Dr. J. Knauss

INTERNATIONAL COUNCIL OF
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WORLD METEOROLOGICAL
ORGANIZATION

THE GARP ATLANTIC TROPICAL EXPERIMENT (GATE)

REPORT ON

SALINITY INTERCOMPARISON

GENEVA, FEBRUARY 1976

PREFACE

This report is the final product of a cooperative intercomparison programme between countries making GATE oceanographic measurements. Water samples were distributed to the participating countries before the GATE Experiment with the request that analyses be made before and after the Experiment using identical instruments and procedures as in the routine sea water analysis. The results were collected by the National Oceanographic Instrumentation Center (NOIC) in the United States for analysis and intercomparison.

In order to aid the widespread usefulness of this report on international intercomparison, the GARP Activities Office has agreed to distribute these results among the national participants in the GATE. I would like to thank Robert J. Farland of the NOIC for the preparation of this report.

David R. Rodenhuis

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GARP Activities Office
World Meteorological Organization

SALINITY INTERCOMPARISON REPORT

* * *

The Oceanographic Sub-Programme

for the

GARP Atlantic Tropical Experiment (GATE)

Robert J. Farland

National Oceanographic Instrumentation Center

Washington, D. C.

November 1975

GARP Activities Office
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CH-1211 Geneva 20
Switzerland

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the GARP Atlantic Tropical Experiment (GATE)

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ABSTRACT. Various valued salinity samples were provided by the National Oceanographic Instrumentation Center (NOIC) to 31 oceanographic vessels participating in the GARP Atlantic Tropical Experiment (GATE) during the summer of 1974. Intercomparison of the sample measurements by these vessels are to be used to evaluate the validity of the GATE salinity data prior to extensive scientific analysis. All the resultant measurements are referenced to NOIC's precision conductivity comparator standard. The intercomparison data revealed that vessels using the titration method had a standard deviation of 23.3 ppm, while those vessels with the inductive salinometers (non-thermostated type) gave a standard deviation of 11.2 ppm. Some vessels used thermostated type salinometers and the standard deviation for the data was 2.3 ppm. The data uncertainty level for the intercomparison project was set at ± 10 ppm over a salinity range of 32 to 38 ppt. Repetitions of measurements are required to establish a more meaningful representation of the quality of the GATE data.

I. INTRODUCTION

Measurements of salinity during the 1974 GARP Atlantic Tropical Experiment (GATE) were obtained from many oceanographic vessels representing several countries using various types of instruments and methods. To evaluate the validity of these measurements, prior to extensive analysis of the GATE data, an intercomparison project was instituted with a goal for the data variance from a standard to be within ± 10 ppm. The project provided at least two sets, X and Y, of various valued salt water samples (Table 1), prepared by the National Oceanographic Instrumentation Center (NOIC), to 31 GATE oceanographic vessels (Table 2), with salinometers or titration equipment (Table 3).

TABLE 1. Salt water sample sets and nominalize salinity values.

X Set		Y Set	
SAMPLE NUMBER	NOMINAL SALINITY(ppt)	SAMPLE NUMBER	NOMINAL SALINITY(ppt)
X01 _ _	38.0	Y07 _ _	38.0
X02 _ _	36.5	Y08 _ _	36.5
X03 _ _	35.0	Y09 _ _	35.0
X04 _ _	33.5	Y10 _ _	33.5
X05 _ _	32.0	Y11 _ _	32.0
X06 _ _	36.5	Y12 _ _	33.5

TABLE 2. Salt water sample sets distributed to GATE vessels.

COUNTRY	VESSEL	SETS	DATA RECEIVED
Brazil	SIRIUS SALDANHA	4 4	No Yes
Canada	QUADRA	4	Yes
France	CAPRICORNE CHARCOT	2 6	Yes Yes
F.R.G.	ANTON DOHRN METEOR	2 2	(1.) (1.)
G.D.R.	VON HUMBOLDT	2	Yes
Mexico	MATAMOROS	4	No
Netherlands	ONVERSAAGD	4	Yes
United Kingdom	DISCOVERY	4	Yes

TABLE 2. (Continued)

COUNTRY	VESSEL	SETS	DATA RECEIVED
U.S.A.	ATLANTIS II	4	Yes
	DALLAS	4	Yes
	H.J.W. FAY	2	Yes
	GILLISS	4	Yes
	OCEANOGRAPHER	6	Yes
	RESEARCHER	4	Yes
	TRIDENT	2	Yes
U.S.S.R.	DEZHNEV	2	Yes
	KOROLOV	4	Yes
	KRENKEL	4	Yes
	KURCHATOV	2	Yes
	LOMONOSOV	2	Yes
	MUSSON	4	Yes
	OCEAN	4	Yes
	PASSAT	2	Yes
	PORYV	6	Yes
	PRIBOY	4	Yes
	VIZE	4	No
	VOLNA	4	No
	ZUBOV	2	No
TOTALS: 10	31	108	

(1.) A data sheet was received from F.R.G. marked: METEOR PLANET DOHRN. Which vessel measured the sets was not identified.

