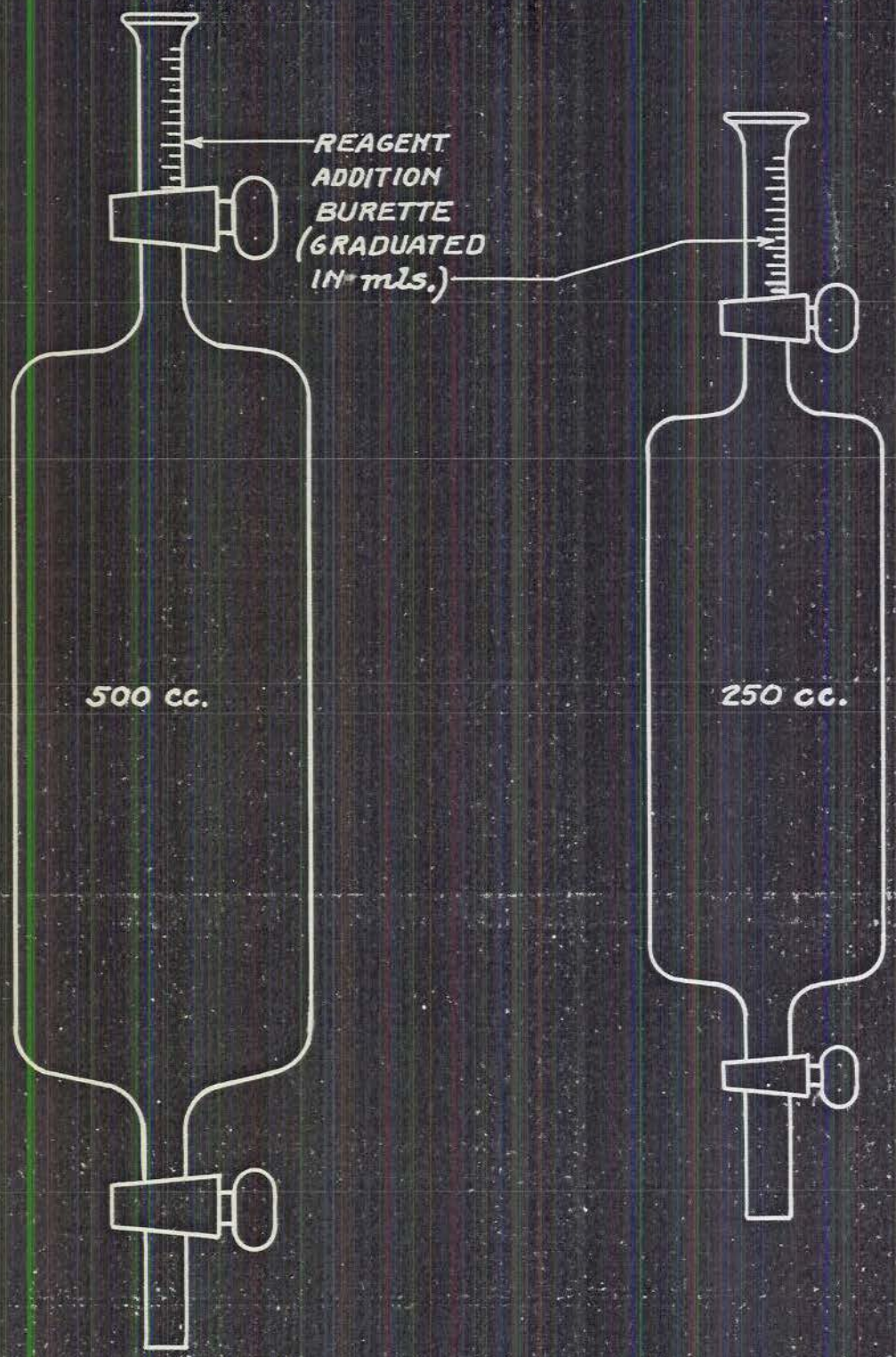


PLATE 17

CIRCUIT DIAGRAM OF APPARATUS USED FOR DEAD STOP, END POINT TITRATION.

