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DEVELOPMENT OF EQUIPMENT FOR CONTINUOUS MEASUREMENT OF pH, CONDUCTIVITY, RELATIVE TURBIDITY AND TEMPERATURE FOR USE IN STUDYING THE CHEMICAL VARIATIONS OF SMALL UNPOLLUTED STREAMS ON A DIURNAL BASIS

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Master of Science in Sanitary Engineering

By

Gerald Maurice Leigh

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DEVELOPMENT OF EQUIPMENT FOR CONTINUOUS MEASUREMENT
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Approved:

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SUMMARY

The purpose of this thesis is to assemble equipment capable of continuous measurement of pH, conductivity, relative turbidity, and temperature using a four-point electrical recorder. This equipment will be used at a later date to study the chemical variations of small unpolluted streams on a diurnal basis.

The pH was measured by a pH meter equipped with a glass electrode and a saturated-calomel electrode. The electrodes were immersed in a 2000 milliliter beaker, and water was supplied to them by a chemical solution-feed pump.

A conductivity bridge with platinum-plated rod electrodes was used to measure the resistance. The electrodes were immersed with the pH electrodes in the 2000 milliliter beaker.

The relative turbidity was measured by a turbidimeter consisting of a fluorescent light source and two photoelectric cells mounted on a float.

To measure temperature a thermocouple circuit and a 56° Centigrade constant temperature bath were employed. The constant temperature bath utilized a thermoregulator, a heater, and a normally closed-circuit relay.

The leads from each of the instruments were connected to one point of a four-point recorder which recorded the data on a strip chart.

The equipment was tested on the Yellow River near Conyers, Georgia, and in the intake well of the Atlanta Water Works Chattahoochee Pumping Station. The results of these tests indicated that:

1. The location for the equipment should be chosen with care; that is, away from possible electrical disturbances.

2. Instrument leads should be kept as short as possible.

3. The pH meter and conductivity bridge should be operated as near their balance point as possible to obtain stability.

4. The heater and relay circuit in the constant temperature bath may well be replaced by an ice bath in order to avoid the disturbance caused by the electrical demand of the heater upon the voltage supply of the pH meter and conductivity bridge.

5. The pH and conductivity electrodes cannot be placed directly in a stream because they are grounded.

6. Commercial flow cells with resistance thermometers for automatic temperature correction for the pH and conductivity electrodes are desirable for extensive measurements.

CHAPTER I

INTRODUCTION

In October, 1953, the U. S. Geological Survey and the Georgia Institute of Technology Engineering Experiment Station instituted a joint study of the headwaters of the Yellow River Basin located thirty miles northeast of Atlanta, Georgia.(1) The purpose of this study was to obtain an understanding of the drainage pattern and the variations in the water quality of small unpolluted streams.

Dissolved oxygen and biochemical oxygen demand values were determined at various times in the Yellow River Basin study until August, 1954. The results obtained indicated that the dissolved oxygen content of the streams underwent a larger drop from the daylight to night hours than could be explained by the value of the biochemical oxygen demand or by the respiration of organisms in the stream. It was reasoned that this phenomenon might possibly be explained if the groundwater contributed water of varying quality to the streams depending upon the length of time the water had been in the ground and upon previous weather conditions,

As a result of the above study, it was proposed to measure the pH, conductivity, relative turbidity, and temperature on a continuous basis in one of the small streams and to supplement these values with dissolved oxygen and biochemical oxygen demand measurements. It was hoped that this more intensive study would present a clearer picture of the variations in the water quality of small unpolluted streams on a diurnal basis and possibly indicate the effects of groundwater contribution upon water quality.

The purpose of this thesis is to assemble equipment capable of continuous measurement of pH, conductivity, relative turbidity, and temperature using a four-point electrical recorder.

CHAPTER II

DESCRIPTION OF EQUIPMENT

Equipment for measuring pH.--pH may be defined as the logarithm of the reciprocal of the hydrogen ion concentration. It may be expressed in terms of the electrical voltage generated between two electrodes.(2) One of these electrodes - the reference electrode - is unaffected by pH changes, while the potential of the second electrode is sensitive to changes in pH.(3) The electrodes are connected to a potentiometer bridge which is balanced when the correct pH is indicated. A change in pH will unbalance the bridge and cause a deflection of a galvanometer needle until the bridge is once more in balance. This deflection is transmitted to a pH indicator scale which records the deflection as a change in pH. As shown by the pH calibration curve, Fig. 1, a linear relationship exists between pH value and voltage.

In this study a Beckman pH meter with a glass electrode and a saturated-calomel electrode was used to measure the pH. The pH meter was connected to one point of a Brown, four-point, electrical recorder which recorded on a strip chart the data supplied to it by the pH meter.

The pH electrodes were immersed in a 2000 milliliter beaker, and water was supplied to them by a chemical solution-feed pump.

