

A STUDY OF PRECISION AND ACCURACY OF
LABORATORIES AND METHODS OF ANALYSIS
OF AMMONIA NITROGEN IN LAKE MICHIGAN WATERS

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A STUDY OF PRECISION AND ACCURACY OF LABORATORIES AND
METHODS OF ANALYSIS OF AMMONIA NITROGEN IN LAKE MICHIGAN WATERS

A Report to the Technical Committee of the Calumet Area-
Lake Michigan Enforcement Conference

by

The Laboratory Directors of the Calumet Area-Lake Michigan
Enforcement Conference

I. INTRODUCTION

This is a report of comparison studies performed by cooperating laboratories concerned with analysis of Lake Michigan waters and stream waters in the Calumet Area of Indiana and Illinois.

A series of comparison studies is to be made for determinations of ammonia nitrogen, phosphate, phenol, cyanide, and threshold odor. Part I presents the findings from a series of five comparison studies on ammonia nitrogen completed between September 9, 1965 and April 26, 1966.

The objectives of the comparison studies are:

1. To determine the reliability (precision and accuracy) of the analytical procedures as normally used in the desired concentration range.
2. To determine if there is a change in the accuracy of these procedures arising from departures from prescribed analytical routine.
3. To determine the degree of variation between the participating laboratories.
4. To find the sensitivity of the methods as used.
5. To recommend necessary changes in procedures.

The laboratories participating in the ammonia nitrogen study were:

1. American Oil Company
2. Cities Service Oil Company
3. City of Chicago, Bureau of Water, Dept. of Water and Sewers
4. Garv-Hobart Water Corporation
5. Great Lakes-Illinois River Basins Project
6. Indiana State Board of Health
7. Inland Steel Company
8. Lake Huron Program Office, GLIRBP
9. Lake Ontario Program Office, GLIRBP
10. Metropolitan Sanitary District of Greater Chicago
11. Robert A. Taft Sanitary Engineering Center

II. PROCEDURES. CHRONOLOGICAL DEVELOPMENT

This section of our report presents a brief chronological commentary on the conditions, implied and explicit, which obtained in the various Test Series. It is intended to provide background for assessment of the results obtained in individual Series and also for comparison of any or all Series. All results, excepting those of Series I, are summarized in Tables 1 to 6 in the Appendix.

SERIES I. September 9, 1965

Number of samples analyzed: Four: Raw Lake Water, preserved and unpreserved, from Gary-Hobart and from Chicago South District Filtration Plant.

Conditions: Samples stored at room temperature 24 hours.

Participating Laboratories:

1. City of Chicago, Bureau of Water, Dept. of Water and Sewers
2. Gary-Hobart Water Corporation
3. Great Lakes-Illinois River Basins Project
4. Metropolitan Sanitary District of Greater Chicago

There was no direct stipulation of the method to be used in this Series. As it turned out, of the four participating laboratories, no two used the same method. The results, as reported, were widely divergent. Average values from the four participating laboratories are shown below in mg/l:

<u>Chicago--SDFP</u>		<u>Gary--Hobart</u>	
<u>Unpreserved</u>	<u>Preserved</u>	<u>Unpreserved</u>	<u>Preserved</u>
0.024	0.082	0.026	0.110
0.160	0.200	0.150	0.260
0.05	0.09	0.06	0.06
0.01	0.02	0.01	0.02

These results revealed that the laboratories were consistent within their own methods, but no two laboratories agreed as to the concentration of ammonia found.

Because of the wide disagreement, the Technical Committee, Calumet Area-Lake Michigan Enforcement Conference, requested that comparison studies be made by laboratories concerned with Calumet Area surveillance. The GLIRBP laboratory prepared a working draft of the proposed comparison studies. These were distributed to the Laboratory Directors for review.

September 30, 1965

A meeting of the Calumet Area Laboratory Directors, under the chairmanship of Mr. Clifford Bisley, Jr., was held to discuss and revise the proposed procedures for future comparison studies. The members of the Technical Committee of the Calumet Area-Lake Michigan Enforcement Conference

met with the Laboratory Directors during the first hour to review the problem and offer their suggestions.

The Laboratory Directors agreed that Series II should consist of ammonia nitrogen, phosphate, phenols, cyanide, and odor standards and samples.

SERIES II. October 13, 1965

Number of samples for ammonia nitrogen: Nine (5 synthetic)
(4 raw water)

Additionally: phosphates - 10 samples
phenols - 5 "
cyanide - 8 "
odor - 5 "

Participating laboratories:

1. American Oil Co.
2. City of Chicago, Bureau of Water, Dept. of Water and Sewers
3. Garv-Hobart Water Corporation
4. Great Lakes-Illinois River Basins Project
5. Indiana State Board of Health
6. Inland Steel Company
7. Metropolitan Sanitary District of Greater Chicago

Analysis date: raw water 10/13/65; synthetic 10/14/65.

Conditions: Collection, preservation, and distribution procedures were standardized and time for analyses synchronized. Forms were distributed for reporting results in triplicate, wherever practicable. Deviations from the above were to be duly recorded on the report forms.

Conditions were stipulated for distillation procedure as follows: The distillation method should be followed as described in Standard Methods for the Examination of Water and Wastewater, 11th Edition, pages 169-173, with emphasis on the following points.

"1. The distillation apparatus should be steamed out by placing 500 ml of distilled water and 10 ml of phosphate buffer solution in the flask; steam out until the distillate is free of ammonia.

2. Preserved samples and standards should be adjusted to a pH of seven, using a pH meter prior to adding the buffer solution.

3. Use a 500 ml sample or standard and distill over approximately 250 ml, collecting the distillate in 0.002N sulfuric acid. The distillate is then concentrated by evaporation on a hot plate. The resulting solution should be made up to 100 ml and nesslerized. This gives a concentration factor of 5. Standards 4 and 5 need not be concentrated by evaporation.

4. The method used to read the sample will be indicated on the report."

The Sodium Phenate method was also outlined for the Technicon AutoAnalyzer.⁽²⁾ However, the final paragraph of these instructions read as follows: "Any method or methods that are being used by any of the laboratories may be employed in these analyses. The method used should be spelled out for the purpose of interpreting the results."

At the November 29 meeting of the Laboratory Directors, the following points were made in discussing the results of the last comparison, Series II. Considerable variation existed among the laboratories both in their procedure and in the results reported. Each laboratory, however, displayed good reproducibility within itself. Values obtained by the Technicon method were judged best, followed in order by distillation and direct nesslerization. The following excerpts from the November 29 meeting are pertinent at this point:

- "1. It appears that some of the laboratories were not experienced at running analyses in the low range (0.00-0.06 mg/l) desired and/or by the prescribed methods. It also appears that too much pressure was placed on the laboratories to accomplish a large amount of work in a short period of time. It was recommended that the study be conducted again, at a more relaxed pace, and with a fixed number of samples and standards for each run.
2. An indispensable condition for conducting a successful inter-laboratory study is skill and familiarity with the method on the part of all participants. The methods used, when applied to the low concentrations found in lake water, i.e. at or near the maximum sensitivity of the method, cannot be used successfully without a great deal of skill and familiarity with the method on the part of the individual analyst. This was not the case in this series of comparison studies.
3. Identical copies of a detailed description of all steps to be followed in this test procedure for comparison studies should be provided to each participant.
4. One standard sample, plus a sample of Gary raw water and Chicago raw water, is enough for each laboratory to check at one time.
5. Although one laboratory used research quality instrumentation, the Spectronic 20 is considered to be good enough to give the desired results."

Under the chairmanship of Mr. LeRoy Scarce, the Laboratory Directors met February 17, 1966. Here it was decided that future studies would be limited to one parameter at a time. Ammonia nitrogen was selected for the next test series, using standard samples only.

SERIES III. March 4, 1966

Number of samples analyzed: Six (synthetic)

Participating laboratories:

1. American Oil Company
2. Cities Service Oil Company
3. City of Chicago, Bureau of Water, Dept. of Water and Sewers
4. Garv-Hobart Water Corporation
5. Great Lakes-Illinois River Basins Project
6. Indiana State Board of Health
7. Inland Steel Company
8. Lake Huron Program Office, GLIRBP
9. Metropolitan Sanitary District of Greater Chicago

Analysis date: March 4, 1966

Conditions: The following conditions were stipulated by advance notice to the participating laboratories.

Distillation Method: Standard Methods, 12th Ed., pp 186-193, with emphasis on the following points:

"Steaming out apparatus to ensure ammonia-free conditions - same as in previous series.

Adjustment to pH 6.6 prior to adding buffer - previous series called for pH 7.0.

Collection of distillate in 0.02N sulfuric acid - previous series called for 0.002N sulfuric acid.

Concentration of distillate to 50 ml instead of 100 ml - as required in previous series."

Procedure for AutoAnalyzer remained unchanged from last Series.

March 17, 1966

Calumet Area Laboratory Directors met for the purpose of reviewing the results obtained from the March 4 Test Series III. The results from Series III showed a substantial improvement over Series II. From a review of these results, it was agreed that an additional study should be made; it was requested and agreed that a prescribed procedure for the ammonia nitrogen test be provided for use in future comparison tests. This was done as requested, with particular emphasis on distillation of standards in preparing calibration curve and volume of distillate.

SERIES IV. March 23, 1966

Number of samples: Six

Participating laboratories:

1. American Oil Company
2. Cities Service Oil Company
3. City of Chicago, Bureau of Water, Dept. of Water and Sewers
4. Garry-Hobart Water Corporation
5. Great Lakes-Illinois River Basins Project
6. Indiana State Board of Health
7. Inland Steel Company
8. Lake Huron Program Office, GLIRBP
9. Lake Ontario Program Office, GLIRBP
10. Metropolitan Sanitary District of Greater Chicago
11. Robert A. Taft Sanitary Engineering Center

Conditions: "All laboratories are to follow the procedure exactly as outlined. For the first time conformity in procedure is insisted upon."

April 21, 1966.

Calumet Area Laboratory Directors met to review latest results of Series IV. There were some laboratory difficulties which still presented a problem - the obtaining of ammonia-free water, ammonia background of laboratory, collection of distillate in boric acid, and use of rubber stoppers. It was agreed that one more comparison series be carried out.

SERIES V. April 26, 1966.

Number of samples: Four

Participating laboratories:

1. American Oil Company
2. Cities Service Oil Company
3. City of Chicago, Bureau of Water, Dept. of Water and Sewers
4. Garry-Hobart Water Corporation
5. Great Lakes-Illinois River Basins Project
6. Indiana State Board of Health
7. Inland Steel Company
8. Lake Huron Program Office, GLIRBP
9. Lake Ontario Program Office, GLIRBP
10. Metropolitan Sanitary District of Greater Chicago
11. Robert A. Taft Sanitary Engineering Center

Conditions: The procedure to be followed was the same as prescribed for the last series with no changes. Points emphasized: collecting 300 ml of distillate and distilling standards in preparation of a standard curve.

At the meeting of the Calumet Area Laboratory Directors May 19, 1966, for the purpose of reviewing recent comparison Series V for ammonia nitrogen, the Laboratory Directors unanimously decided that further testing would be of little value. Series V showed that when all laboratories followed the same procedure, most of the laboratories obtained an accuracy of ± 0.02 mg/l or better, in analyzing standard samples containing 0.00 and 0.04 mg/l ammonia nitrogen.

The subject of direct nesslerization was again brought up and the opinion was expressed that this method should not be entirely excluded from the future thinking of the members of this group.

Problems which existed throughout the Series were as follows:

From the beginning of the Series there was a question of ammonia-free water and ammonia-free reagents (buffer and sulfuric acid). Ordinary distilled water was found to contain significant amounts of ammonia. Redistilled water, upon concentration, still contained some ammonia. The best procedure for obtaining ammonia-free water was found to be the addition of sulfuric acid to the redistillation, if a carbon or ion-exchange column couldn't be attached to the still. Once the ammonia-free water was prepared, keeping it free from ammonia contamination was an important factor.

Clean glassware was imperative. Cleaning glassware with chromic acid solution and then rinsing with ammonia-free water was found to be the best preparation for glassware.

It was suggested that rubber stoppers be replaced with special neoprene stoppers since ammonia does adsorb to rubber.

This section on procedures indicates that with conformity of procedure, reliable results can be obtained.

The results of the above comparison series are discussed and summarized in detail in the next section of this report.

III. FINDINGS AND DISCUSSION

Distillation Method

As indicated in the preceding section, progressive improvement in agreement of results from the individual laboratories was realized in application of the distillation method. Uniform test procedures were not followed by all laboratories for the first three series and results were erratic. After uniform procedures were followed, the results were more consistent and gave better indications of the accuracy that can be achieved when the recommended procedure is carefully followed.

