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SUBJECT

Methods for the Determination of Chlorides in Battery Water.

DEPARTMENT OF THE NAVY
BUREAU OF ENGINEERING

BY

NAVAL RESEARCH LABORATORY
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NAVY DEPARTMENT

Report

on

Methods for the Determination of Chlorides in Battery Water.

FR-1608

NAVAL RESEARCH LABORATORY
ANACOSTIA STATION
WASHINGTON, D.C.

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ABSTRACT

Three methods for the determination of chlorides in battery water have been studied. Two of these methods have used the turbidity of silver chloride solutions as a means of measurement. In the first, this is done visually and in the second, a photoelectric cell is used. Both methods require about 20 minutes for a constant and reproducible reading. The third method uses the conductivity of the water as a measure of its chloride content.

The third method has been recommended as superior to the others because of its simplicity. It requires no chemicals and gives an instantaneous reading. It is actually only a modification of the present Navy salinity indicator.

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INTRODUCTION

(a) Authorization

1. This problem was authorized by Bureau of Engineering letter S62-4/L5 (8-8-Ds) of 11 August 1939.

(b) Statement of Problem

2. The purpose of this problem was to develop a method which could be used aboard a submarine for the determination of chlorides in battery water.

(c) Known Facts Bearing on the Problem

3. The battery water which is prepared by distillation aboard the submarine is collected in small measuring tanks. Before these are emptied into the larger storage tanks, the water must be tested for its chloride content; if this is above 5 parts per million, it is not allowed to enter the storage tanks.

4. The method which is used at the present time for determining the chloride content is carried out by adding a few cubic centimeters of silver nitrate solution to the water contained in a glass tube and observing the amount of precipitate that results from the formation of silver chloride. The Bureau of Engineering feels that this method is not sufficiently accurate for the present purpose. Another method which is sometimes used as given in Chapter 6 of the M.E.I. for the chlorides in boiler water is not suitable for this range of concentrations.

5. Any method which is selected should be capable of detecting at lease one part per million and have a range up to about 9 or 10 parts per million. The latter range, although above the limit set for the chloride content of battery water, is desirable to show the magnitude of the contamination.

(d) Theoretical Considerations

6. Three methods for determination of chlorides were studied in the course of this investigation. The first two make use of the same chemical reaction as that of the present method, this being the formation of a precipitate of silver chloride when silver nitrate is added to the water to be tested. The third method measures the conductivity of the water.

7. The precipitate which is formed in the above reaction has a tendency to remain in suspension for a considerable length of time, thus giving rise to an opportunity for its measurement. Therefore, any method that could be used to determine the extent of this precipitate would be a possible solution to the problem.

8. The first of these methods studied makes use of an instrument known as the Hellige Turbidimeter to measure the turbidity

of the solution by comparing visually the intensity of the beam of light passing through a definite depth of the solution with the Tyndall effect produced from a lateral illumination of the solution from the same light source. After this instrument has once been calibrated, there is no need for a standard suspension as long as the light source is constant. A more complete description of the instrument will be given later.

9. In the second method the light absorbed by the precipitate is measured by means of a photoelectric cell in conjunction with a light source and a suitable galvanometer. In this method the personal factor in the visual observations of light is eliminated and the accuracy depends only upon the construction of the instrument.

10. In the third method the conductivity of the water in question is measured by using a conductivity cell in series with an a.c. milliammeter and a source of 60 cycle, 110 volt alternating current.

11. In precise conductivity work the resistance of the solution must be measured by means of a bridge and alternating current of at least 1000 cycles. For the present purpose 60 cycle current will give sufficiently accurate results provided the voltage and the cell constant of the electrodes are so adjusted that no more than 50 milliamperes are used at the upper range of the instrument.

12. The fact that this type of instrument would not only indicate the presence of chloride ions, but that of any other ions, would be of no disadvantage since the presence of any other ion would mean that contamination was present.

13. The possibility of using such a method can best be illustrated by referring to the table of approximate values given below. The resistance values have been calculated from the conductivity of sodium chloride solutions at the indicated concentration of chloride ion at 80°F. and when a conductivity cell with a constant of 0.10 is used. The current in milliamperes is the calculated value when 110 volts is used and assuming no polarization. Slight polarization occurs when 60 cycle alternating current is used.

Parts per Million of Chloride Ion	Resistance in Ohms at 80°F. - Cell Constant, 0.10	Milliamperes
1	26,000	4.2
3	12,000	9.2
5	7,800	14.1
7	5,800	19.0
9	4,500	24.5

EXPERIMENTAL DETAIL

(a) Preparation of Solutions

14. A standard solution of chloride ion was prepared by dissolving 0.165 gram of sodium chloride in water and diluting to a liter. This solution contains 100 parts per million of chloride ion. The chloride solutions used in the measurements were prepared by diluting the above solution. One cubic centimeter of this solution, when diluted to 100 cc, is equivalent to 1.0 part per million of chloride ion.