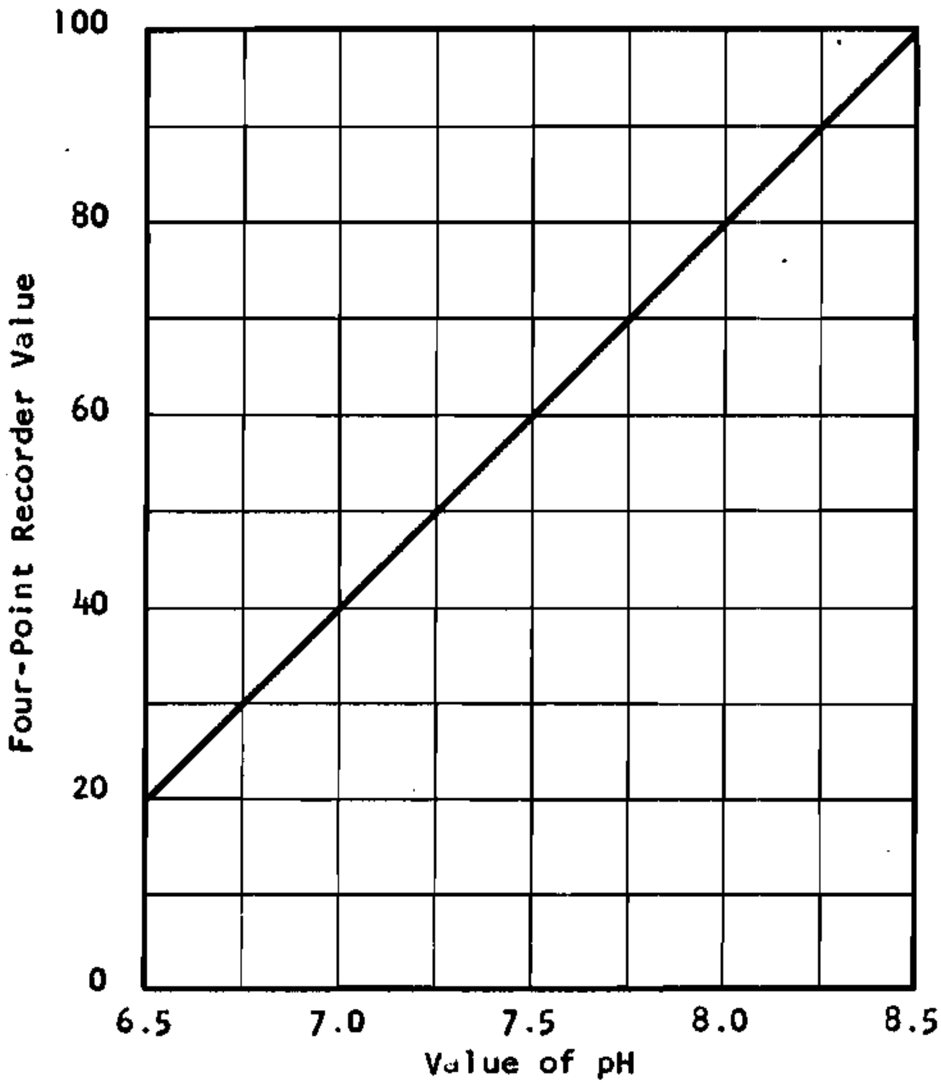

Fig. 1.-Calibration Curve for pH

Equipment for measuring conductivity.--Electrical conductivity of a liquid is the reciprocal of the specific resistance of the liquid. Conductivity is a measure of the ability of a solution to carry current. A voltage is applied to the solution through an electrode system, and the resistance of the solution is measured by a conductivity meter, which is essentially an ohmmeter.

The conductivity of a solution is dependent upon the concentration of ions present in the solution. Measurement of the conductivity of streamwater should give an indication of the role played by groundwater infiltration upon variations in water quality because of the higher concentration of ions in groundwater. As the percentage of groundwater infiltration in a stream increases the specific resistance of the streamwater should decrease because of its greater current-carrying ability.

In this study an Industrial Instruments, Inc., Type RC-1, conductivity bridge with platinum-plated rod electrodes was used. The electrodes were immersed with the pH electrodes in a 2000 milliliter beaker with streamwater supplied by a chemical solution-feed pump. The conductivity bridge was connected to the four-point electrical recorder for continuous recording of the measurements.

The calibration curve for measured resistance is shown in Fig. 2.