(**)

TABLE 3. Salinity measuring equipment used in GATE intercomparison.

MANUFACTURER	MODEL	TYPE
NOIC	PCC	Inductive-thermostated
Beckman	RS-7B&C	Inductive-nonthermostated
Plessey	6230	Inductive-nonthermostated
Auto Laboratory	601MKIII	Inductive-nonthermostated
Hydrometpribor	GM65	Inductive-nonthermostated
Guildline	8400	Electrode-thermostated
Woods Hole	3	Electrode-thermostated

(**) **NOTE by GARP Activities Office: All samples from these FRG ships were analyzed by equipment in laboratories at Kiel.**

Each vessel was instructed to determine the salinity of one set of samples before the start of a GATE phase and the other set at the conclusion of a phase. The resultant data were recorded on data sheets (Example 1) which were transmitted to NOIC.

The nominal salinity values were repeated once in each set. For example, in the X set samples, the value 36.5 ppt was repeated and in Y set the value 33.5 ppt was repeated. Also each set had a sample with a nominal value of 35.0 ppt. It was assumed that each participating vessel would standardize their equipment by using a standard sea water of 35.0 ppt. This scheme, therefore, provided repeatability data at two points for each set during the intercomparison measurements: 36.5 and 35.0 for the X set and 33.5 and 35.0 for the Y set.

All the water samples (more than 950) were initially measured by NOIC utilizing its salinity reference standard system as the designated standard for this project. Approximately 25 percent of these samples were randomly selected and retained at NOIC to be measured for quality assurance monitoring purposes. The measurement schedule was designed to be carried out before, during and after the at sea portion of GATE. Also, several of these samples were measured by other national and international laboratories, recognized for their quality salinity measuring capabilities. The resultant data provided a quality control check on the performance of the NOIC salinity standard. The overall flow of the various intercomparison salinity measurements for GATE is shown in Chart 1.

II. INTERCOMPARISON REFERENCE STANDARDS

Several standards were referenced throughout the salinity intercomparison project. In all of NOIC's measurements, the traceable chain was from its instrumental standard, the Precision Conductivity Comparator (PCC), to I.A.P.S.O. standard sea water and eventually the Unesco oceanographic tables for the final salinity readings.

The PCC is a self-contained thermostated system, that compares the conductivity ratio of an unknown sample with that of a known reference standard. The conductivity measuring circuit consists of an oscillator, a precision ratio transformer, a null detector and six conductivity cells, each 40 cc, one cell being used for the standard water, and the other five for the water under test. The cells are fabricated in quartz and immersed in a 26.5 litre temperature-controlled oil bath. A specially adapted inductive bridge is employed with a platinum thermometer in the bath, to monitor the temperature stability of oil surrounding the cells to

INTERCALIBRATION
(INCAL)

EXAMPLE 1

SALINITY DATA SHEET

1. PROGRAM NAME

2. PARTICIPANT'S ORGANIZATIONAL NAME

COUNTRY	VESSEL	MEASURER'S NAME

3. TYPE OF SALINITY MEASUREMENT (CHECK ONE)
   - ☐ INDUCTIVE SALINOMETER
   - ☐ OTHER
   - ☐ TITRATION (METHOD & EQUIPMENT) ______

4. INSTRUMENT MANUFACTURER

MODEL NUMBER	SERIAL OR IDENTITY NUMBER

5. STANDARD FOR SALINITY MEASUREMENT (CHECK ONE)

☐ IAPSO STANDARD SEA WATER	BATCH NUMBER	DATE

☐ OTHER (EXPLAIN)

6. TABLE OR EQUATION USED TO COMPUTE SALINITY (CHECK ONE)
   - ☐ INTERNATIONAL OCEANOGRAPHIC TABLES (UNESCO)
   - ☐ OTHER (EXPLAIN) ______