15. The silver nitrate solution contained 164 grams of the salt per liter of solution.

16. The 2 normal nitric acid solution was prepared by diluting the concentrated acid.

(b) Description of the Apparatus

(1) Hellige Turbidimeter as used in the turbidimetric method

17. This instrument was obtained from the Hellige Company of New York and was first described in the literature in reference (1) as used in a method for determining sulphates.

18. Its chief advantage over the usual turbidimetric methods which compare the turbidity of an unknown solution to that of a known solution is that it does not require a standard after it has once been calibrated, provided a constant source of light is available.

19. Its principle of operation depends on the well known Tyndall effect which is produced when light falling on small particles in suspension is reflected at right angles to the light beam. Thus, if a solution having only a few particles in suspension is being illuminated from the side, little light will be observed from above the solution due to the Tyndall effect, but if there were a large number of particles present, there would be a considerable amount of light reflected. Hence, the intensity of light from this source depends upon the number of particles present at a given depth of solution. The light passing directly through a turbid solution depends upon the number of particles present, the larger the number the less the light passing through. These are two opposing tendencies, and if one can be compared with the other under a given condition, there would only be one point at which the two were equal. This is the principle in which the instrument works. Its description as taken from reference (1) is given below:

> "The apparatus as diagrammed in Figure 1, Plate 1 consists of a metal housing 7x5x16 inches in size. Mounted in this housing is an opal-glass lamp (B), a large reflector (R), and a precision slit (S), which is operated by a graduated drum knob. At the side of the apparatus to which

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(1) Ind. and Eng. Chem., Anal. Ed. 7, 292 (1939).

the door is attached is a platform for the tubes with the mirror (M) in a removable frame beneath it, and a circular milk-glass filter (MR), in a metal frame. The rays emanating from the lamp (B) are reflected into the liquid column in the tube and the Tyndall effect is produced by this side illumination of the suspended particles. The observation of the Tyndall effect through the ocular on top of the apparatus is facilitated by a silver mirror which rests horizontally beneath the tube. Light rays from the lamp also pass through a precision slit and illuminate a circular milk-glass reflector and from there are reflected through a circular aperture in the silver mirror and then through the liquid to the tube and to the ocular. These light rays appear to the observer as a circular spot in the center of the Tyndall effect of the illuminated liquid which is seen lighter or darker than the Tyndall light, depending upon the size of the opening of the slit (see Figure 2, Plate 1). By revolving the drum knob and thereby adjusting the opening of the slit, the brightness of this spot can be regulated so as to be of the same intensity as the brightness of the surrounding field.

"The tubes which are used in this instrument are made for liquid depths of 10, 20, 50 and 100 millimeters. The tubes have fused-on plano-parallel bottom plates of optical glass while the upper end of the filled tubes are covered with a short glass plunger (P) with a plano-parallel plate which automatically adjusts for the proper liquid depth.

"Different ranges of turbidity can be covered by inserting standard filter plates over the precision slit."

(2) <u>Photometric measurements of turbidity by means of a photoelectric cell</u>

20. In this method a General Electric blocking layer-type photoelectric cell was used in conjunction with a low resistance microammeter to measure the amount of light passing through a 5 centimeter cell containing the suspension of silver chloride precipitate.

21. The amount of light falling on a photocell after passing through a 5 centimeter depth of water is first adjusted by means of an iris diaphragm so as to give a full scale deflection on the meter. The solution containing the precipitate is then placed in a tube of the same size and the amount of light absorbed measured. This, of course, requires the use of a constant light source. The light source was an ordinary automobile head light bulb using current from a constant voltage transformer. This light was rendered approximately parallel by use of proper lenses.

(3) Conductivity method

22. The apparatus used in the study of this method consisted simply of a conductivity cell, a constant source of 60 cycle, 110 volt alternating current, and an a.c. milliammeter. The conductivity cell was the type used in the Navy salinity indicator. The source of 110 volt alternating current was a Raytheon constant voltage transformer.

(c) Description of the Methods

23. Since the first two methods depend upon the formation of a precipitate of silver chloride, the procedures for the two were the same up to the time of actual measurement. The chloride solutions were prepared as described above. A few drops of the dilute nitric acid were added and then 5 cc of silver nitrate solution. In both methods, readings were taken over a period of about 1/2 hour.

24. In the third method the chloride solutions were made up as above and then placed in contact with the electrodes of the conductivity cell. Readings were taken over a period of time. This was repeated for the various concentrations. The effect of temperature and voltage on the readings was also determined.