Equipment for measuring relative turbidity.--Turbidity is a

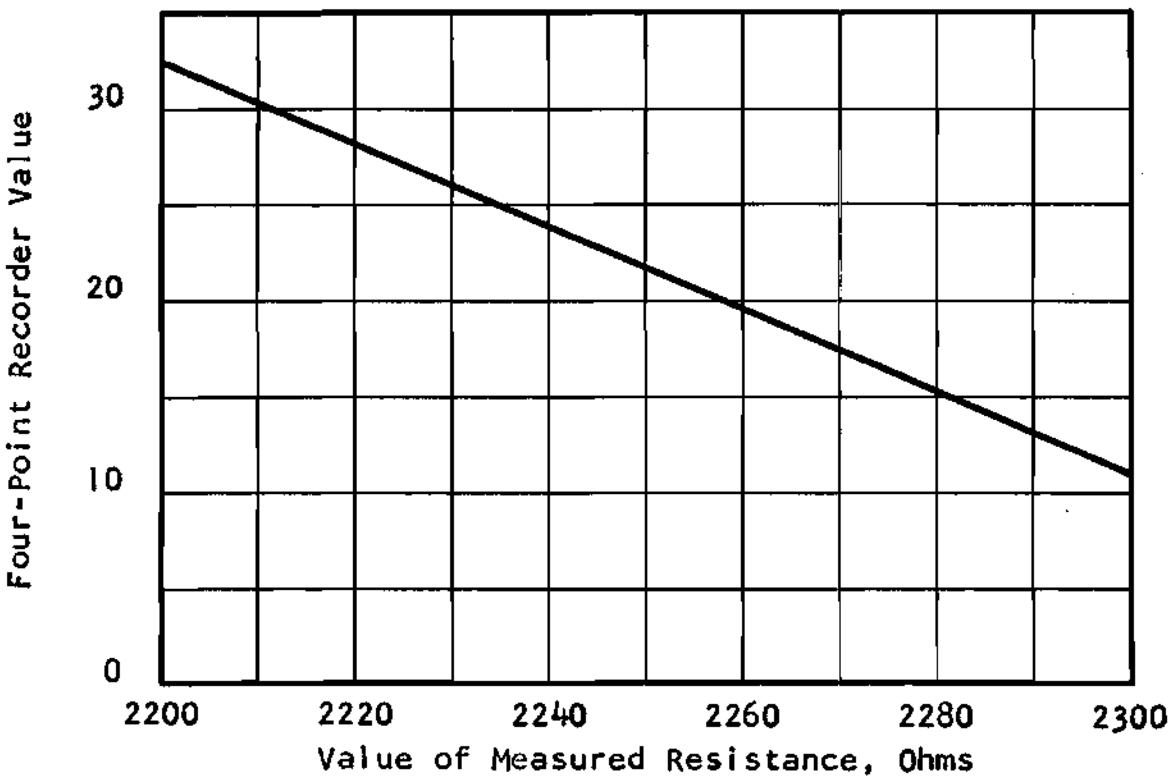

Fig. 2.-Calibration Curve for Resistance

measure of the amount of suspended matter in a liquid. It is termed "relative" turbidity here because no attempt was made to compare the samples tested against prepared standards. The relative turbidity is important in this study because higher than normal turbidity values would indicate precipitation on the watershed and an increase in surface runoff.

The instrument used in this study may be termed a turbidimeter because it measures the decrease in light transmitted by a turbid media. The turbidimeter consisted of a fluorescent light source and two photoelectric cells mounted on a float as shown in Fig. 3.

The float was constructed of plastic and was mounted on a frame to which four one-gallon cans were attached. This frame supported the float in the water so that the top of the float was submerged about one inch. The fluorescent light and the two photoelectric cells were each mounted in separate watertight compartments.

The two photoelectric cells were connected as shown in Fig. 4. The positive terminal of each cell was connected to the negative terminal of the other and the 2000 ohm variable resistor, R1, so set that the current through a galvanometer indicated zero when there was full light transmission. This arrangement gives a maximum response to changes in light as well as the most nearly linear relationship between current flow and decrease in light transmission. The 3000 ohm variable resistor, R2, was used to reduce the current flow and