Tables 1a and 1b present individual laboratory average results chronologically and anonymously. When analyzing samples containing 0.00 mg/l of ammonia nitrogen, an accuracy of ± 0.04 mg/l (one standard deviation) was obtained in Series II, whereas in a repeat analysis in the last series, an accuracy of ± 0.02 mg/l was realized. The same improvement was noted when

analyzing standard samples containing concentrations in the range of 0.02 to 0.05 mg/l. In general, the average values indicate a slight tendency to be on the high side in these determinations.

Even closer agreement was demonstrated when analyzing Lake Michigan samples from the City of Chicago and Gary-Hobart water intakes, where a precision of ± 0.04 mg/l was obtained in October 1965 (Series II), and in April 1966 the precision had improved to ± 0.01 mg/l.

Recoveries of known amounts of ammonia nitrogen by the distillation process are shown in Table 3. The precision and accuracy were, in this instance, the same and was ± 0.02 mg/l for recoveries of 0.10 and 0.05 mg/l ammonia from Lake Michigan water. The precision and accuracy for recovery of 1.0 mg/l ammonia nitrogen from river water (collected from the Indiana Harbor Canal) was ± 0.29 mg/l.

AutoAnalyzer Method

From the inception of the studies, the AutoAnalyzer method provided results demonstrating precision and accuracy superior to those of the distillation method. These results are shown in Tables 2, 5, and 6. Precision and accuracy, in terms of one standard deviation for standard and lake samples, was most often ± 0.01 mg/l. For the recoveries of the known amounts (0.05, 0.10, and 1.0 mg/l) added to lake and river water, the accuracy was ± 0.01 , ± 0.01 , and ± 0.09 mg/l, respectively.

Data Evaluation

Figures 1 through 7 summarize the results from both methods in terms of deviation from the known amounts of ammonia nitrogen. The range of deviation from known amount and distribution of individual values are presented as percent of all determinations accruing from all participating laboratories. The reliability of the method as used in the various laboratories may, in this manner, be estimated. Approximately 32 to 96% of all the distillation determinations for standard samples ranging from 0.00-0.06 mg/l are within ± 0.02 mg/l (one standard deviation). It is to be noted that a significant percentage of AutoAnalyzer determinations showed no deviation at all from the known amounts (60 to 90%).

Forty-nine to 67% of all distillation results were within ± 0.02 mg/l for standard samples in the range 0.11-0.15 mg/l ammonia nitrogen; 22-31% were within ± 0.04 for standard samples in the range 0.30-0.38 mg/l ammonia nitrogen; and 45-61% were within ± 0.08 mg/l for standard samples containing 0.72-0.97 mg/l ammonia nitrogen.

The findings are presented in further graphic detail in Figures 9 through 14, located in the Appendix in the form of probability curves for each sample in the entire study.

Laboratory Evaluation

Since the data are herein presented anonymously, a direct comparison of laboratory performance in using the distillation method is not possible. However, all laboratories, of course, did not show equal performance. As indicated in the Procedure Section, consistency of relative achievement was present at the beginning of these comparisons. Most of the laboratories

did demonstrate that, with enough effort and special precautions, the data so generated might be considered as interchangeable if a standard deviation of ± 0.02 mg/l is allowable.

A statement by Mr. Dwight G. Ballinger, consultant to the Laboratory Directors, is quoted below:

"Adequate data is lacking on the precision and accuracy of the ammonia nitrogen determination at concentrations below 0.1 mg/l. Standard Methods, Twelfth Edition (1965), indicates a reproducibility of 5% for the distillation procedure, but this figure was obtained at concentrations found in polluted waters.

In a recent study, Dr. David Jenkins, University of California, investigated ammonia nitrogen concentrations of approximately 0.03 mg/l in San Francisco Bay waters. Dr. Jenkins found that the standard deviation of the distillation-Nessler procedure, using 10 replicate determinations of the same sample, was ± 0.005 mg/l. Experience in the Analytical Reference Service of the Taft Center indicates that a comparison of results between laboratories yields a deviation at least three times greater than the deviation within the single laboratory. Thus, an extrapolation of the Jenkins data suggests an interlaboratory comparison of approximately ± 0.02 mg/l at the 0.03 mg/l level.

It should be noted that the University of California studies were conducted with 10 replicate determinations, in a very carefully controlled test. The results obtained are probably superior to those normally found in routine survey work.

On the basis of the available information on the precision and accuracy of the ammonia nitrogen determination, it is my opinion that the values reported by the average laboratory may be expected to deviate from the true concentration by at least ± 0.02 mg/l at ammonia nitrogen levels below 0.05 mg/l. However, in order to ensure the best possible results, only those laboratories demonstrating ability to meet this precision level should be included in a nutrient monitoring operation."

In conclusion, this section on procedure shows that good results can be attained in the distillation method for ammonia nitrogen, especially at the low levels encountered in Lake Michigan water, provided that: a great amount of care in preparation and skill in technique are exercised, and that there is strict adherence to the method outlined in Standard Methods with the modifications as described in the Appendix of this report.

IV. CONCLUSIONS AND RECOMMENDATIONS

1. This study indicated that an accuracy of ± 0.02 mg/l, expressed as one standard deviation, can be achieved when analyzing Lake Michigan open water, inshore, and harbor samples by distillation. When samples from the above waters are analyzed employing the AutoAnalyzer, an accuracy of ± 0.01 mg/l can be achieved. The precision that can be obtained by distillation is ± 0.01 mg/l (one standard deviation), and when employing the AutoAnalyzer, the precision is better than this value.

2. The above distillation results have been obtained by modifying the method for ammonia nitrogen, as given in Standard Methods, 12th Edition, to comply strictly with the procedure as presented in the Appendix of this report.

3. The AutoAnalyzer procedure was demonstrated to be superior (more accurate with greater precision) to the distillation procedure for the relatively uncontaminated lake waters.

4. Of the 11 participating laboratories, the majority was able to achieve the above accuracy using the distillation procedure. These results were not achieved on a routine basis, but under conditions requiring extraordinary care and precautions. Laboratories exposed to extreme air pollution problems, and those small laboratories where all analyses must be performed in one room, will most likely not be able to obtain these accuracies at the concentrations under investigation.

5. The limit of detectability using the modified distillation procedure, as presented herein for the detection of ammonia nitrogen in Lake Michigan waters, appears to be 0.02 mg/l. With the AutoAnalyzer, the limit appears to be 0.01 mg/l. It is possible that the sensitivity of the distillation procedure can be improved. However, such a possibility can be verified only through further applied research.

6. Only those results from laboratories showing the continuing capability to analyze at an accuracy of ± 0.02 mg/l, or better, should be accepted in a monitoring operation when analyzing for ammonia nitrogen levels below 0.06 mg/l.

7. Historic data reporting ammonia nitrogen levels below 0.1 mg/l should be evaluated with extreme caution. There appears to be no practical way to develop a correction factor to apply to the latter data which would provide acceptable correlations in the lower concentration ranges.

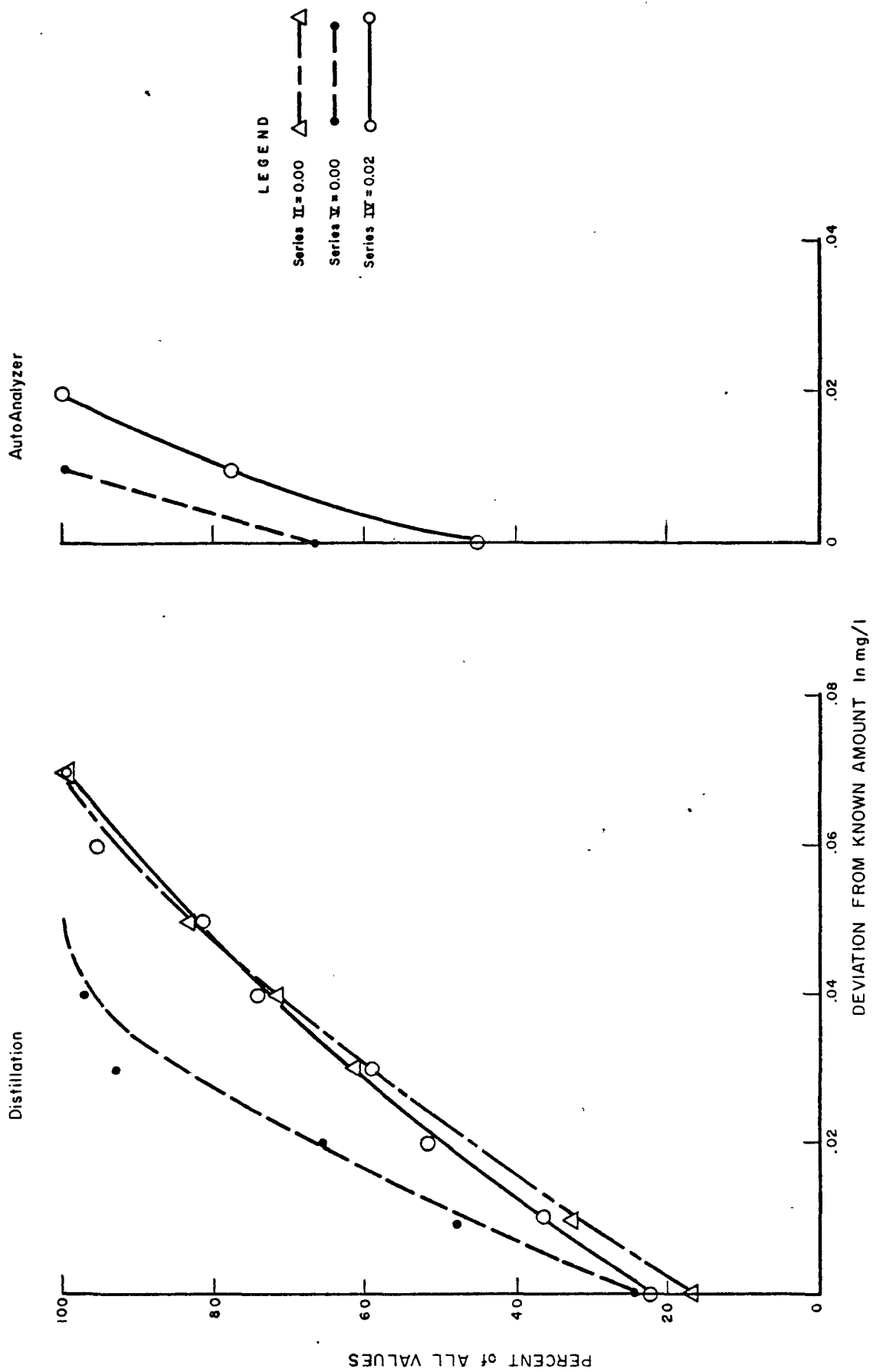
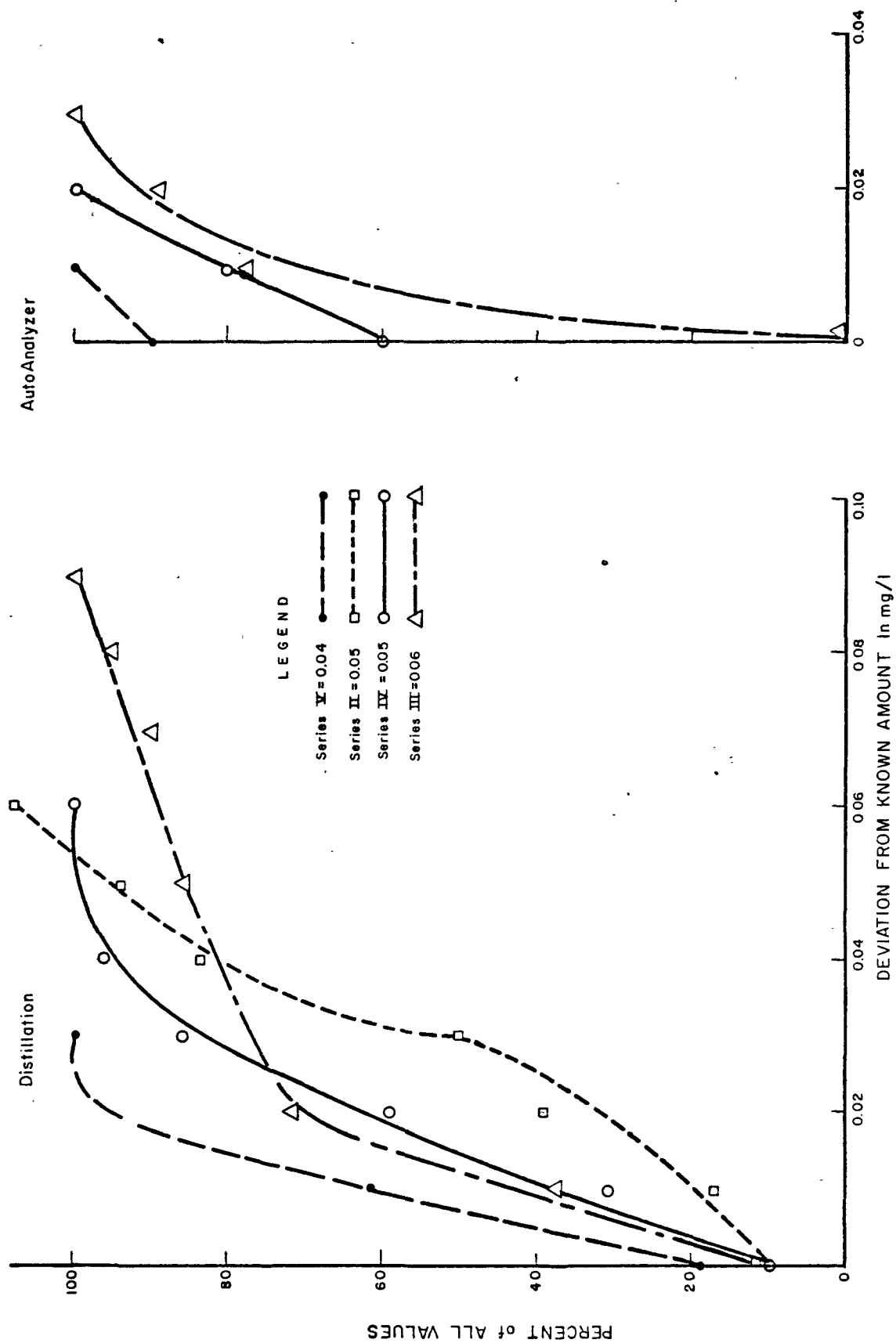
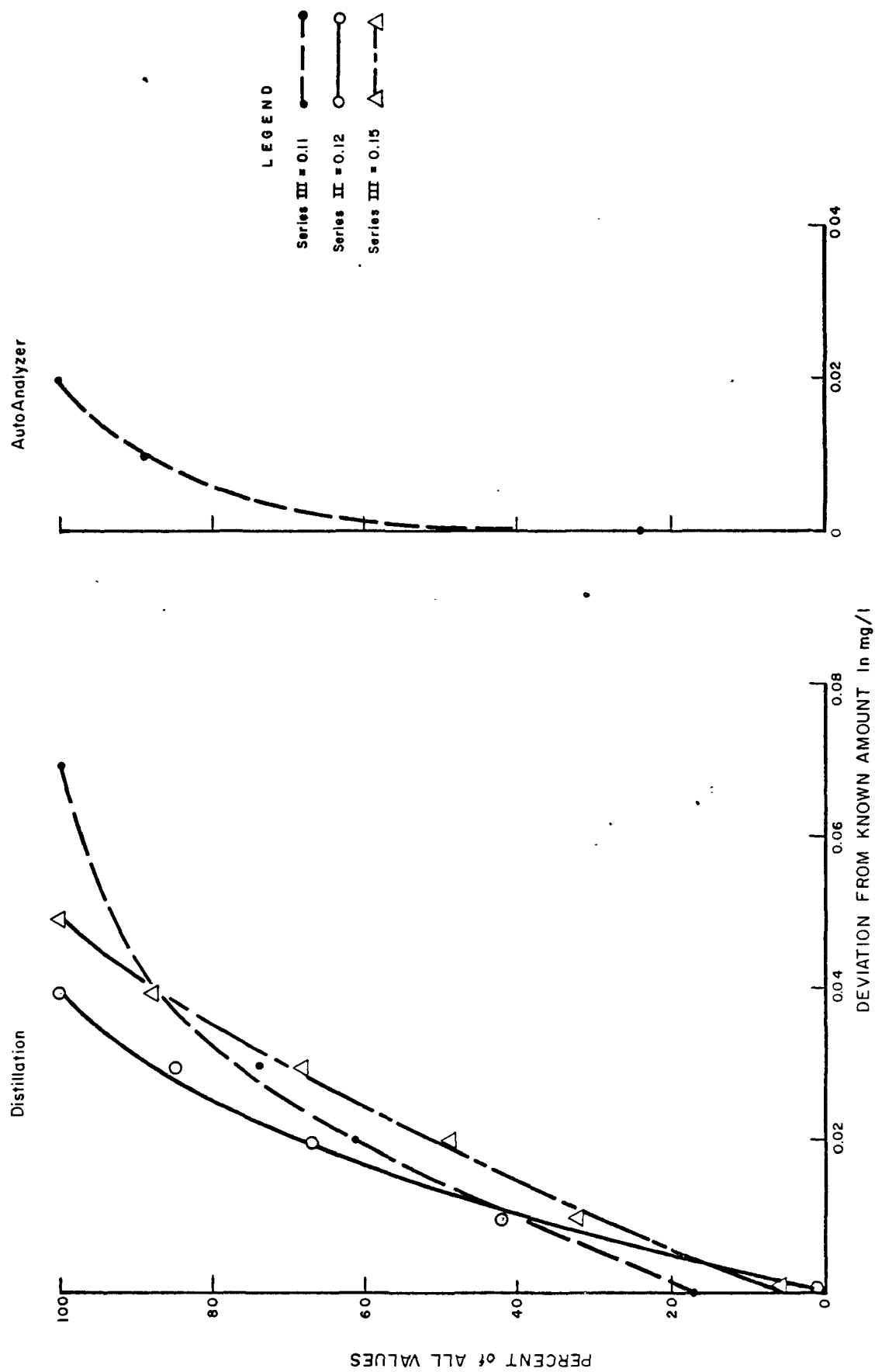