DISCUSSION OF DATA AND RESULTS OBTAINED

(a) Turbidimetric Methods

25. It was at once apparent that the formation of the precipitate of silver chloride required a considerable length of time to reach a constant and maximum value. This was indicated by the change in the readings with time. An exploratory calibration curve was run with the Hellige instrument, taking readings after about 5 minutes in order to get the range of the instrument. The results are shown by the curve on Plate 2 in which the readings are plotted against parts per million of chloride.

26. Since the method in which the photoelectric cell was used to measure the amount of turbidity was more adaptable to taking readings over a period of time and which also eliminates the personal factor in a visual observation, it was used to make a careful study of the change in turbidity with time. Any results obtained by this method would also apply to the first method.

27. The results obtained by this method indicate that the formation of the precipitate of silver chloride is not complete until after about 20 minutes and that any attempt to obtain a reading before that time would result in an appreciable error. The curves plotted on Plate 3 show the change in readings with time for several runs each of 1, 3, and 5 parts of chloride per million. The curves show that after about 20 minutes, constant and reproducible values may be obtained. Plate 4 gives the calibration curve for values taken at the end of 20 minutes. The range covered by this method can be changed by

simply using a different length of absorption tube. A shorter tube would give a higher range but would also cut down the sensitivity in the low concentrations. This latter factor could be increased by using the longer tube.

28. The results of these two methods in which the amount of turbidity is measured indicate that very good results can be obtained by either one if the time factor as well as the requirement of a fair amount of skill in technique are not important in the actual use of the method.

(b) Conductivity Method

29. A number of preliminary calibration curves were first made using a small panel model Weston a.c. 0 to 25 milliammeter. This meter had a resistance of about 650 ohms. Three runs were made using 100 volt, 60 cycle alternating current to show the reproducibility of the readings. The results are shown by curve 1 on Plate 5. In order to show the effect of voltage on the readings, runs at 90 and 110 volts were also made and the results are shown by curves 2 and 3 on Plate 5.

30. The remainder of the runs were made using a Raytheon constant voltage transformer as a source of 110 volt alternating current and a multiple range alternating current milliammeter of 30 ohms resistance in each of its three ranges of 10, 30, and 100 milliamperes. These runs were made at 30°C. or 86°F. In addition, the conductivity was taken at 26°C. or 79°F. and at 36°C. or 96.8°F. for a chloride content of 3.5 parts per million in order to show the effect of temperature. The readings at 79°F. were 17, at 86°F. 18.6, and at 96.8°F. 20 milliamperes.

31. As expected, slightly better results were obtained with the precision meter and a source of constant voltage. The curve drawn through the results of several runs was slightly different than the former because of the difference in resistances of the meters. This curve is shown on Plate 6.

32. It is, of course, evident that the range can be adjusted to suit the required needs by either changing the cell constant (i.e., by changing the size of the electrodes or their distance apart) or by changing the voltage. The range of the current could be changed by a limited amount only, since the current through the cell should be as small as possible in order to reduce the amount of polarization.

33. If the temperature of the water to be tested does not vary by more than 5°F., it is believed that no correction would be necessary. If the water varies more than 5°, calibration curves should be made for each 5°F. If the temperature change is not too great, a partial correction can be made by use of an auxiliary adjustable resistance. This is limited in use since each concentration has a different temperature coefficient of resistance.

CONCLUSIONS AND RECOMMENDATIONS

(a) Facts Established

34. The results of these investigations have shown that any of the above methods can be used to determine the chloride content of battery water.

35. The two methods which depend upon the turbidity of the precipitate of silver chloride that results when silver nitrate is added to a solution of chloride ion require about 20 to 30 minutes for the attainment of a maximum and constant reading. In addition, careful technique is required in order to obtain reproducible results. Of these two methods the one employing a photoelectric cell is more accurate and also eliminates the personal factor that is always present in any visual observation of light.

36. The method in which the conductivity is measured is the simplest to use. If properly designed there would be no operation other than turning on a switch and reading a meter. It does not require the use of chemicals and readings are instantaneous.

(b) Opinions

37. This Laboratory believes that any of the methods selected by the Bureau of Engineering can be successfully installed. Since the actual selection is left to the Bureau, this Laboratory has not developed any of these methods to a place where they are ready for installation; however, enough has been done on all the methods so that only the actual mechanical details remain to be worked out. This, of course, should be done with the idea of using as much as possible of the equipment that is available in industry so that the time and cost of manufacture would be at a minimum.

38. It is highly possible that there are a number of manufacturers equipped to construct an instrument for whichever method is selected.