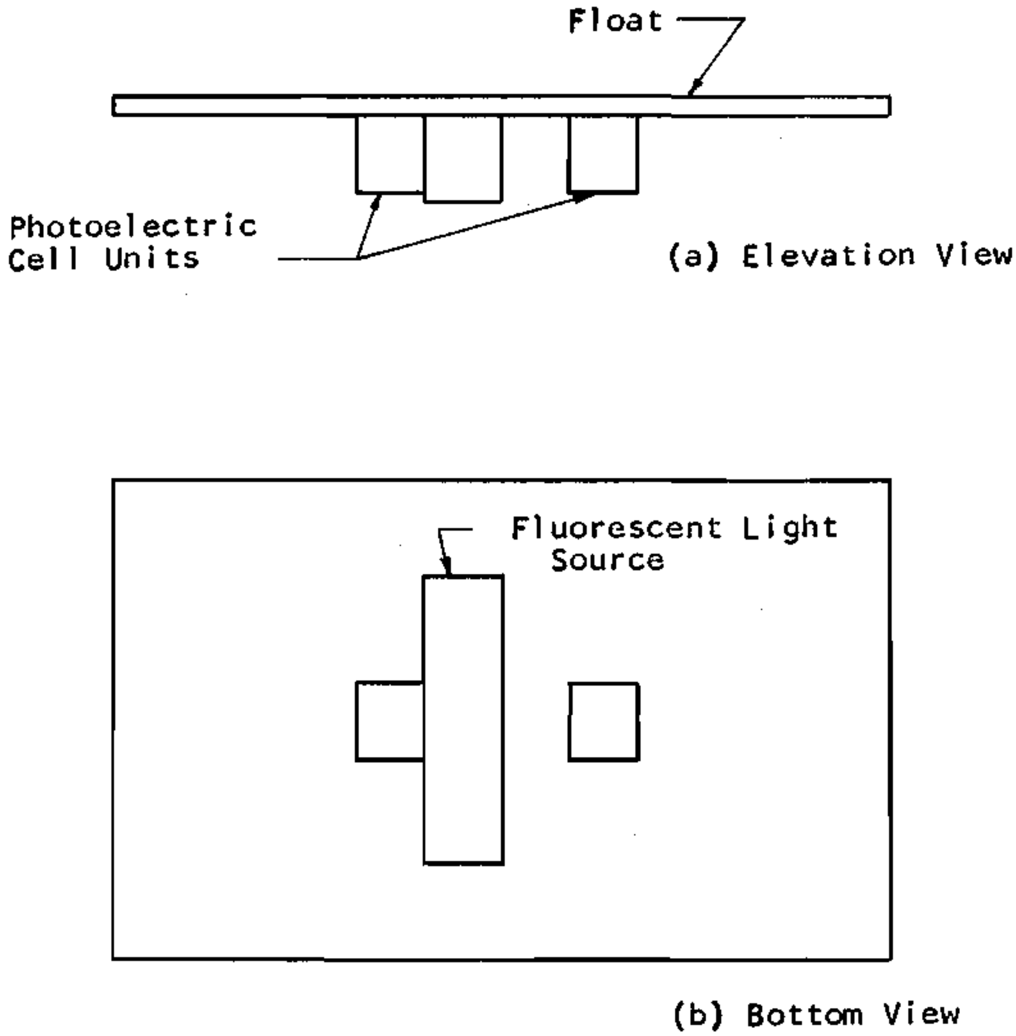

Fig. 3.-Turbidimeter Mounting

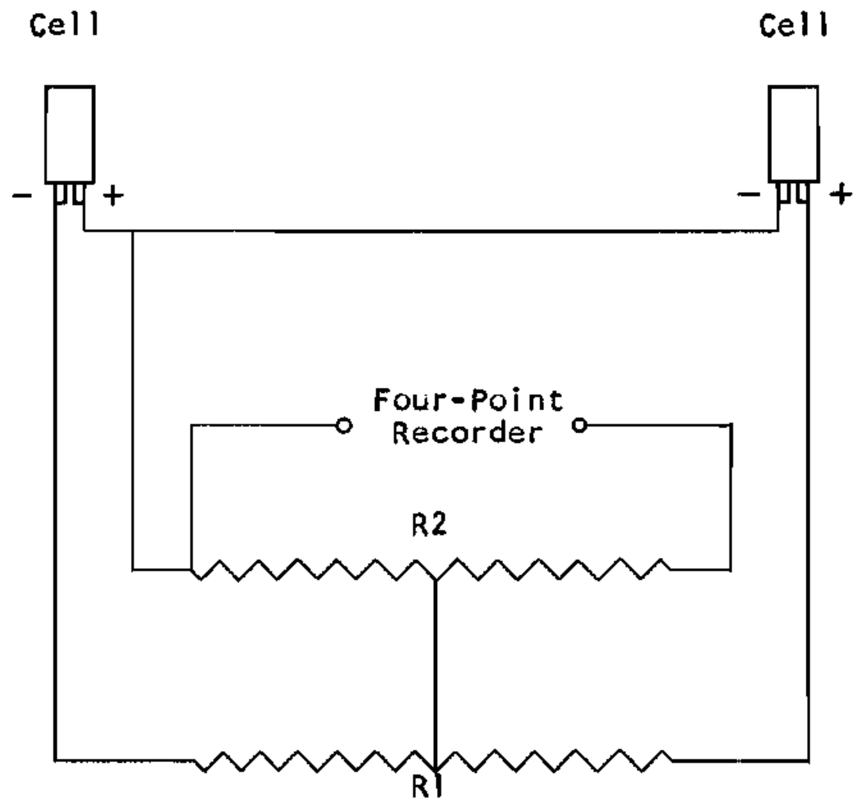

Fig. 4.-Photoelectric Cell Connections

bring it within the range of the electrical recorder.

Final adjustments resulted in a four-point recorder value of five with full light transmission and 91 with no light transmission on a scale range of 0 to 100.