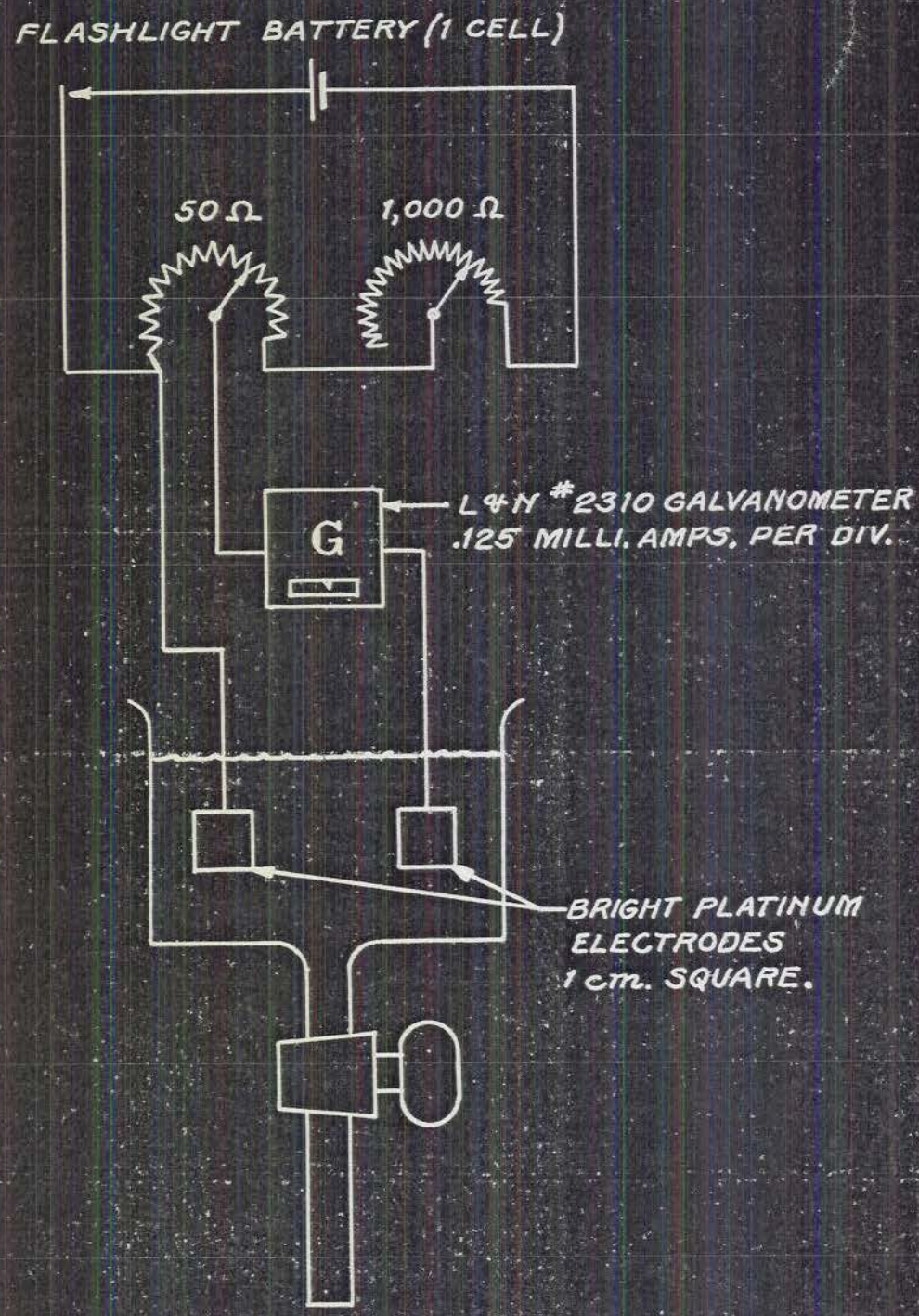


PLATE 18