(c) Recommendations

39. The Laboratory, in view of its experience with the three methods studied, recommends the conductivity method as the one best suited for the purpose. It is the simplest because no chemicals or careful technique are required, and it gives an instantaneous reading. In addition to these advantages it will also show the presence of any other ion that may be contaminating the water. This method has been used for a long time for higher ranges of chloride content and it actually becomes only a modification of a well established method.

40. Of the two turbidimetric methods, the one employing a photoelectric cell is recommended over the other since it gives more accurate results and eliminates the personal factor in the visual observation of light.

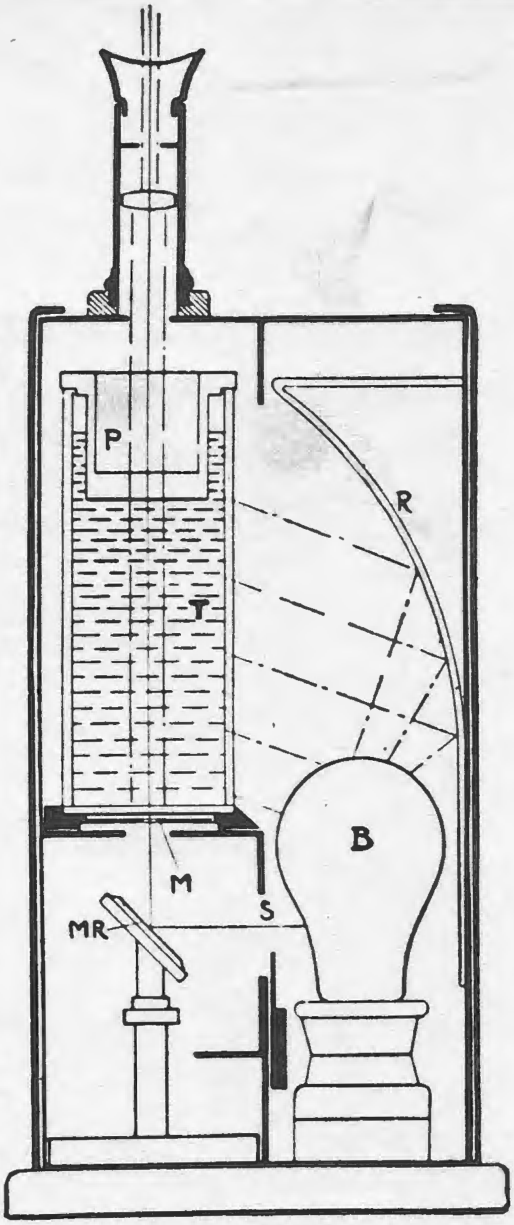

FIGURE 1. DIAGRAM OF TURBIDIMETER

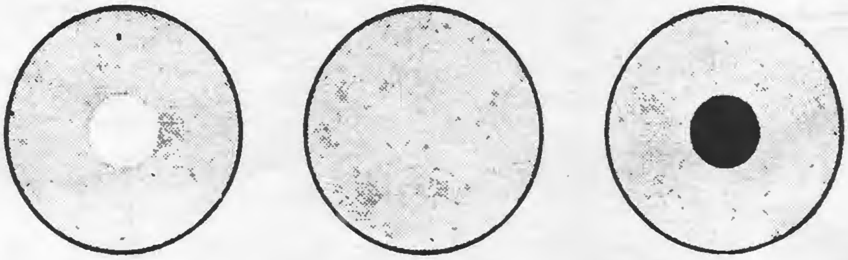

FIGURE 2. OBSERVATION FIELDS

Center, balanced; left and right, unbalanced

PLATE I

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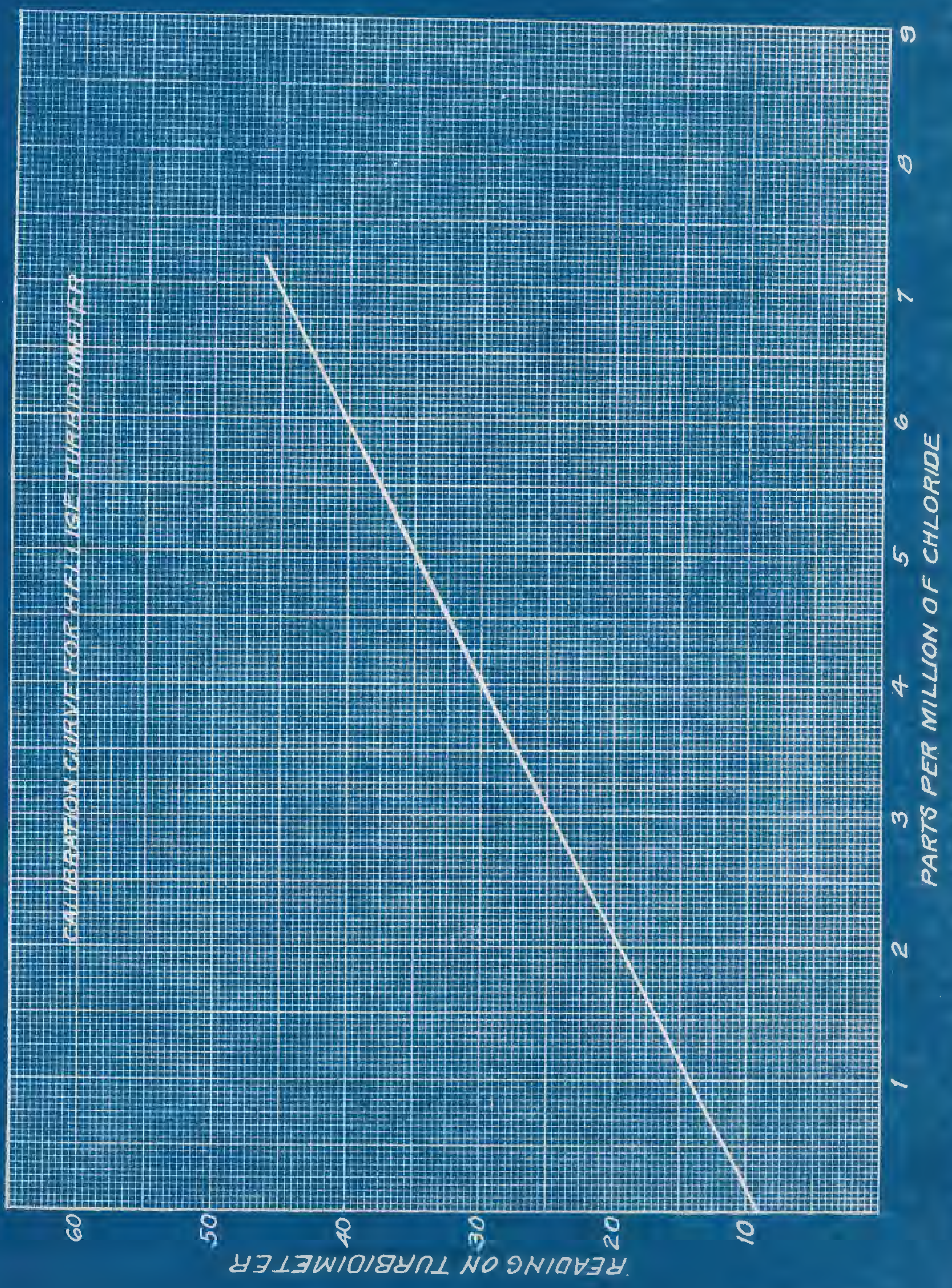