Equipment for measuring temperature.--In this study temperature was measured by a thermocouple. A thermocouple is a combination of wires of two different metals in which a thermoelectric electromotive force may be generated. The electromotive force in a thermocouple circuit depends on the difference in temperature between the two dissimilar metal junctions. Therefore, temperature differences can be measured by measuring the thermoelectric electromotive force. If the temperature of one junction--the reference junction--is maintained constant, and if the thermocouple circuit has been previously calibrated, the temperature of the other junction may be determined.

In this case the thermocouple junctions were protected by enclosing them in test tubes. The reference junction was maintained at a temperature of 56° Centigrade in a constant temperature bath; the sensitive junction was set in position on the float mentioned above at such a depth so that it was sensitive only to changes in streamwater temperature.

The constant temperature bath was maintained by using a 200 watt heater, a 56° Centigrade thermoregulator, and a normally closed-circuit relay. The heater and thermoregulator were contained in a one-gallon water bath.

The calibration curve for temperature using the above equipment is shown in Fig. 5.

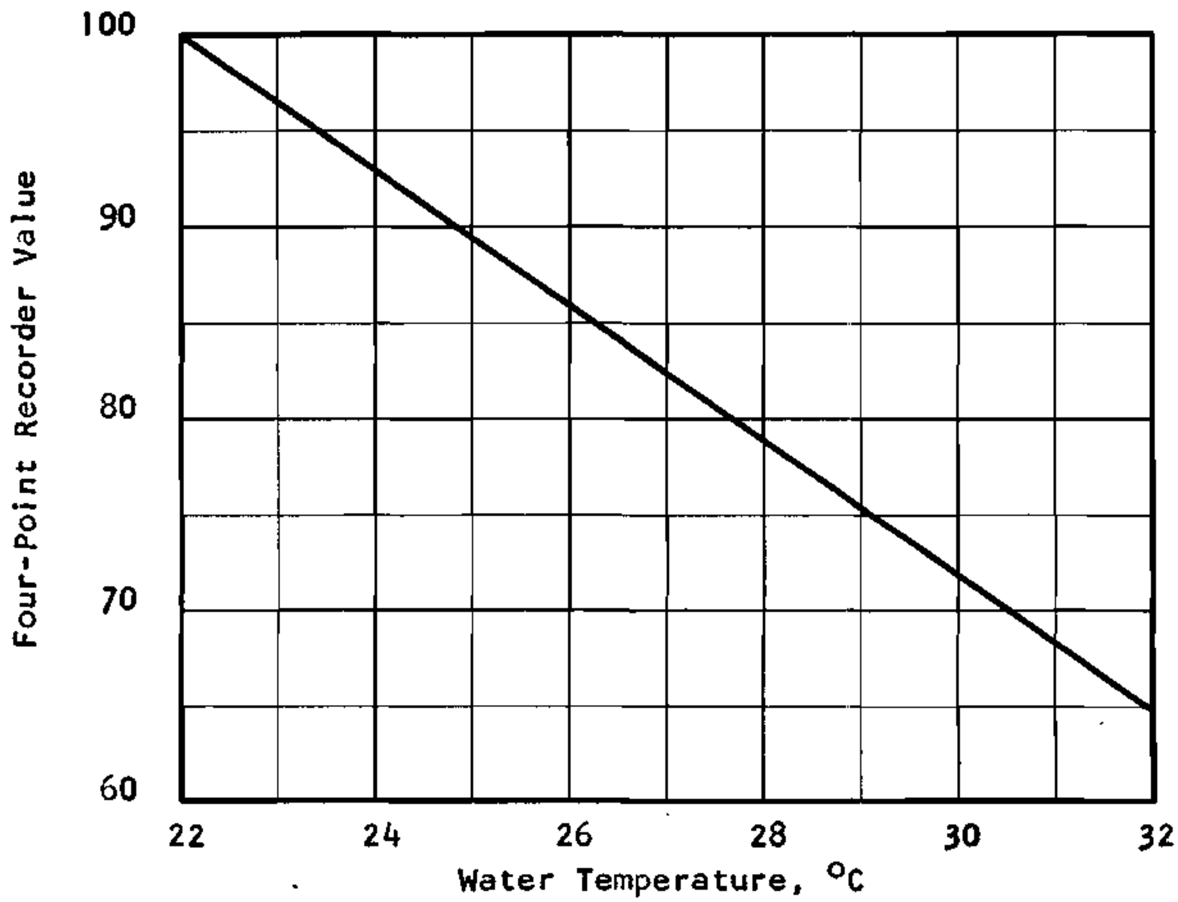

Fig. 5.-Calibration Curve for Temperature

CHAPTER III

TESTING OF EQUIPMENT

On September 9, 1955, the equipment was placed on the Yellow River at Conyers, Georgia, to test its operation. Considerable difficulty was encountered. At this time there was a 500 watt heater in the constant temperature bath. This heater was large enough to cause enough voltage drop when it was operating to affect the other instruments. Its intermittent operation through the relay circuit caused a noticeable variation in instrument readings. Even when the heater was not in operation there were unexplained fluctuations in the readings of the pH and conductivity meters. Also the float compartments containing the photoelectric cells began leaking after a few weeks of trial operation.