FIGURE 1

CALUMET AREA-LAKE MICHIGAN COMPARISON SAMPLES
Percent Distribution of All Ammonia Nitrogen Determinations, 0.00 and 0.02 mg/l

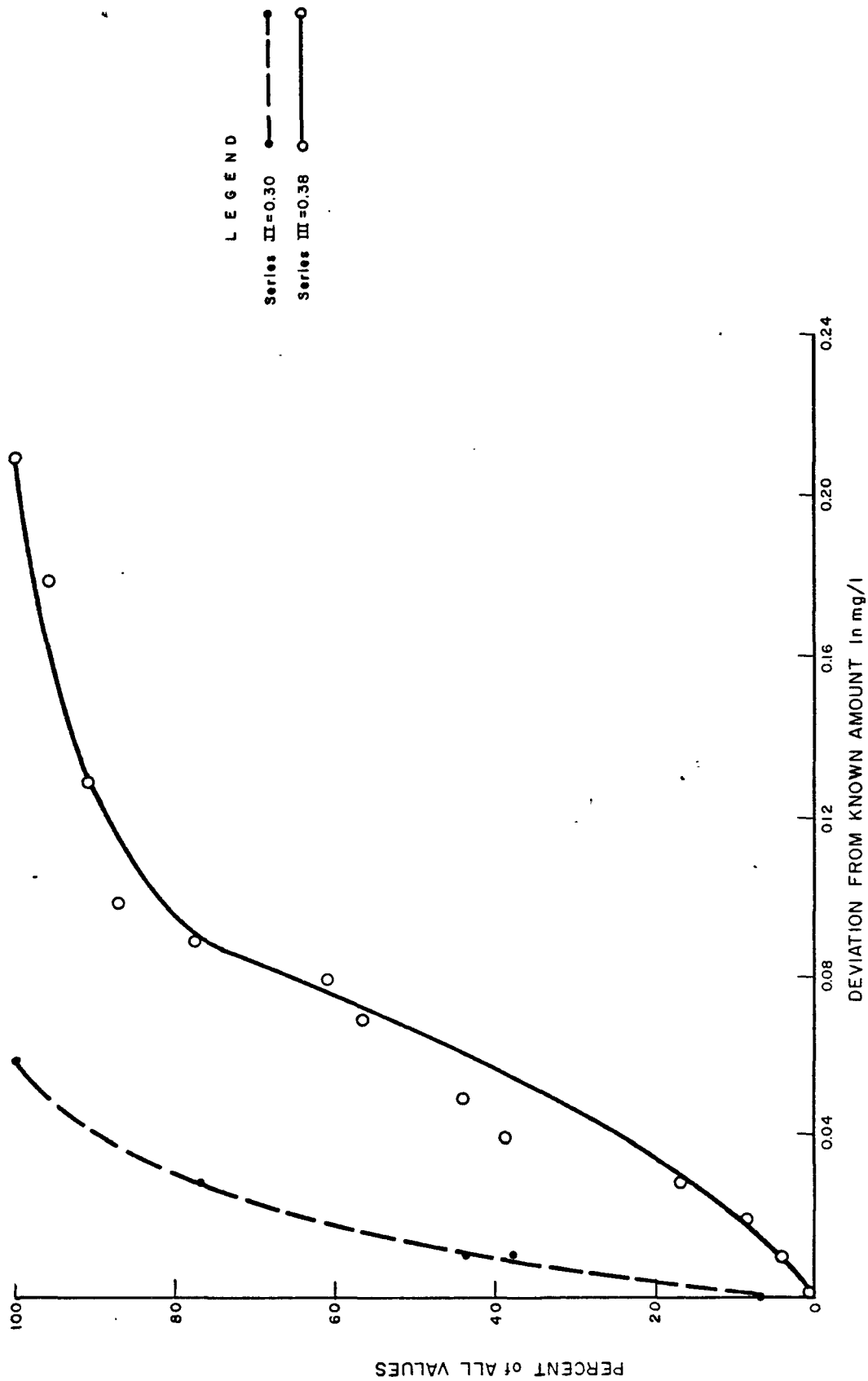


CALUMET AREA-LAKE MICHIGAN COMPARISON SAMPLES
Percent Distribution of All Ammonia Nitrogen Determinations, 0.04, 0.05 and 0.06 mg/l

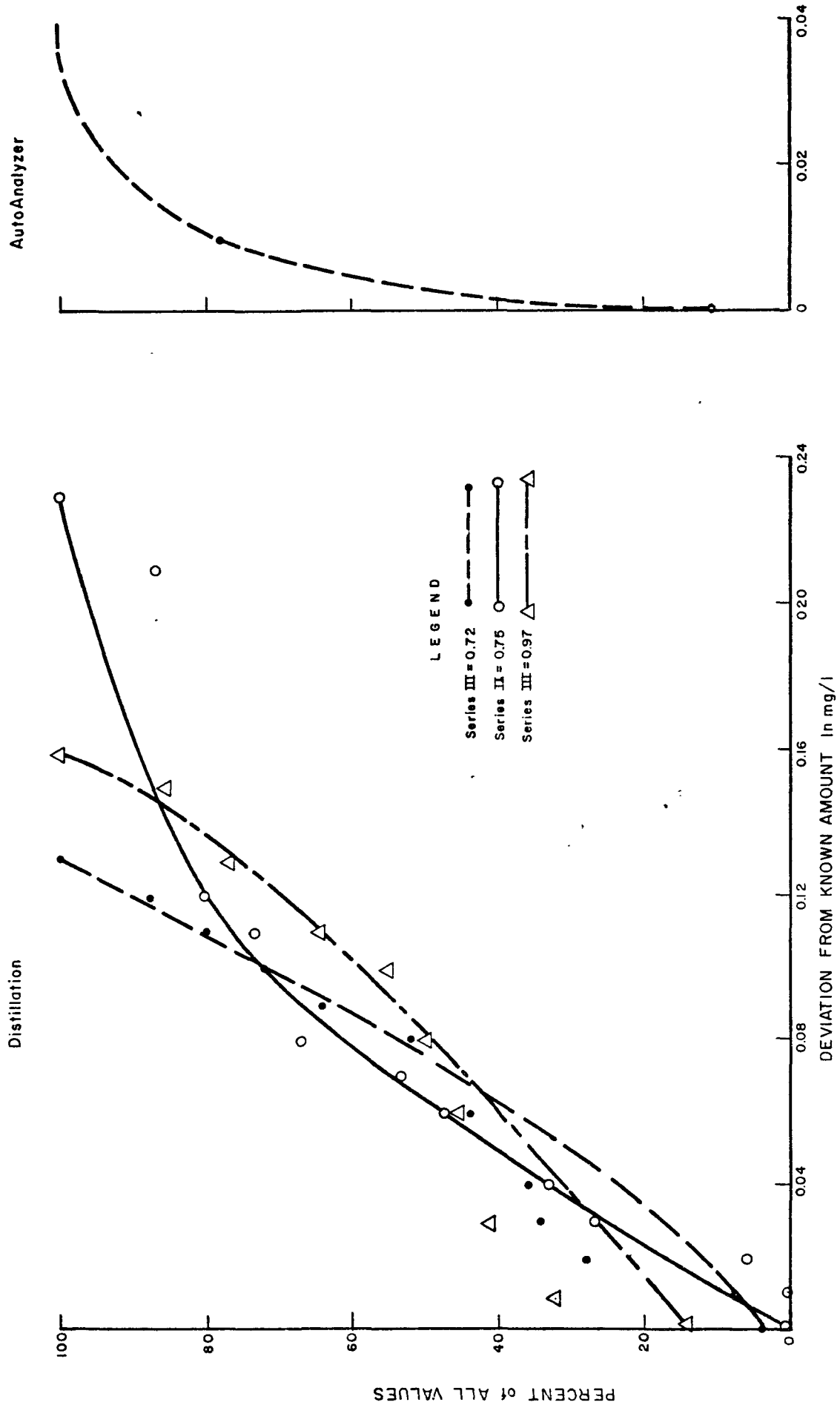


CALUMET AREA-LAKE MICHIGAN COMPARISON SAMPLES

Percent Distribution of All Ammonia Nitrogen Determinations, 0.11, 0.12 and 0.15 mg/l