7. SALINITY DATA

GROUP X — MEASUREMENT DATE

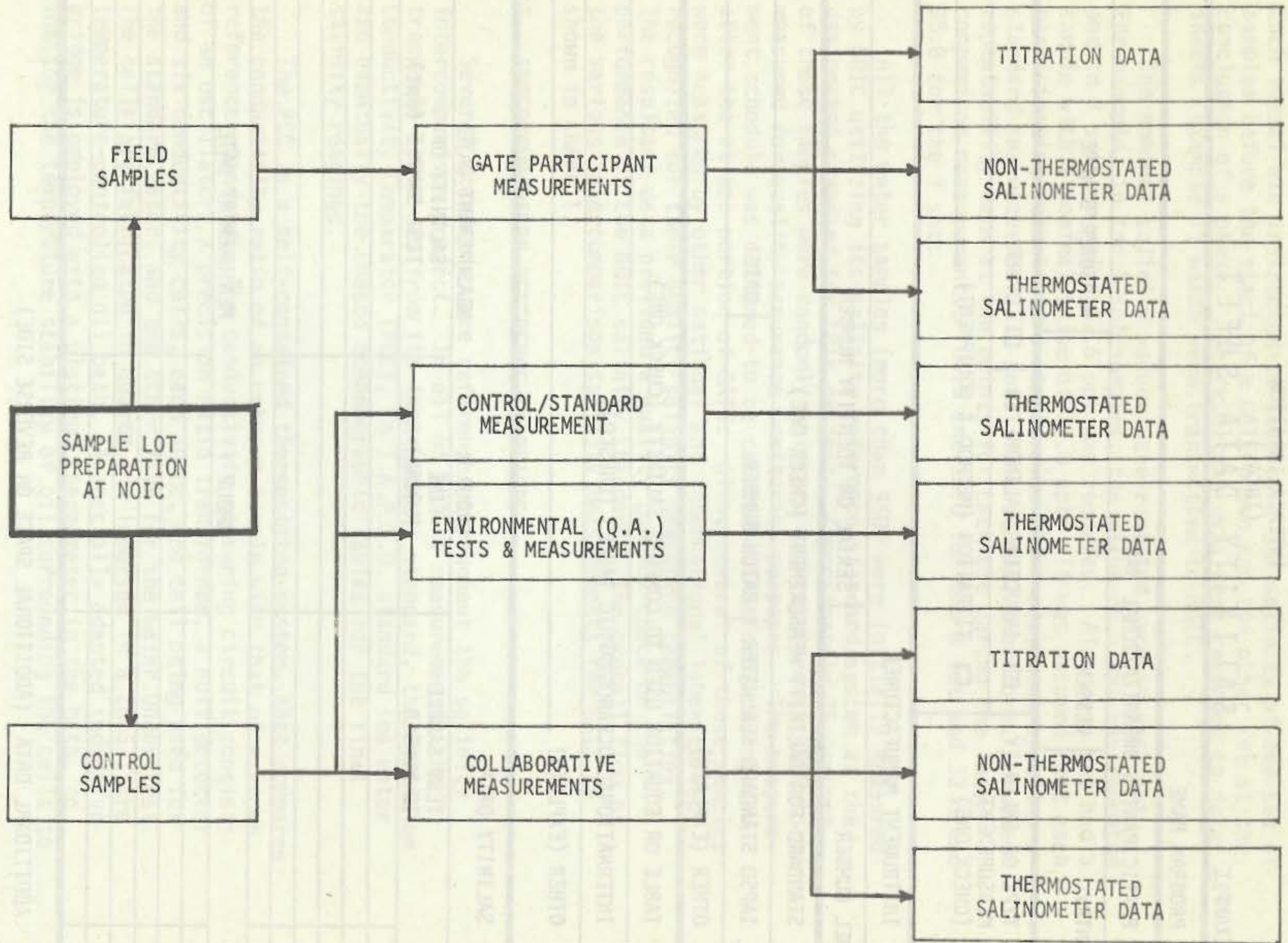
	TEST SAMPLE ID NUMBER	TIME (LOCAL)	SALINITY OF TEST SAMPLE (ppt)
1			
2			
3			
4			
5			
6			

GROUP Y — MEASUREMENT DATE

	TEST SAMPLE ID NUMBER	TIME (LOCAL)	SALINITY OF TEST SAMPLE (ppt)
7			
8			
9			
10			
11			
12			

8. ADDITIONAL DATA (ADDITIONAL SPACE ON REVERSE SIDE)

CHART 1. Flow of the GATE Salinity Intercomparison Measurements



±0.2 mK. The dimensional stability of quartz incorporated in the design of the test cells effectively minimized changes in their cell constant with time and temperature. The PCC facilitates salinity measurements from 40 to 60 ppt over a temperature range from -5°C to 40°C with an uncertainty of 1 ppm.

Data obtained from other laboratories were referenced to such instrumental standards as: Guildline Salinometer, Model 8400 (Bedford Institute of Oceanography, Canada); Autolab Model 601, Mk. III (Institute of Oceanographic Sciences, England); and WHOI Salinometer, Model 3 (Woods Hole Oceanographic Institution, USA). Generally, salinity measurements from inductive type salinometers were traced to I.A.P.S.O. standard seawater and the Unesco oceanographic tables.