N. R. L. 31A

PLATE 2

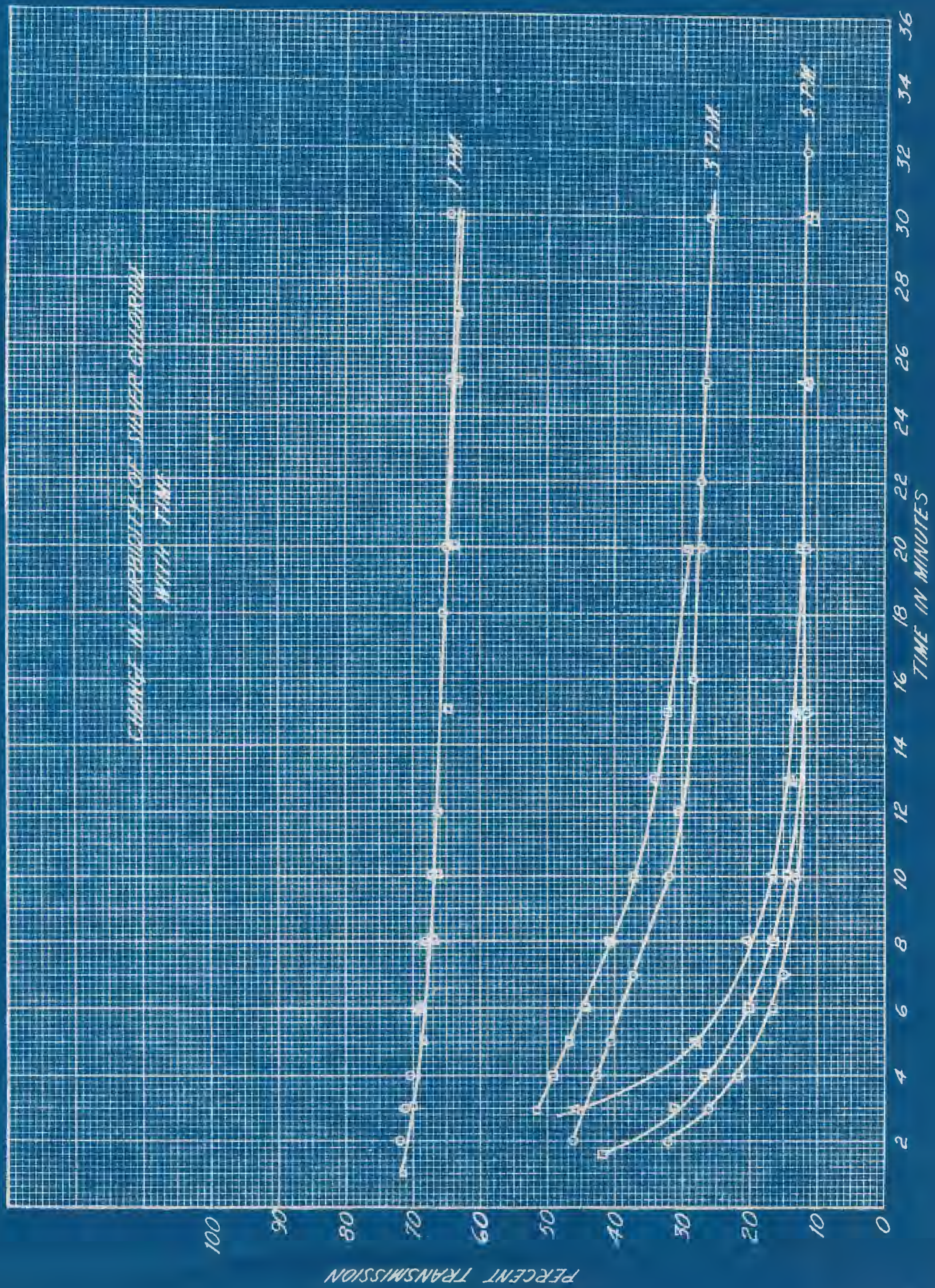