CALUMET AREA-LAKE MICHIGAN COMPARISON SAMPLES
 Percent Distribution of All Ammonia Nitrogen Determinations, 0.30 and 0.38 mg/l



CALUMET AREA-LAKE MICHIGAN COMPARISON SAMPLES
Percent Distribution of All Ammonia Nitrogen Determinations, 0.72, 0.75 and 0.97 mg/l

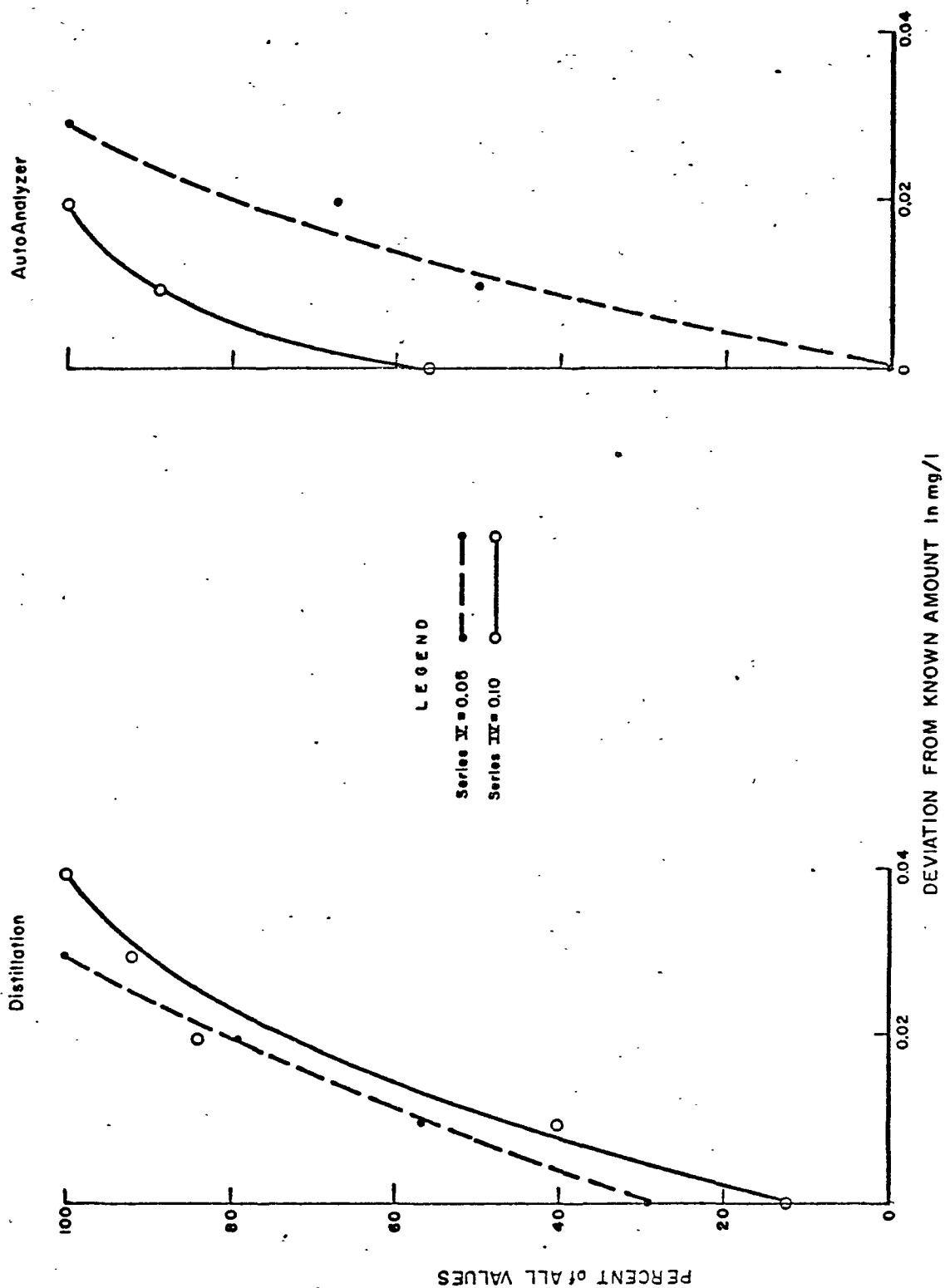
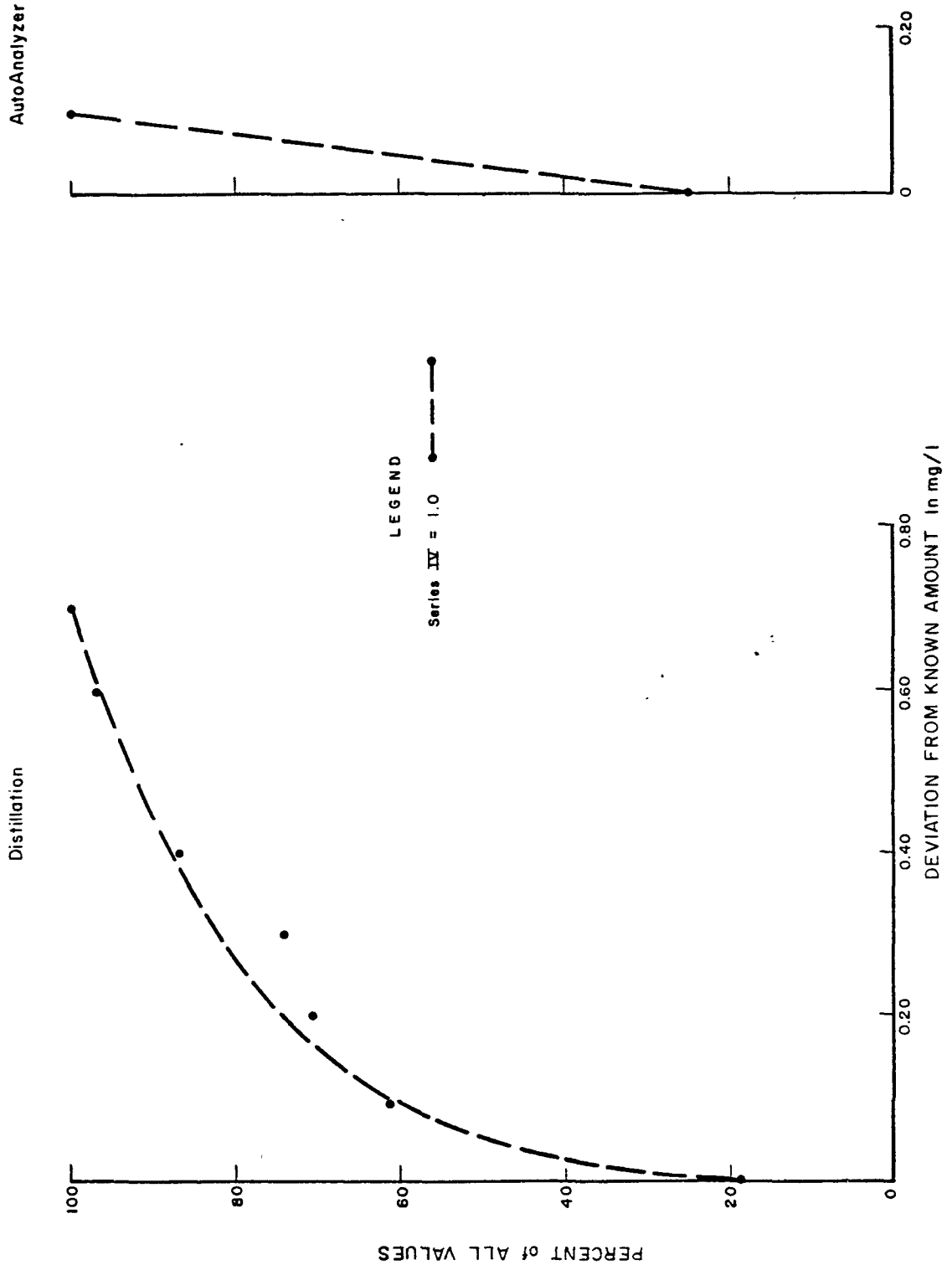


FIGURE 6

CALUMET AREA-LAKE MICHIGAN COMPARISON SAMPLES

Ammonia Nitrogen Recoveries from Spiked Lake Samples by Distillation and Auto Analyzer. 0.5 and 0.10mg/l



CALUMET AREA-LAKE MICHIGAN COMPARISON SAMPLES
Ammonia Nitrogen Recoveries from River Samples by Distillation and AutoAnalyzer 1.0 mg/l

BIBLIOGRAPHY

1. Standard Methods for the Examination of Water and Wastewater, 12th Edition, American Public Health Association, Inc., New York, N.Y., 1965.
2. O'Brien, James E. and Fiore, Janece. "Ammonia Determination by Automatic Analysis." *Wastes Engineering*, July 1962.
3. Jenkins, David. "A Study of Methods Suitable for the Analysis and Preservation of Nitrogen Forms in an Estuarine Environment." SERL Report No. 65-13. U.S. Dept. of Health, Education, and Welfare, Water Pollution Control Administration, San Francisco, California, August 1965.

APPENDIX

ANALYTICAL PROCEDURAL DETAILS FOR THE ANALYSIS OF AMMONIA NITROGEN

The sodium phenate method, using the AutoAnalyzer, is recommended by the authors of this report for the analysis of ammonia nitrogen, as are the methods found in the 12th Edition of Standard Methods for the Examination of Water and Wastewater, in particular the distillation-nesslerization method (pages 186 through 194), with the modifications presented herein.

1. AutoAnalyzer Procedure - Ammonia Nitrogen

Sodium Phenate Method:

Reagents:

1. Alkaline phenol solution: Dissolve 83 g phenol in 200 ml of distilled water at room temperature and add 180 ml of 5-N-sodium hydroxide solution to the phenol solution. Make up the volume to 1000 ml with distilled water and store in an amber bottle; keep in refrigerator when not in use. If the sodium phenate turns dark, discard it.
2. Sodium hypochlorite solution: 5% available chlorine.
3. Sodium nitroprusside, 0.005%: Dissolve 1 g in 100 ml of distilled water. Dilute 5 ml of this solution to 1000 ml with distilled water. Store in refrigerator at 4°C.
4. Standards: Dissolve 3.819 g of ammonium chloride in ammonia-free water, add 0.8 ml conc. H_2SO_4 and make up to 1000 ml. This solution contains 1 mg of nitrogen per ml. Appropriate standards are prepared by diluting this stock solution.

Procedure:

1. Set up the analytical system in accordance with the attached flow diagram. Allow 30 minutes for instrument to warm up and establish a base line using distilled water as the sample.
2. Filter turbid samples through a pledget of cotton or membrane filter, discarding the first 10 ml of filtrate.
3. Arrange five standards, ranging from 0-0.75 mg/l, and samples on the turntable with a single distilled water wash between each sample and standard.
4. There should be a set of standards placed in each row.
5. Set the cycle time at two minutes and the sample time at one minute and 59 seconds.
6. All readings made at a magnification of 2X when the NH_3 -N levels are very low, and at 1X at higher levels.

2. Distillation Procedure - Ammonia Nitrogen

Of all the methods listed in Standard Methods, 12th Edition, the distillation method is preferred for the determination of ammonia nitrogen, in trace or appreciable amounts, especially when interferences of any nature are suspected. The distillates may be titrated* or nesslerized. Nesslerization of the distillate is the method of choice for distillates containing 1 mg or less of ammonia nitrogen. (In the absence of interfering substances, the direct nesslerization method may be used but this method is reserved for samples containing ammonia nitrogen in excess of 0.2 mg/l.)

Nesslerization Method:

Apparatus:

1. All-glass distilling apparatus with 800-2000 ml capacity flask.
2. Spectrophotometer or filter photometer for use at 425 mμ, and providing a light path of 1 cm or longer.
3. Nessler tubes 50 ml tall form.

Reagents:

All reagents prepared in ammonia-free distilled water.