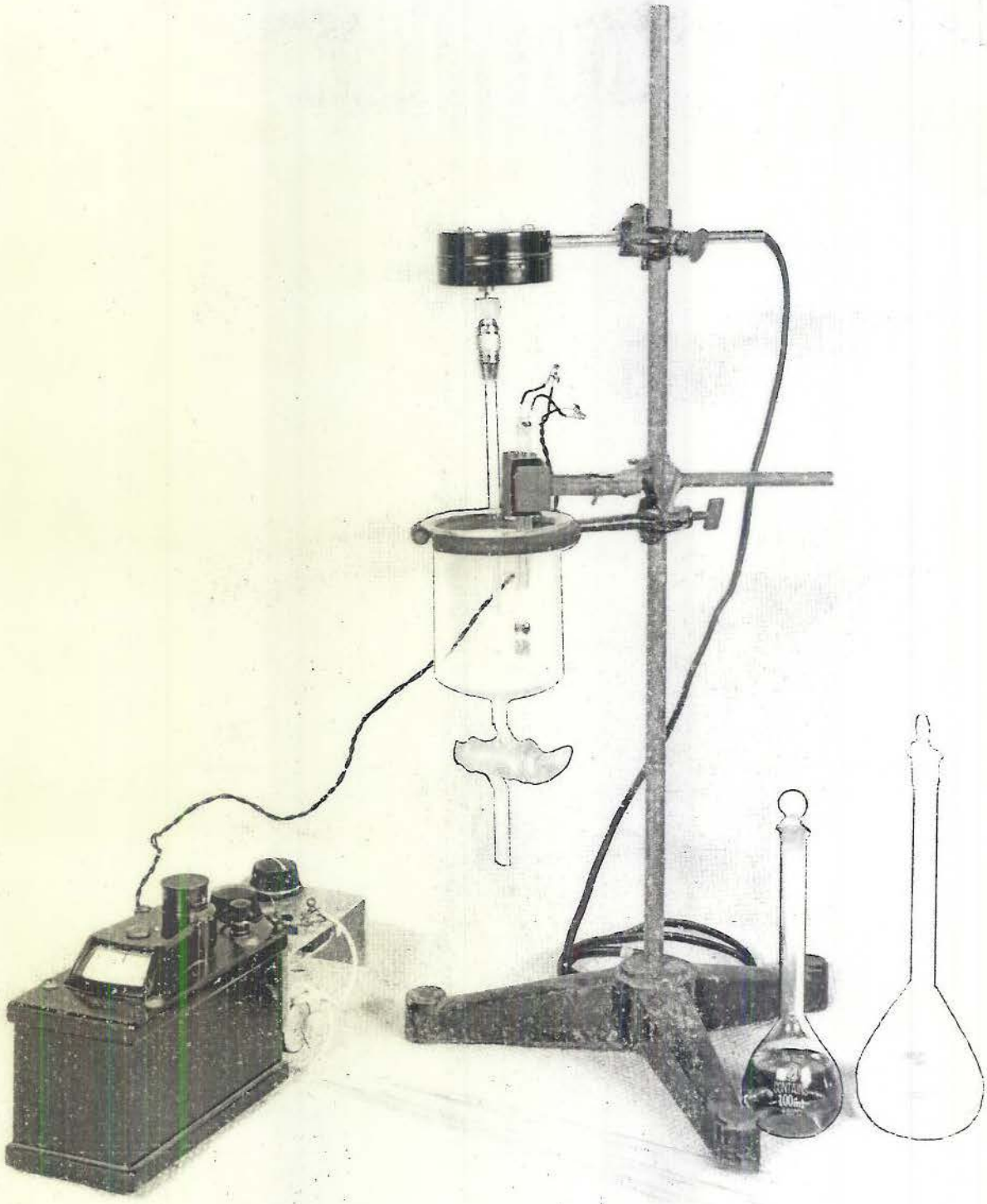


PLATE 19

SKETCH OF CALIBRATING