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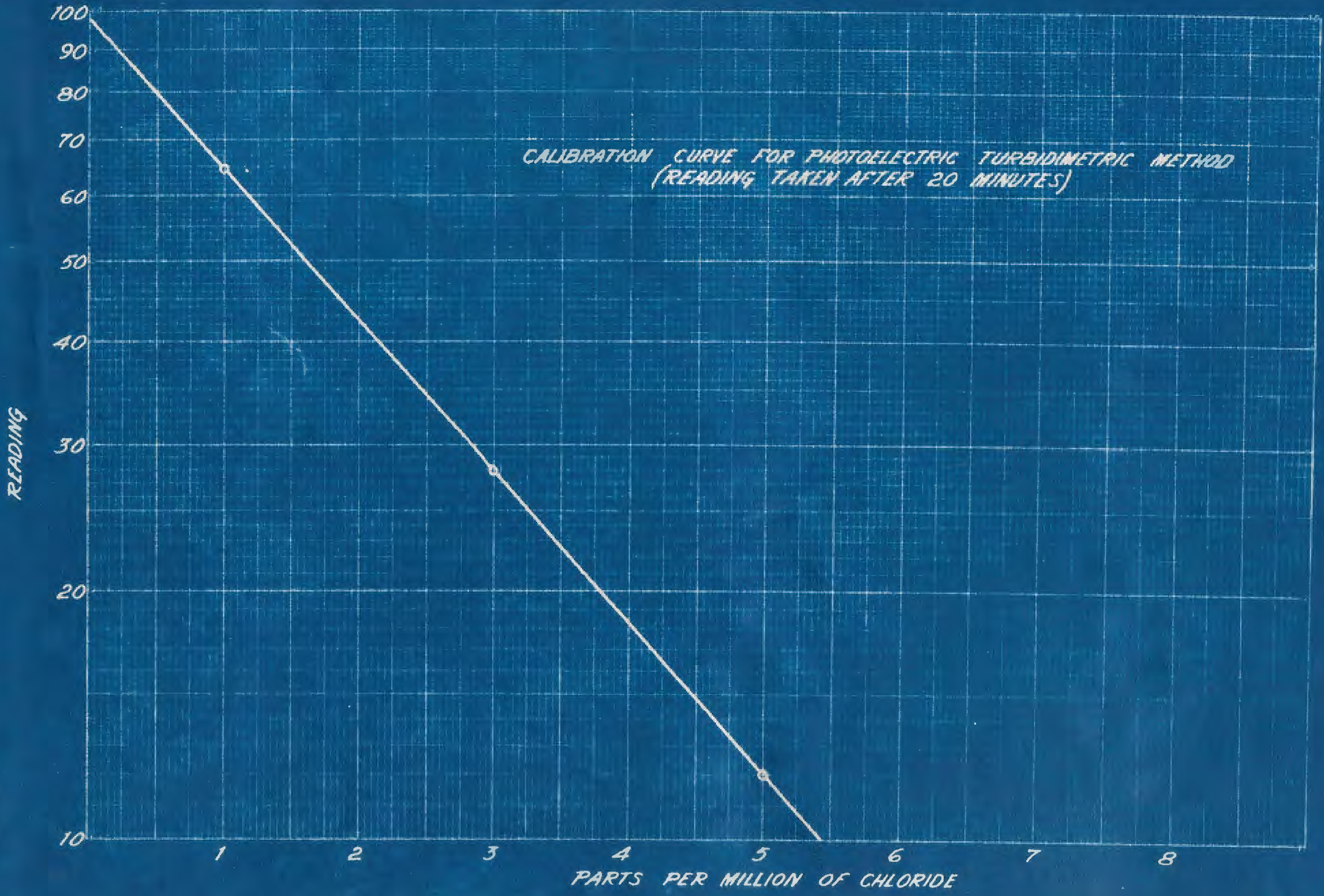
PLATE 3