On October 20, 1955, the equipment was returned to the laboratory for improvements. The constant temperature bath was reduced in size, and the 500 watt heater was replaced by a 300 watt heater. A voltage regulator was installed to maintain a constant input voltage. The float compartments containing the photoelectric cells were redesigned so as to be watertight.

The equipment was then moved to the intake well of the Atlanta Water Works Chattahoochee Pumping Station for further tests. This was a much more convenient site than the Yellow River, and, although not a small unpolluted stream, served amply for testing the equipment.

The temperature and turbidimeter equipment presented no difficulties other than properly connecting the various components. The pH and conductivity instruments, however, were quite troublesome. Wildly erratic fluctuations took place. The indicators of the instruments were at times completely off scale. The electrodes of these instruments were at this time attached to the float which was suspended in the water. It was determined that the electrodes were being grounded when attached in this manner. To prevent this grounding, the electrodes were removed from the float and placed in a 2000 milliliter beaker which was supplied with water by a chemical solution-feed pump. This arrangement proved to be satisfactory.

The variations in pH, resistance, relative turbidity, and temperature were obtained for the intake well of the Chattahoochee Pumping Station on the 23 and 24 of June, 1956. These curves are shown in Figs. 6, 7, 8, and 9. The measured resistance values were corrected by two per cent per degree Centigrade variation from 18^{o} Centigrade which was used as a datum. It is interesting to note that the values of pH, resistance, and temperature began to decrease during the late evening hours and reached a minimum value near 10 a.m. This trend may possibly indicate the influence of groundwater infiltration. However, since the variation of pH was larger than may be expected in a river the size of the Chattahoochee,