ELECTROLYSIS CELL

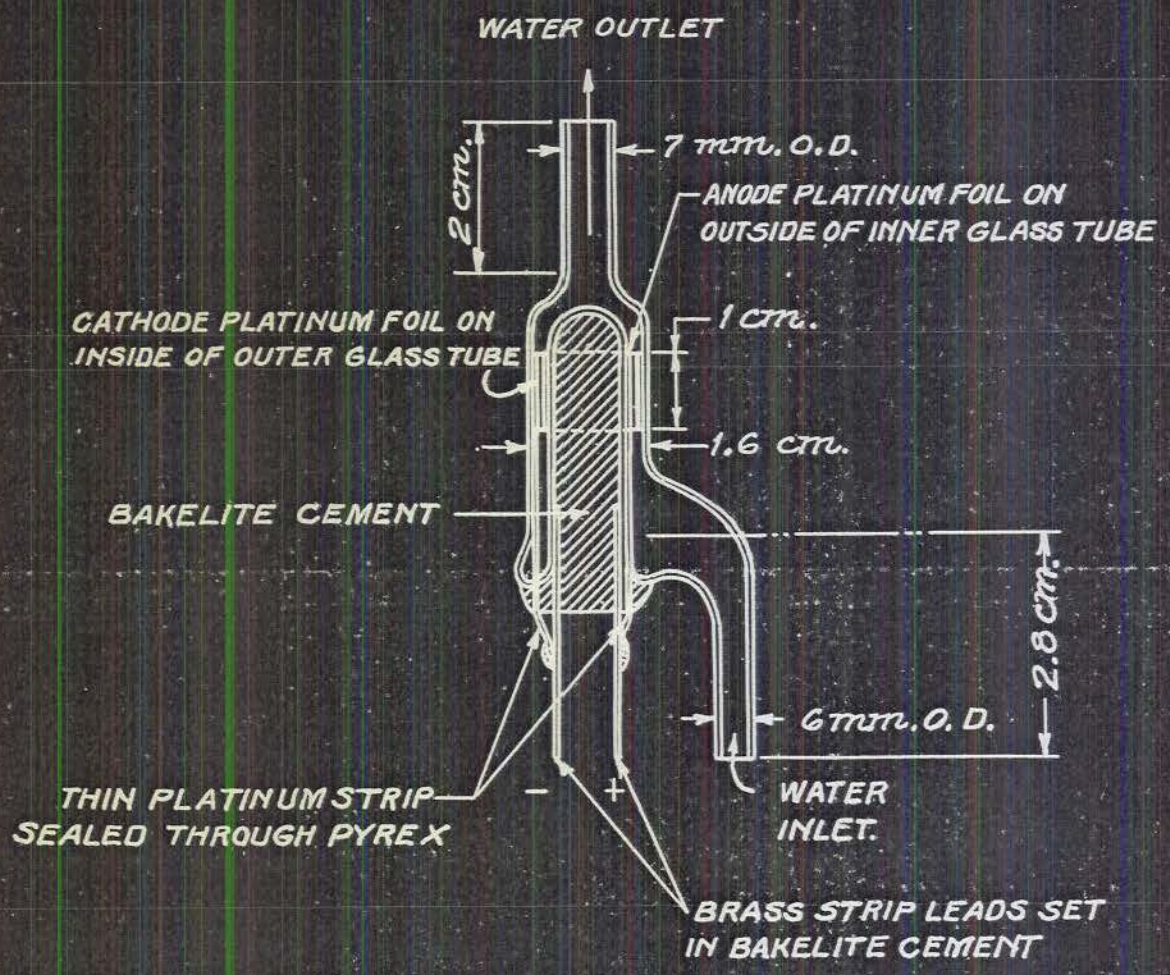


PLATE 20