1. Ammonia-free water may be prepared by redistilling distilled water containing 1 ml of concentrated sulfuric acid per liter, or as stated in Standard Methods, p. 189.
2. Phosphate buffer solution, p. 189-190.
3. Stock ammonium solution, p. 190.
4. Standard ammonium solution, p. 190.
5. Neutralization reagent 1.0N sodium hydroxide, p. 190.
6. Neutralization reagent 1.0N sulfuric acid, p. 190.
7. Nessler reagent, p. 190.
8. Rochelle salt solution, p. 194.
9. Sulfuric acid 0.02N, p. 50.
10. Boric acid solution, p. 190.

Procedure:

1. Preparation of equipment: Add 500 ml of distilled water, 10 ml of phosphate buffer solution, and a few boiling chips to a 800 ml flask. Steam out the distillation apparatus until the distillate shows no trace of ammonia, p. 190.
2. Sample preparation: Use 500 ml of sample. Neutralize to a pH of about 6.6 using a pH meter for the measurement. Add 10 ml of the phosphate buffer, mix and check the pH which should now be 7.4. If it is not, add another 10 ml of the buffer solution and again check the pH, p. 190.

* If titration is used, collect in boric acid as given in Standard Methods, p. 191, Sec. 4.4 and p. 404, Sec. 4.3.

Distillation:

Distill over 300 ml into a 500 ml Erlenmeyer flask containing 50 ml of 0.02N sulfuric acid for nesslerization (or 50 ml 2% boric acid if titration is used). Distill at the rate of 6-10 ml/min. Lower the collected distillate free of contact with the delivery tube, and continue distillation during the last minute or two to cleanse the condenser and delivery tube.

Preliminary nesslerization:

Nesslerize a 50 ml portion of the distillate to determine if the concentration of ammonia in the distillate is in the satisfactory reading range for the colorimetric equipment used. For example, for a Spectronic 20 with a 1 inch cell, the satisfactory range is 0.10 to 1.4 mg/l. If the concentration is below 0.10 mg/l, the ammonia in the distillate should be concentrated by boiling. If the ammonia nitrogen is above 1.0 mg/l, the titrimetric method may be employed for measuring the ammonia in the distillate, or by nesslerization of a suitable aliquot.

Concentration of ammonia in the distillate:

Since the distillate is in the presence of acid (0.02N sulfuric acid) it may be boiled with no loss of ammonia.

1. Add boiling chips to the flask and boil on a hot plate to a volume of about 100 or 50 ml depending upon results from the preliminary nesslerization.
2. If the concentration of ammonia is less than 0.10 mg/l, the sample should be concentrated by evaporation. Transfer to 50 ml nessler tubes and bring the volume up to the 50 ml mark with ammonia-free water. The concentration factor in this case is $\frac{500}{50}$ or 10.
3. If the concentration of ammonia nitrogen in the distillate is in the satisfactory range (0.10 to 1.4 mg/l) the concentration factor is $\frac{500}{300 \div 50}$ or 1.43.
4. To each 50 ml sample or aliquot in the nessler tubes, add 1.0 ml of nessler reagent and mix by inverting the tube six times. Allow for color development at least 10 minutes, but not more than 20 minutes if the ammonia nitrogen is very low, but in any event run the samples and the standards the same length of time. Read at 425 mμ wavelength. The occasional formation of cloudiness following nesslerization may be prevented by the use of two drops of Rochelle salt solution (Standard Methods, p. 189).

Preparation of standard curve:

The standard curve should be prepared under the same conditions as the samples. The blank (reagent blank) and the appropriate aliquot of standards - diluted to 500 ml each - are distilled in the same manner as the samples. The 300 ml distillate and 50 ml of 0.02 N sulfuric acid are brought up to the 500 ml volume before taking the 50 ml portion for nesslerization. The phosphate buffer, Rochelle salt solution, and nessler reagent are used as for the samples.

3. Sample Preparation and Collection

Several $\text{NH}_3\text{-N}$ standards were prepared by the Great Lakes-Illinois River Basins Project and Indiana State Board of Health. Standards were prepared from anhydrous ammonium chloride dried at 100°C and dissolved in ammonia-free water. Ammonia-free water was prepared by redistilling distilled water containing sulfuric acid.

Lake samples were collected from the water intakes of the Gary-Hobart Water Corporation and Chicago's Central District Filtration Plant. These samples were collected in three five-gallon carboys and then blended in a small drum or tank in order to obtain a homogeneous sample. One-half gallon samples were drawn off for the 11 laboratories and the remainder of the sample was spiked with the standard $\text{NH}_3\text{-N}$ solution. A second set of 11 half-gallon samples were drawn off for the participating laboratories.

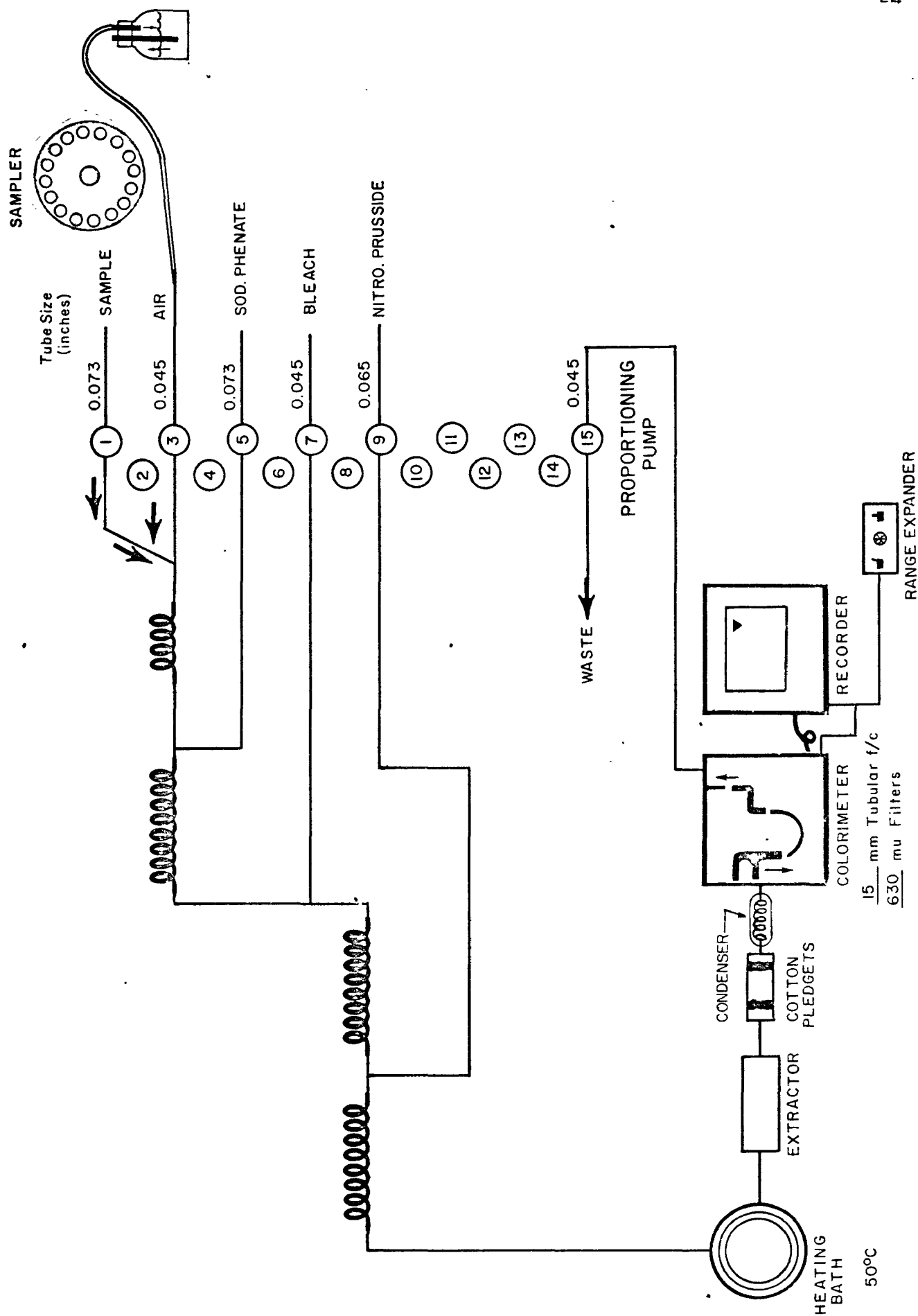
River samples were collected from Indiana Harbor Canal at 151st St. These samples were collected and prepared in the same manner as the lake samples. All samples were preserved with 0.8 ml of conc. H_2SO_4 per liter.

4. Analysis of Data

The data were analyzed according to the method of least squares to obtain one and two standard deviations. A line of best fit was plotted on probability paper. The slope of this line was based on one standard deviation: the mean (or known) value, plus and minus 34 percent, plotted at 16 and 84 percent on the abscissa.

The standard deviations were plotted in relation to the known amount of ammonia nitrogen, or in relation to the mean, in the case of lake and river samples. The standard deviations are indicated by broken lines and the known amounts or means are indicated by a solid line.

Probability curves like those shown in Figures 9-14 were prepared for each individual sample.



CALUMET AREA-LAKE MICHIGAN COMPARISON SAMPLES
AutoAnalyzer Methodology. Ammonia Nitrogen Flow Diagram

50°C

FIGURE 8

Key to Symbols and Abbreviations in the Tabulated Data

*	Data deleted; ()* number of results deleted before final computation
** GRW-P	Gary Raw Water, Preserved
GRW-NP	Gary Raw Water, Not Preserved
SDFP-RW-P	South District Filtration Plant, Raw Water, Preserved
SDFP-RW-NP	South District Filtration Plant, Raw Water, Not Preserved
Lake	Lake Michigan water taken at Gary-Hobart Water Corp. Raw Water Intake
River	Indiana Harbor Canal water taken at 151st St.

TABLE 1a
CALUMET AREA-LAKE MICHIGAN COMPARISON SAMPLES
AMMONIA NITROGEN DETERMINATIONS BY DISTILLATION
Average Results (mg/l)

SERIES II - 10/10/65

Sample	Individual Laboratory Averages						Range	Avg.	No. Results	10 ⁻⁶ - mg/l	
	0.01	0.03	0.00	0.06	0.03	0.05				Prec.	Accuracy
0.00	0.01	0.03	0.00	0.06	0.03	0.05	0.00-0.07	0.03	18 (2)*	0.02	0.04
0.05	0.05	0.07	0.02	0.10	0.09	0.09	0.01-0.11	0.07	18 (2)*	0.03	0.04
0.12		0.13		0.15	0.15	0.13	0.13-0.16	0.14	12 (7)*	0.01	0.02
0.30	0.33	0.28	0.24	0.29	0.31	0.54	0.24-0.33	0.30	13 (5)*	0.03	0.03
0.75	0.85	0.69	0.53	0.69	0.78		0.52-0.87	0.71	15 (5)*	0.11	0.12
**GRW-P	0.03	0.07	0.00	0.08	0.03	0.10	0.00-0.10	0.05	18 (2)*	0.04	
GRW-NP	0.01	0.05	0.00	0.04	0.04	0.09	0.00-0.09	0.04	18 (2)*	0.04	
SDFP-RW-P	0.01	0.04	0.00	0.07	0.10		0.00-0.10	0.04	15 (2)*	0.04	
SDFP-RW-NP	0.03	0.05	0.00	0.05	0.04	0.08	0.00-0.08	0.04	18 (2)*	0.02	
SERIES III - 3/4/66											
0.06	0.05	0.11	0.08	0.05	0.14	0.08	0.04-0.15	0.08	21 (3)*	0.03	0.04
0.11	0.10	0.15	0.11	0.08	0.17	0.13	0.07-0.18	0.12	23 (3)*	0.03	0.03
0.15	0.11	0.18	0.14	0.11	0.18	0.14	0.10-0.20	0.14	19 (3)*	0.03	0.03
0.38	0.47	0.29	0.42	0.36	0.41	0.44	0.28-0.59	0.43	23 (0)*	0.08	0.09
0.72	0.59	0.64	0.62	0.66	0.62	0.74	0.59-0.84	0.68	25 (0)*	0.07	0.09
					0.71	0.75					
0.97	0.81	0.89	0.87	0.97	0.83	0.97	0.81-1.1	0.93	22 (0)*	0.09	0.10

TABLE 1b
CALUMET AREA-LAKE MICHIGAN COMPARISON SAMPLES
AMMONIA NITROGEN DETERMINATIONS BY DISTILLATION
Average Results (mg/l)