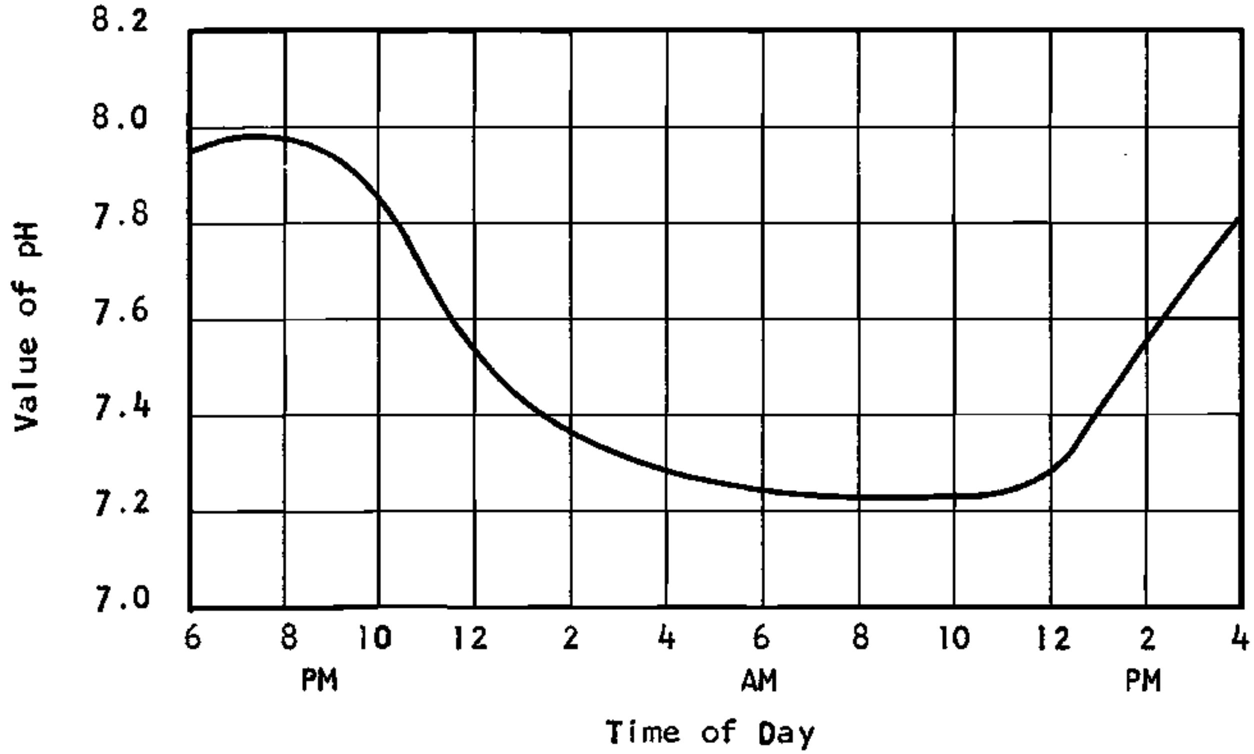

Fig. 6.-Variations in pH at Chattahoochee Pumping Station, June 23 and 24, 1956

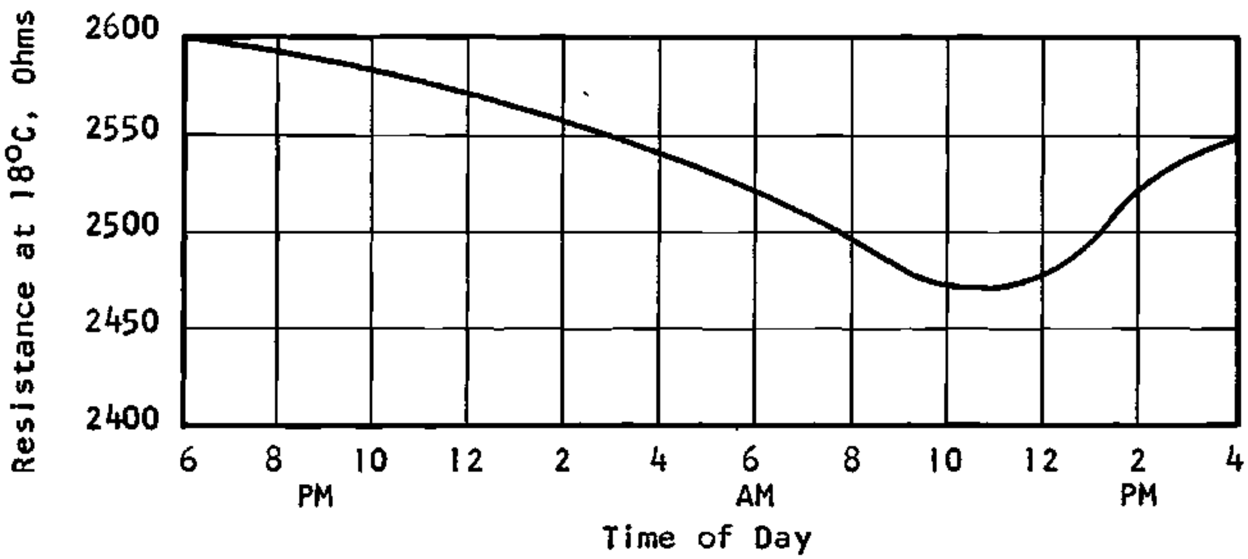

Fig. 7.-Variations in Resistance at Chattahoochee Pumping Station, June 23 and 24, 1956

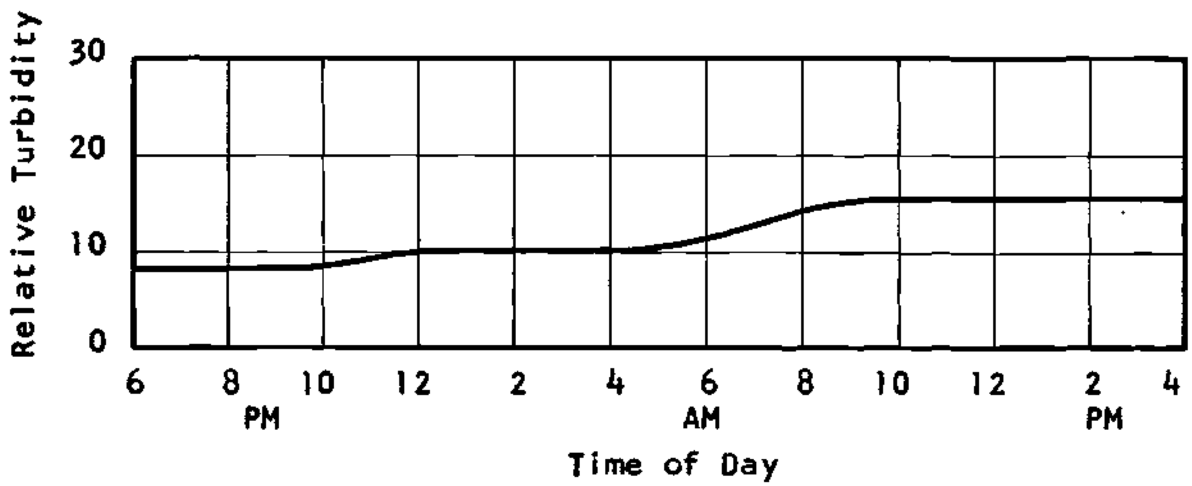

Fig. 8.-Variations in Relative Turbidity at Chattahoochee Pumping Station, June 23 and 24, 1956.