CALIBRATION CURVE FOR PHOTOELECTRIC TURBIDIMETRIC METHOD
(READING TAKEN AFTER 20 MINUTES)

PLATE 4

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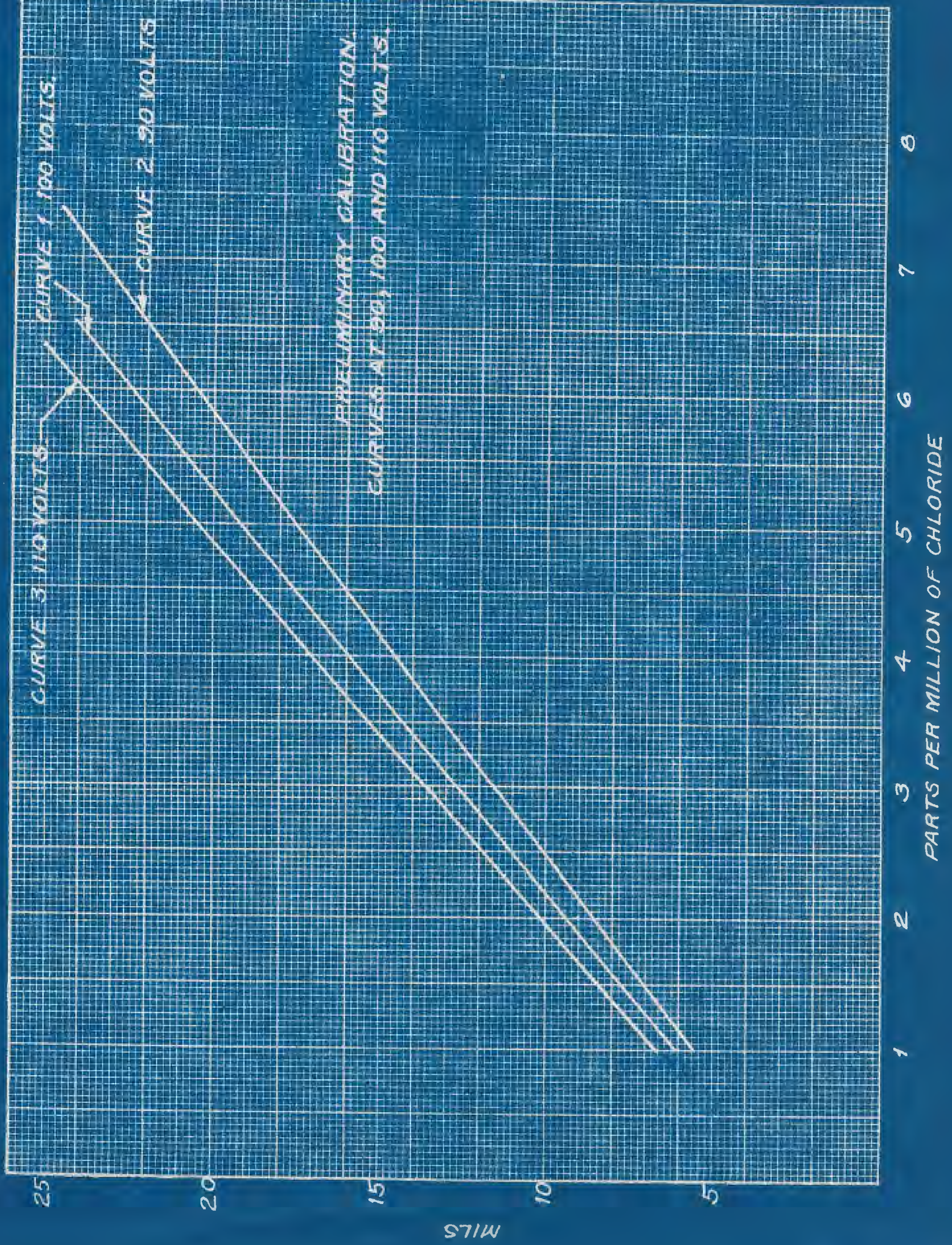