Sample	Individual Laboratory Averages										Range	Over- all Avg.	No. Results	15 - mg/l.	
	0.02	0.02	0.08	0.07	0.01	0.01	0.06	0.02	0.03	0.02				Prec.	Accuracy
SERIES IV - 3/23/66															
0.02	0.02	0.02	0.08	0.07	0.01	0.01	0.06	0.02	0.03	0.02	0.00-0.09	0.04	27 (1)*	0.03	0.04
0.05	0.05	0.05	0.08	0.10	0.02	0.03	0.06	0.06	0.03	0.03	0.02-0.11	0.05	29 (0)*	0.03	0.03
Lake	0.05	0.06	0.09	0.13	0.04	0.08	0.08	0.08	0.06	0.06	0.03-0.13	0.08	26 (0)*	0.03	
Lake, Spiked	0.12	0.13	0.18	0.25	0.13	0.19	0.18	0.14	0.14	0.14	0.12-0.29	0.17	27 (0)*	0.04	
River	3.0	3.2	2.4	3.6	2.9	3.2	3.4	3.7	3.1	3.1	1.6-3.9	3.0	31 (0)*	0.57	
River, Spiked	4.0	4.2	3.3	4.8	4.0	4.3	4.0	4.4	4.3	4.3	2.9-4.9	4.0	31 (0)*	0.50	
SERIES V - 4/26/66															
0.00	0.01	0.02	0.03	0.00	0.00	0.01	0.03	0.00	0.04	0.01	0.00-0.05	0.02	29 (0)*	0.01	0.02
0.04	0.04	0.05	0.06	0.02	0.03	0.06	0.06	0.05	0.04	0.06	0.02-0.07	0.05	26 (1)*	0.01	0.02
Lake	0.03	0.03	0.06	0.04	0.02	0.05	0.02	0.06	0.04	0.05	0.02-0.06	0.04	30 (0)*	0.01	
Lake, Spiked	0.07	0.10	0.14	0.07	0.07	0.07	0.09	0.08	0.08	0.07	0.06-0.14	0.09	28 (0)*	0.02	

TABLE 2
CALUMET AREA-LAKE MICHIGAN COMPARISON SAMPLES
AMMONIA NITROGEN DETERMINATIONS BY AUTOANALYZER
Average Results (mg/l)

SERIES III - 3/4/66

Sample	Individual Laboratory Averages			Range	Over- all Avg.	No. Results	10 ⁻⁶ - mg/l.	
							Prec.	Accuracy
0.06	0.07	0.07	0.07	0.07	0.07	9 (0)*	0.01	0.02
0.11	0.12	0.10	0.11	0.09-0.12	0.11	9 (0)*	0.01	0.01
0.72	0.73	0.75	0.73	0.72-0.76	0.73	9 (0)*	0.02	0.02

SERIES IV - 3/23/66

0.02	0.02	0.01	0.03	0.00-0.03	0.02	9 (3)*	0.01	0.01
0.05	0.05	0.07	0.05	0.04-0.07	0.05	10 (2)*	0.01	0.01
**Lake	0.07	0.05	0.06	0.04-0.08	0.06	9 (3)*	0.01	0.01
Lake, Spiked	0.17	0.15	0.16	0.15-0.20	0.17	11 (1)*	0.01	0.01
River	3.2	3.2	3.2	3.2-3.5	3.3	12 (0)*	0.09	0.09
River, Spiked	4.2	4.4	4.3	4.0-4.4	4.3	11 (0)*	0.12	0.12

SERIES V - 4/26/66

0.00	0.01	0.00	0.00	0.00-0.01	0.00	9 (3)*	< 0.01	< 0.01
0.04	0.04	0.04	0.04	0.03-0.04	0.04	10 (1)*	< 0.01	< 0.01
Lake	0.02	0.03	0.05	0.02-0.05	0.04	12 (0)*	0.01	0.01
Lake, Spiked	0.06	0.09	0.07	0.06-0.09	0.07	12 (0)*	0.01	0.01

TABLE 3
CALUMET AREA-LAKE MICHIGAN COMPARISON SAMPLES
AVERAGE RECOVERIES OF AMMONIA NITROGEN BY DISTILLATION (mg/l)

SERIES IV - 3/23/66															
Sample	Individual Laboratory Averages										Range	Over- all Avg.	No. Results	10 ⁻⁶ - mg/l.	
														Prec.	Accuracy
Lake 0.10	0.07	0.09	0.12	0.09	0.11	0.11	0.08	0.10	0.08	0.10	0.06-0.12	0.10	25 (1)*	0.02	0.02
River 1.0	1.0	0.90	1.2	1.1	1.1	0.60	1.0	1.4	0.80	1.2		0.97	31 (0)*	0.29	0.29
SERIES V - 4/26/66															
Lake 0.05	0.05	0.08	0.02	0.05	0.05	0.04	0.07	0.05	0.04	0.04	0.02-0.08	0.05	28 (0)*	0.02	0.02
AVERAGE RECOVERIES OF AMMONIA NITROGEN BY AUTOANALYZER															
SERIES IV - 3/23/66															
Lake 0.10	0.10	0.10	0.10	0.10							0.09-0.12	0.10	9 (2)*	0.01	0.01
River 1.0	1.0	1.1	1.1								1.0-1.1	1.1	8 (3)*	0.05	0.09
SERIES V - 4/26/66															
Lake 0.05	0.04	0.06	0.02	0.02							0.02-0.06	0.04	12 (0)*	0.02	0.02

TABLE 4a
CALUMET AREA-LAKE MICHIGAN COMPARISON SAMPLES
AMMONIA NITROGEN DETERMINATIONS BY DISTILLATION
Original Data (mg/l)

SERIES II - 10/10/65

Sample	Individual Laboratory Results						
	0.00	0.01	0.70*	0.03	0.00	0.07	0.04
0.00	0.00	0.01	0.70*	0.03	0.00	0.04	0.06
		0.01	0.70*	0.03	0.00	0.04	0.05
		0.01		0.03	0.00	0.06	0.05
0.05		0.05	0.77*	0.07	0.02	0.09	0.09
		0.05	0.77*	0.07	0.01	0.09	0.09
		0.06		0.07	0.02	0.11	0.09
0.12		0.03*	0.46*	0.13	0.07*	0.16	0.14
		0.04*	0.41*	0.13	0.06*	0.14	0.13
				0.13	0.07*	0.14	0.13
0.30		0.33	0.65*	0.29	0.24	0.29	0.32
			0.72*	0.28	0.24	0.30	0.31
				0.27	0.24	0.28	0.31
							0.53*
							0.58*
							0.50*
0.75		0.83	1.69*	0.71	0.54	0.72	1.4*
		0.87	1.68*	0.69	0.52	0.69	1.3*
		0.86		0.68	0.52	0.67	1.3*
**GRW-P		0.03	0.23*	0.08	0.00	0.08	0.10
		0.03	0.26*	0.07	0.00	0.08	0.10
		0.03		0.07	0.00	0.09	0.09
GRW-NP		0.01	0.17*	0.06	0.00	0.05	0.09
		0.01	0.22*	0.06	0.01	0.04	0.08
		0.01		0.04	0.00	0.04	0.09
SDFP-RW-P		0.01	0.19*	0.04	0.00	0.07	0.10
		0.01	0.14*	0.04	0.00	0.08	0.10
		0.01		0.04	0.00	0.07	0.09
SDFP-RW-NP		0.03	0.14*	0.06	0.00	0.06	0.04
		0.03	0.12*	0.06	0.00	0.04	0.08
		0.03		0.04	0.00	0.04	0.05
							0.07

TABLE 4b
CALUMET AREA-LAKE MICHIGAN COMPARISON SAMPLES
AMMONIA NITROGEN DETERMINATIONS BY DISTILLATION
Original Data (mg/l)

SERIES III - 3/4/66

Sample	Individual Laboratory Results											
0.06	0.04	0.10	0.07	0.04	0.13	0.08	0.07	0.27*	0.06			
	0.05	0.11	0.08	0.05	0.14	0.08	0.05	0.25*	0.08			
			0.08	0.05	0.15		0.06	0.30*	0.10			
0.11	0.10	0.15	0.10	0.07	0.17	0.13	0.09	0.28*	0.11			
	0.10	0.15	0.11	0.08	0.17	0.12	0.13	0.30*	0.12			
	0.09	0.15	0.11	0.08	0.18		0.09	0.28*	0.11			
0.15	0.11	0.19	0.14	0.10	0.17	0.14	0.13	0.38*				
	0.10	0.16	0.14	0.12	0.18	0.14	0.14	0.37*				
	0.12		0.15	0.11	0.20		0.12	0.37*				
0.38	0.46	0.28	0.42	0.34	0.40	0.45	0.59	0.51				
	0.47	0.29	0.41	0.34	0.41	0.43	0.45	0.45				
	0.48	0.30	0.42	0.39	0.42		0.56	0.47				
0.72	0.59	0.63	0.62	0.66	0.60	0.74	0.70	0.80	0.70	0.75		
	0.59	0.64	0.62	0.63	0.61	0.73	0.70	0.82	0.72			
	0.59		0.61	0.68	0.66		0.70	0.84				
0.97	0.81	0.91	0.86	0.97	0.82	0.97	0.96	1.0				
	0.81	0.87	0.86	0.98	0.82	0.97	0.96	1.1				
	0.81		0.89	0.96	0.84		1.0	1.1				

TABLE 4c
CALUMET AREA-LAKE MICHIGAN COMPARISON SAMPLES
AMMONIA NITROGEN DETERMINATIONS BY DISTILLATION
Original Data (mg/l)

SERIES IV - 3/23/66

Sample	Individual Laboratory Results												
	0.02	0.02	0.08	0.06	0.00	0.02	0.07	0.02	0.01	0.08	0.06	0.02	0.02
0.02	0.02	0.02	0.08	0.07	0.01	0.06	0.06	0.02	0.04	0.13*	0.04	0.06	0.04
0.05	0.05	0.05	0.08	0.09	0.02	0.03	0.07	0.03	0.04	0.03	0.09	0.03	0.03
	0.05	0.05	0.08	0.11	0.02	0.03	0.06	0.03	0.04	0.06	0.08	0.08	0.08
	0.08	0.08	0.08	0.06	0.02	0.04	0.06	0.03	0.05	0.09	0.02	0.02	0.02
Lake	0.05	0.05	0.09	0.13	0.04	0.08	0.07	0.06	0.06	0.09	0.09	0.06	0.06
	0.05	0.05	0.09	0.13	0.03	0.08	0.09	0.09	0.05	0.08	0.09	0.09	0.09
	0.06	0.06	0.09		0.04	0.08	0.07			0.05	0.09		
Lake, Spiked	0.12	0.12	0.18	0.25	0.12	0.18	0.19	0.13	0.13	0.21	0.29	0.14	0.14
	0.12	0.12	0.18	0.25	0.13	0.20	0.18	0.13	0.13	0.16	0.19		
	0.12	0.12	0.17		0.13	0.20	0.18	0.14	0.14	0.16	0.18		
River	3.0	3.0	2.4	3.6	2.9	3.2	3.5	3.3	1.6	3.1	3.5	3.1	3.1
	3.0	3.0	2.4	3.8	2.9	3.2	3.0	3.2	1.6	2.9	3.9		
	2.9	2.9	2.4	3.4	2.9	3.2	3.6	3.2	1.8	2.9	3.8		
River, Spiked	4.0	3.9	3.3	5.0	4.0	4.3	3.9	4.2	2.9	3.7	4.1	4.3	4.3
	3.9	3.9	3.3	4.9	4.0	4.3	4.0	4.2	3.3	3.8	4.3		
	4.0	4.0	3.2	4.4	4.0	4.2	4.0	4.3	3.2	3.7	4.9		

TABLE 4d
CALUMET AREA-LAKE MICHIGAN COMPARISON SAMPLES
AMMONIA NITROGEN DETERMINATIONS BY DISTILLATION
Original Data (mg/l)

SERIES V - 4/26/66

Sample	Individual Laboratory Results												
	0.01	0.02	0.00	0.00	0.01	0.03	0.03	0.03	0.04	0.01	0.03	0.01	0.01
0.00	0.01	0.02	0.00	0.00	0.01	0.03	0.03	0.03	0.04	0.01	0.03	0.03	0.01
	0.01	0.03	0.00	0.00	0.00	0.03	0.03	0.02	0.02	0.01	0.03	0.03	0.01
		0.03	0.00	0.00	0.01	0.03	0.03	0.02	0.02		0.05		
0.04	0.04	0.06	0.02	0.03	0.06	0.06	0.06	0.05	0.05	0.06	0.05	0.04	0.04
	0.04	0.07	0.03	0.03	0.06	0.06	0.06	0.05	0.05	0.11*	0.05	0.05	
		0.06	0.02	0.03	0.05				0.04		0.04		
Lake	0.02	0.06	0.05	0.02	0.02	0.05	0.05	0.03	0.03	0.05	0.06	0.06	0.04
	0.03	0.06	0.04	0.02	0.02	0.05	0.05	0.03	0.05	0.03	0.06	0.06	
		0.05	0.04	0.02	0.02	0.04	0.04	0.04	0.04	0.02	0.05	0.05	
Lake, Spiked	0.07	0.14	0.07	0.07	0.07	0.09	0.09	0.09	0.09	0.08	0.09	0.09	0.08
	0.07	0.14	0.06	0.07	0.07	0.09	0.09	0.10	0.08	0.07	0.09	0.09	
		0.13	0.07	0.07	0.07	0.09	0.09		0.10		0.07	0.07	