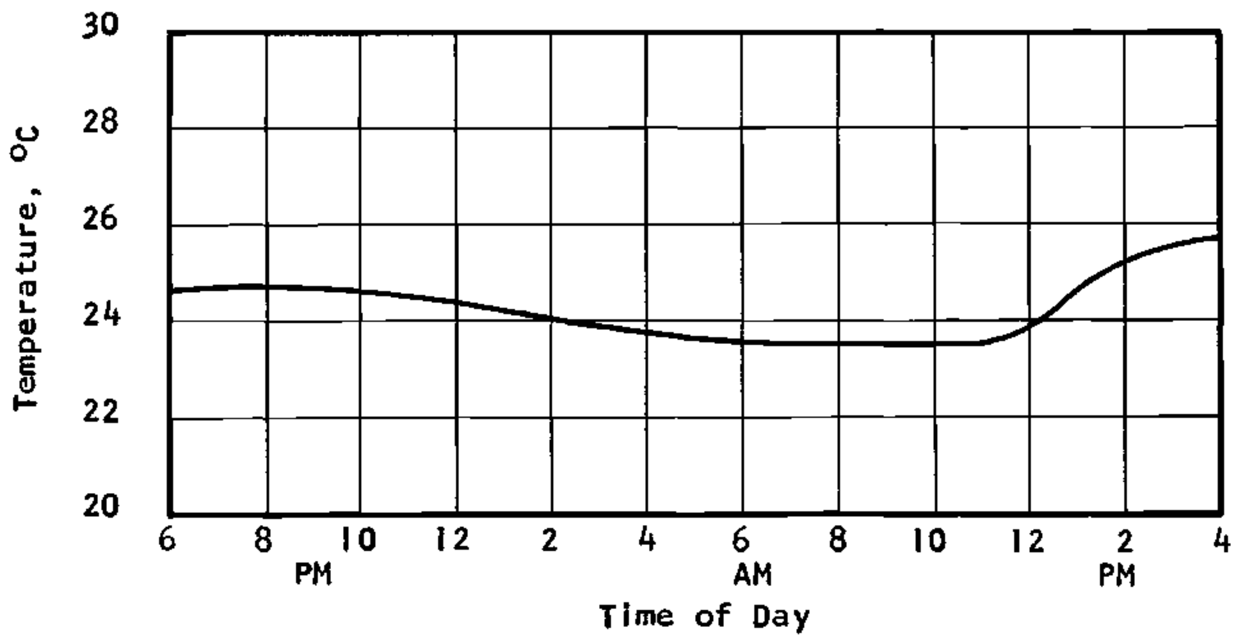

Fig. 9.-Variations in Temperature at Chattahoochee Pumping Station, June 23 and 24, 1956

the variations might have been caused by pollution. The relative turbidity was fairly constant. The water was slightly more turbid on June 24 than it was on June 23.

The equipment operated well during the above tests, and it seems to be capable of further and more extensive field use.

CHAPTER IV

RECOMMENDATIONS

The following recommendations are offered for consideration in improving the operation and reliability of the equipment.

The position for placing the equipment should be chosen with care. The equipment should not be placed near high tension wires, radio stations, or any industry using large electrical equipment as these factors seem to aggravate instrumental operation.

The leads to the instruments should be kept as short as possible. The voltage in the leads is small and increased length of leads increases the resistance and chance for error.

The pH meter and conductivity bridge should be operated as near their balance point as possible. In this position they operate with the most stability.

The constant temperature bath should possibly be operated as an ice bath rather than at 56° Centigrade. The ice bath could be contained in a vacuum bottle and would need little attention. Also the ice bath could replace the relay circuit containing the heater and thermoregulator. This replacement would reduce the amount of equipment needing attention and would eliminate the undesirable influence the relay and heater seem to have on the pH meter and conductivity bridge.

If much work is to be done with this equipment, it would be desirable to obtain commercial flow cells with resistance thermometers for automatic temperature correction for the pH and conductivity electrodes.

BIBLIOGRAPHY

BIBLIOGRAPHY

Literature Cited

1. Ingols, Robert S. and George M. Jacobs, "Variations in the Chemical Character of Small Streams," Bulletin of the Georgia Academy of Science, 13, 1955, pp. 94-100.

2. Streatfield, E. L., "Instrumentation in Water Usage," Chemistry and Industry, 53, December, 1951, pp. 1208-17.

3. Rosenthal, Robert, "Some Practical Aspects of the Measurement of pH, Electrical Conductivity, and Oxidation-Reduction Potential of Industrial Water," Symposium on Continuous Analysis of Industrial Water and Industrial Waste Water, American Society for Testing Materials Special Technical Publication No. 130, 1953, pp. 12-20.

Other References

Bates, Roger G., Electrometric pH Determinations, New York: John Wiley and Sons, Inc., 1954.

Weber, Robert L., Temperature Measurement and Control, Philadelphia: The Blakiston Company, 1941.

American Society for Testing Materials Committee D-19, Manual on Industrial Water, American Society for Testing Materials Special Technical Publication No. 148, Philadelphia: American Society for Testing Materials, 1953.