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PLATE 5

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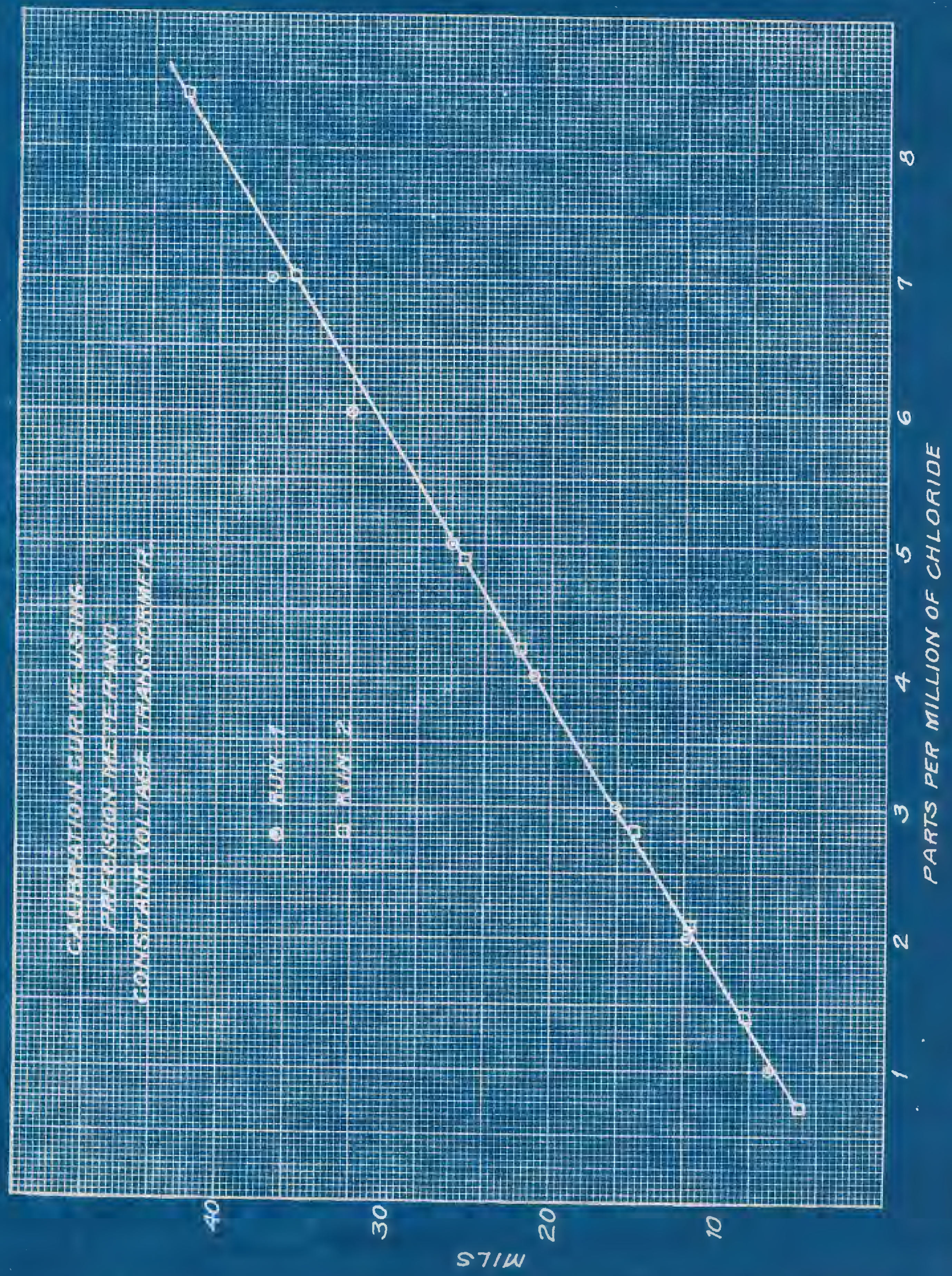

N.R.L. 34A

PLATE 6