TABLE 6
CALUMET-AREA-LAKE MICHIGAN COMPARISON SAMPLES
AMMONIA NITROGEN RECOVERIES BY DISTILLATION
Original Data (mg/l)

SERIES IV - 3/23/66		Individual Laboratory Recoveries									
Sample		0.07	0.09	0.12	0.08	0.10	0.12	0.07	0.12	0.08	0.20*
0.10 Lake		0.06	0.09	0.12	0.10	0.12	0.09	0.08	0.08	0.10	0.09
1.0 River		1.0	0.90	1.4	1.1	1.1	1.0	1.3	0.60	1.2	0.60
		0.90	0.90	1.1	1.1	1.1	1.0	1.7	0.90	0.40	0.40
		1.1	0.80	1.0	1.1	1.0	0.40	1.1	0.80	1.1	1.1
SERIES V - 4/26/66											
0.05		0.05	0.08	0.02	0.05	0.05	0.04	0.06	0.03	0.04	0.03
		0.04	0.08	0.02	0.05	0.05	0.04	0.07	0.03	0.04	0.03
		0.08	0.08	0.03	0.05	0.05	0.05	0.06	0.02		0.02
SERIES IV - 3/23/66		AMMONIA NITROGEN RECOVERIES BY AUTOANALYZER									
0.10 Lake		0.10	0.09	0.10	0.00*						
		0.11	0.10	0.10	0.16*						
		0.09	0.12	0.10							
1.0 River		1.1	1.1	1.1	0.70*						
		1.0	1.1	1.1	0.80*						
		1.0	1.1	1.1	0.70*						
SERIES V - 4/26/66											
0.05 Lake		0.04	0.06	0.02	0.03						
		0.04	0.06	0.03	0.02						
		0.04	0.06	0.02	0.02						

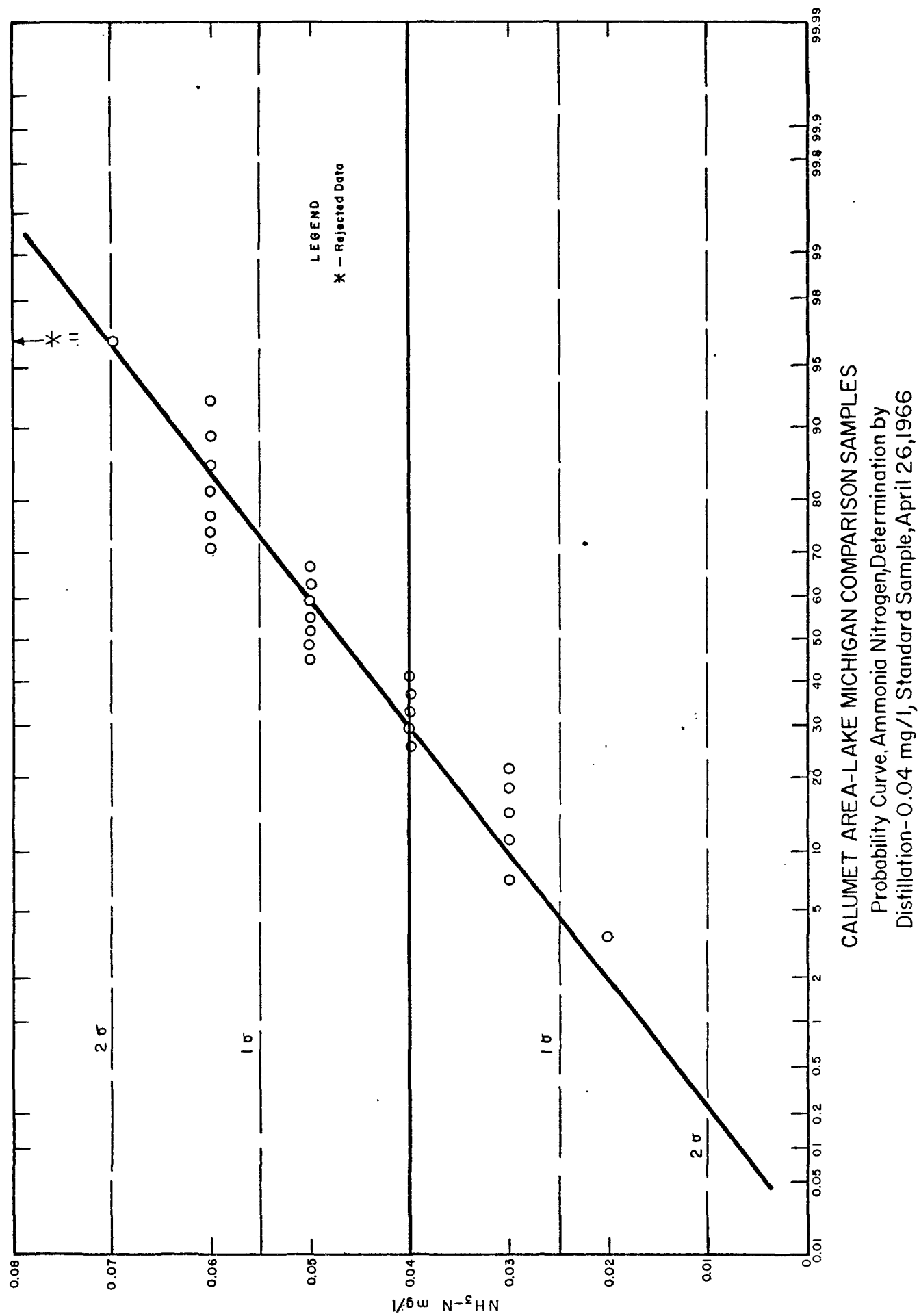
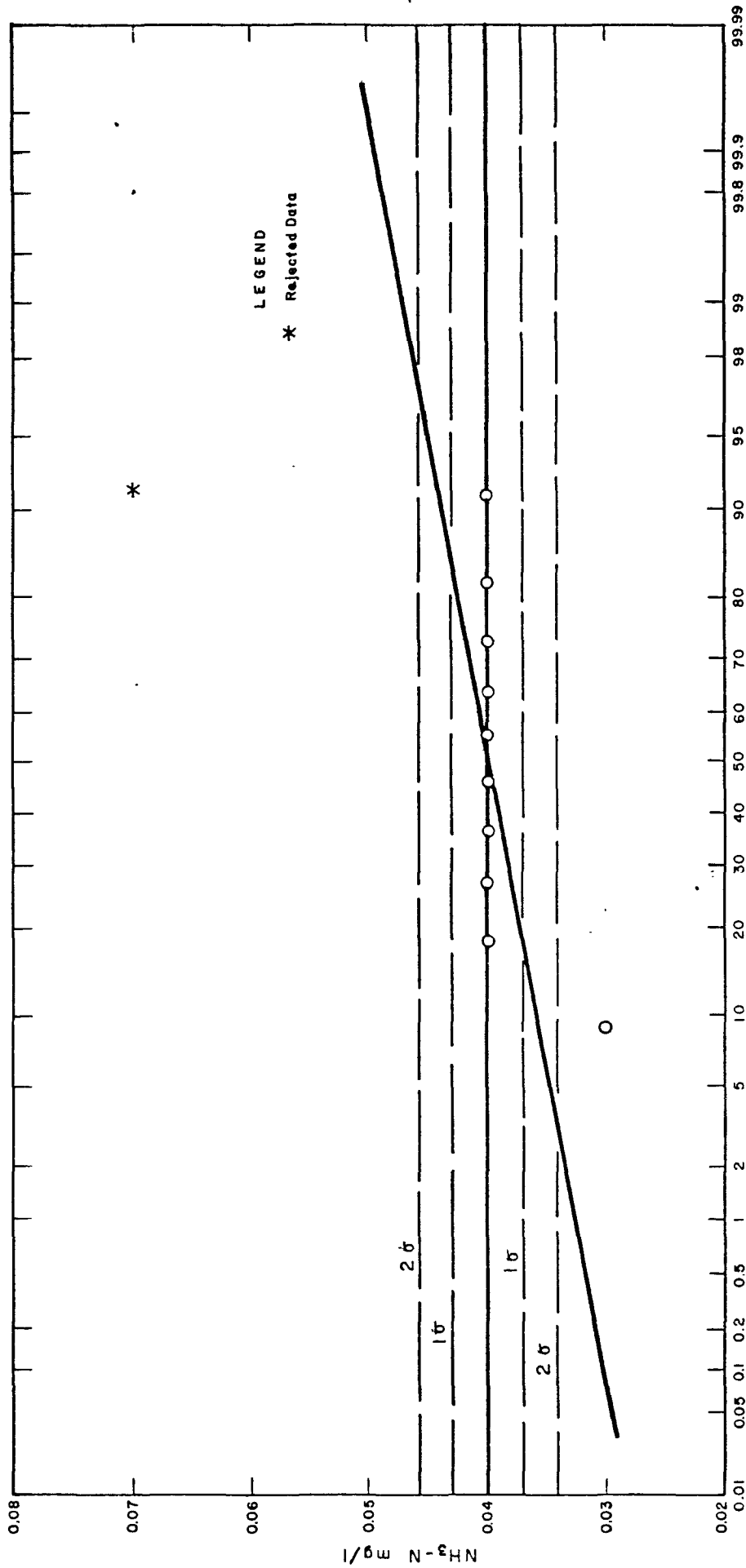
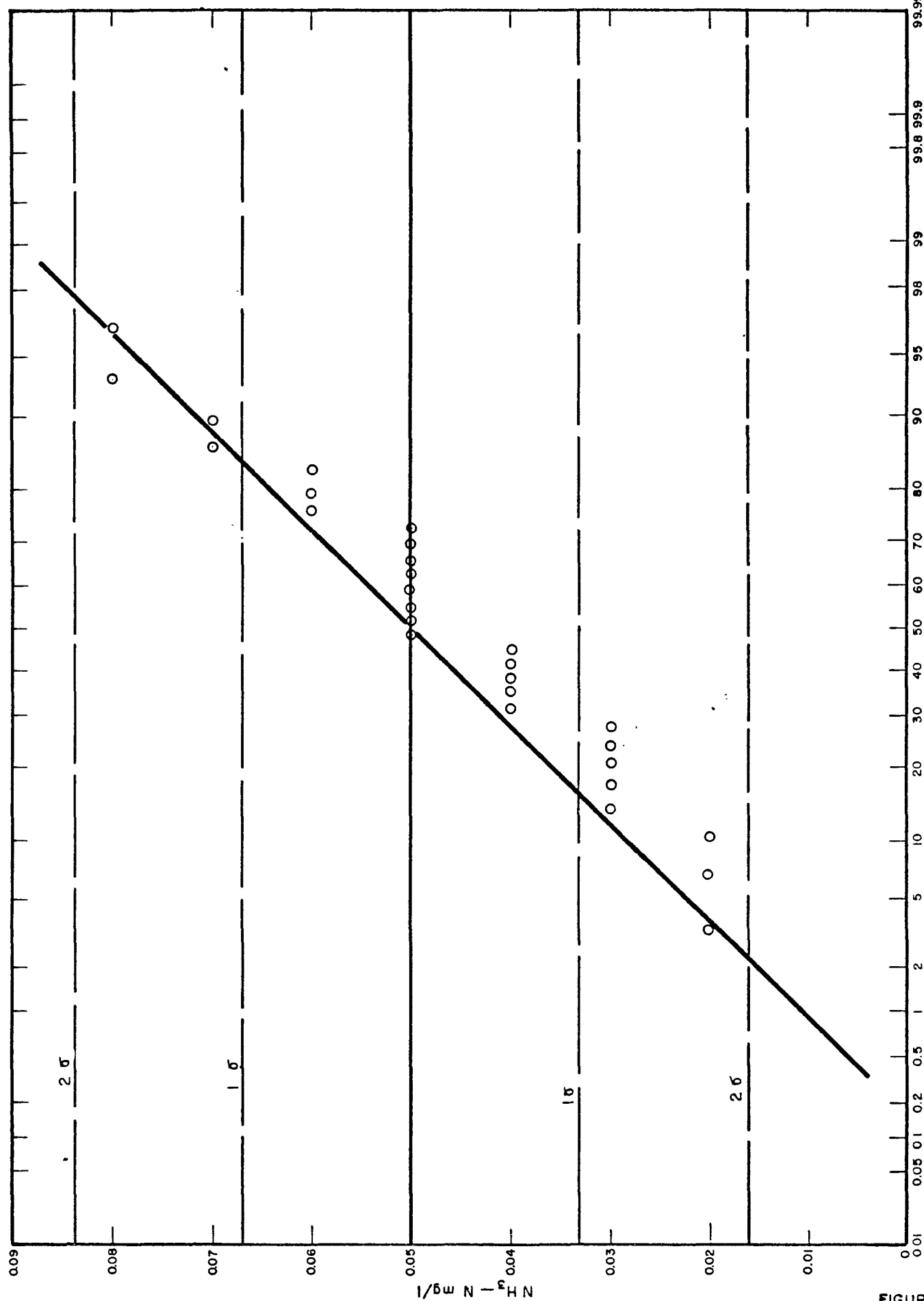


FIGURE 9

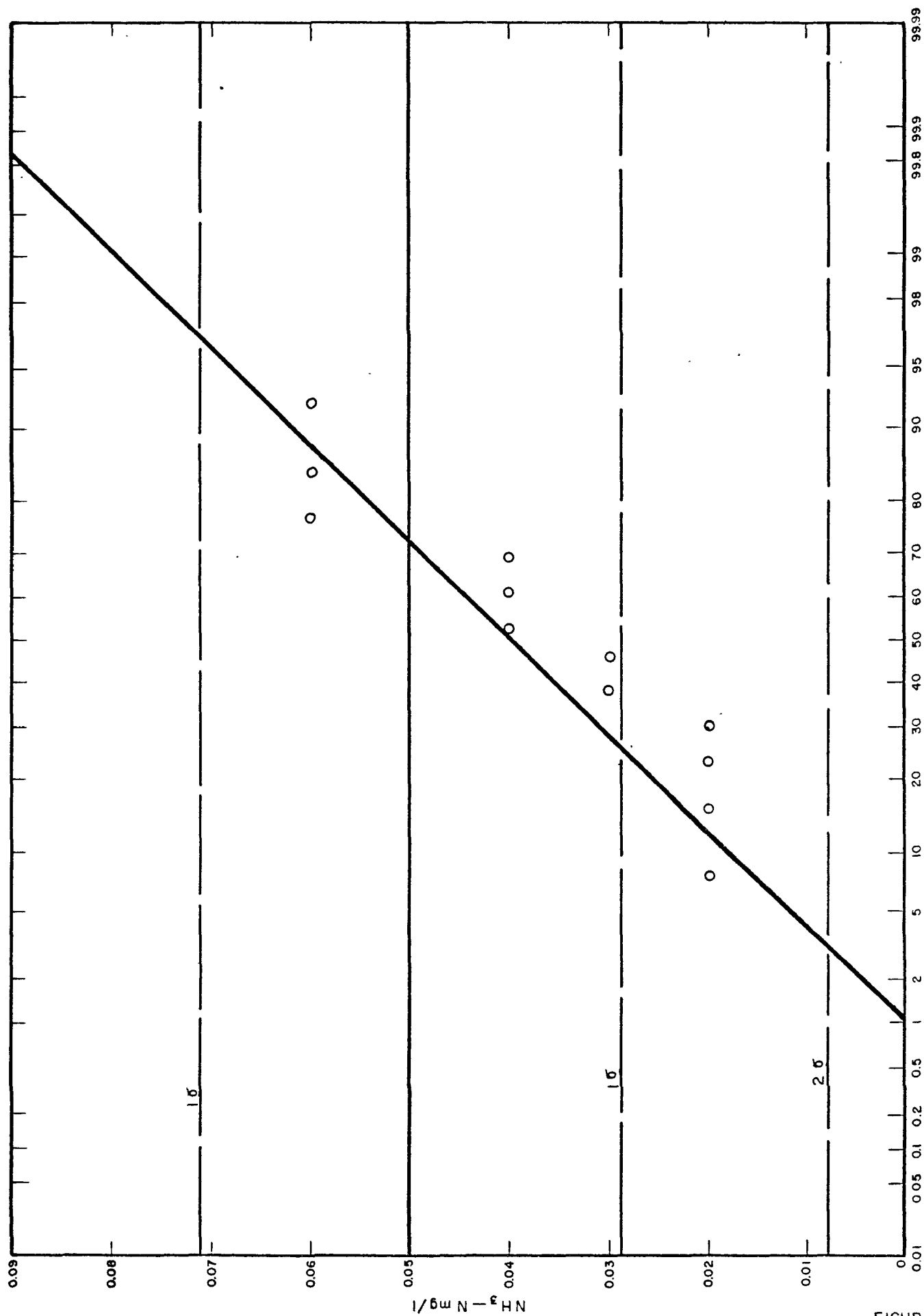


CALUMET AREA-LAKE MICHIGAN COMPARISON SAMPLES
Probability Curve. Ammonia Nitrogen Determination by
Auto Analyzer - 0.04 mg/l Standard Sample, April 26, 1966



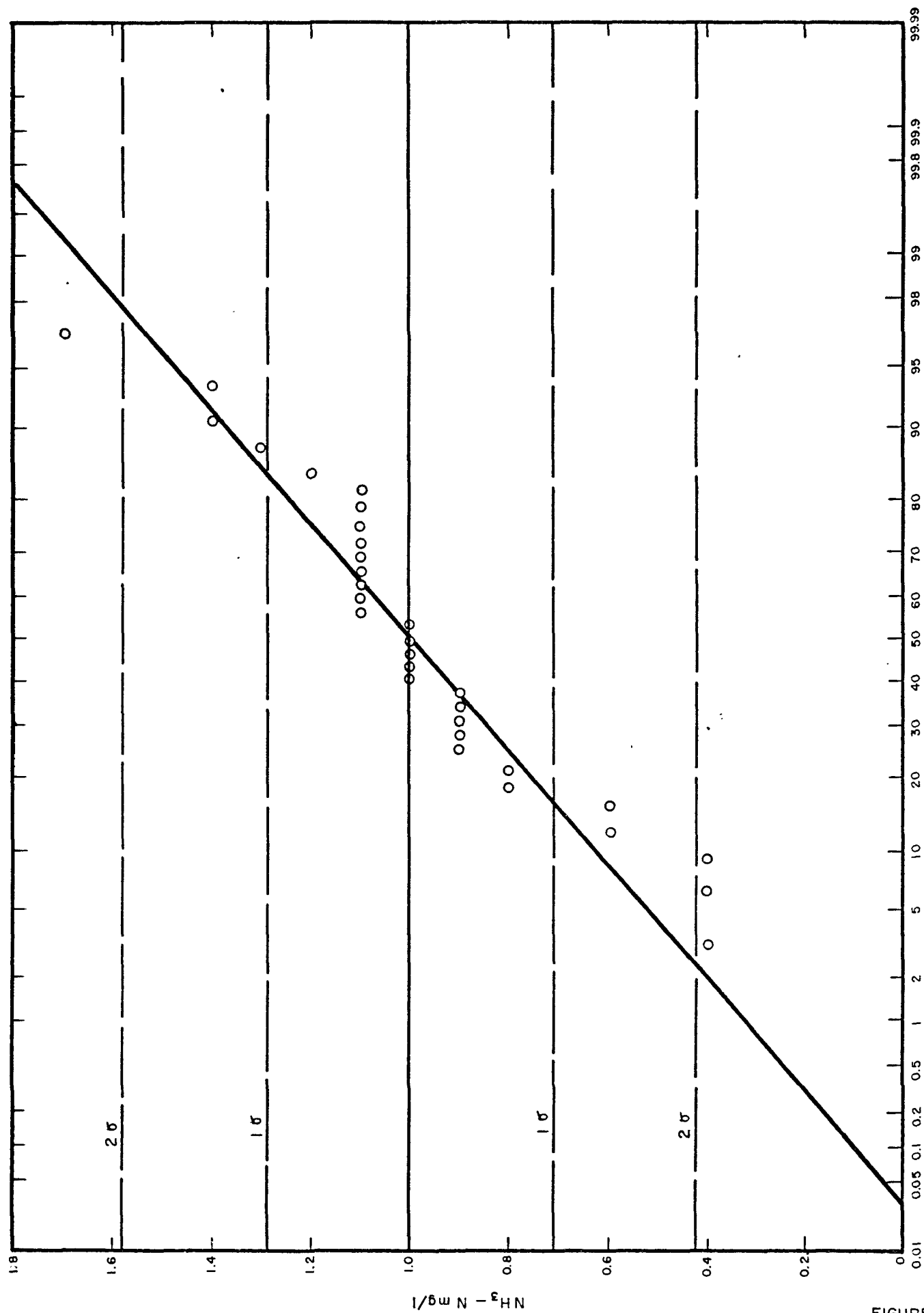
CALUMET AREA-LAKE MICHIGAN COMPARISON SAMPLES
Probability Curve. Recovery of Ammonia Nitrogen, Determination
by Distillation - 0.05 mg/l, April 26, 1966

FIGURE 11



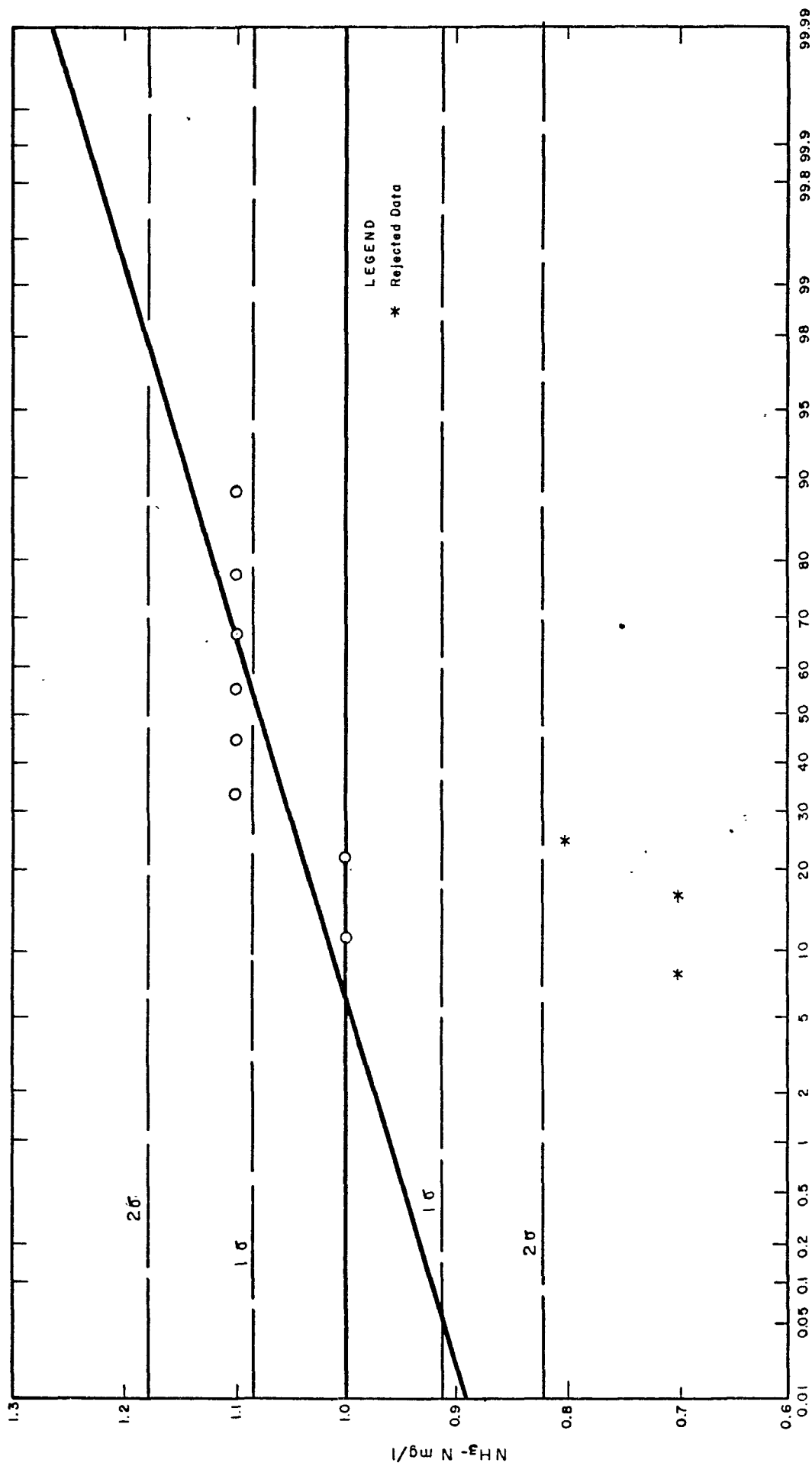
CALUMET AREA-LAKE MICHIGAN COMPARISON SAMPLES
 Probability Curve. Recovery of Ammonia Nitrogen, Determination
 by AutoAnalyzer -0.05 mg/l, April 26, 1966

FIGURE 12



CALUMET AREA-LAKE MICHIGAN COMPARISON SAMPLES
Probability Curve. Recovery of Ammonia Nitrogen, Determination
by Distillation-1.0mg/l, March 23, 1966

FIGURE 13



CALUMET AREA-LAKE MICHIGAN COMPARISON SAMPLES
 Probability Curve Recovery of Ammonia Nitrogen, Determination by
 Auto Analyzer - 1.0 mg/l, March 23, 1966

FIGURE 14