During the intercomparison project, information received from the participants indicated that other standards were used in their traceability of salinity measurements. The Canadians utilized the conductivity-salinity tables of A.S. Bennett, Bedford Institute of Oceanography. A few of the Soviet vessels traced their measurements to standard seawater prepared by the Institute of Oceanology (USSR Academy of Sciences) and the N. N. Zubov (Leningrad 1957) tables.

In anticipation that some vessels would measure the samples by the titration method, a minority of NOIC's quality control samples were titrated by the U.S. Naval Oceanographic Office (Washington, D.C.) who used the Knudsen method with a phenosafranim indicator as described in their publication entitled: "Instruction Manual for Oceanographic Observations" No. 607, 1968.

III. QUALITY ASSURANCE

a. Solution Preparation

The samples, represented by sets X01 through X06, Y10 and Y12, were prepared from natural seawater obtained from the Sargasso Sea area with a salinity range of 36 to 38 parts per thousand. This seawater was concentrated to approximately 40 ppt by evaporation at 40°C. For sample sets Y07 through Y09 and Y11, the solution was constructed synthetically by the use of a commercial salt known as Sea Salt. The salts were dissolved by weight in deionized water, producing a solution of about 45 ppt. The absolute solution value was not critical at this time. The solution was allowed to settle for a week and then the clear salt water was drawn off and filtered.

All the concentrates were filtered as they entered a 50 litre mixing and dispensing bottle. The deionized water was added to dilute to the desired nominal salinity. A partial vacuum was drawn for about a half hour on the solution while stirring with a magnetic stirrer to degas well below saturation at room temperature. Atmospheric pressure was restored and the solution constantly stirred until half-way through the bottling.

b. Bottling

The sample bottles used in the intercomparison were all borosilicate type at 650 ml size. Soda-lime glass bottles were first considered because of their low cost and easy accessibility. These bottles would then be acid rinsed (10% HCL) and subsequently washed with distilled water. Soda-lime glass (or flint glass) has approximately four times more soda (Na_2CO_3) than borosilicate glass. The soda will leach out from the glass surface at a rate decreasing with time. Table 4 is an example of test results using distilled water in a 10 oz. soda-lime container which was heated to 120°C for 1 hour. This is equivalent to 1 to 2 years on the shelf at ambient temperature.

TABLE 4. Reactions of soda-lime containers, distilled water and heat.

OXIDES	QUANTITY (ppm)
SiO_2	26.0
Al_2O_3	0.6
CaO	4.1
MgO	0.4
Na_2O	6.5
K_2O	0.01
B_2O_3	0.01

These oxides will increase by 2 to 5 times if the pH of the water were 8.4. Alkalinity therefore accelerates the leaching process.

To assure quasi absolute non-contamination and stability of the water sample composition, the borosilicate bottle was chosen over the cheaper soda-lime glass container. Measurement integrity was of prime importance.

The sample bottles were prepared prior to filling with the desired solution by rinsing in deionized water, drying in an oven for 30 minutes at a temperature of 150°C, then allowed to cool in an inverted position in a drying rack.

The bottles were readied to receive the various valued salinities. The solution was drawn off the bottom of the 50 litre mixing and dispensing bottle via a glass dip tube (the only entrance to the bottle except for a small air vent at the top) and gravity fed via tygon tubing to the sample bottle. The tygon tubing was flexible enough to stop the solution flow by pinching the tubing by hand. This eliminated spillage of water on the sealing surface of the bottles. The sample bottles were then sealed with two layers of a highly flexible thermoplastic, known as parafilm, and a layer of aluminum foil. Parafilm is waterproof and prevents sample evaporation and contamination. The aluminum foil allowed the cap to be screwed on with no pulling of the parafilm. The cap was tightened down snugly with a pair of pliers, and the bottle labeled. The first and last samples bottled for each salinity value were measured to check for any differences. The standard deviation for the twelve salinities was 0.6 ppm.

c. Quality Control Testing

A control sample lot of the bottled seawater was retained by NOIC and measured over a period from April to November 1974 on the PCC. The dates were: April 2 and 5; June 7; July 15 and 16; August 7, 20 and 28; September 17; October 1 and 4; and November 27. Twenty sets (120 measurements) were tested during this period with results in Table 5.

The results of the control samples measured by other laboratories are shown in Table 6.

TABLE 5. Measurement results of NOIC control salinity samples.

SAMPLE NUMBER	PCC MEAN (ppt)	PCC STD. DEV. σ (ppm)
X01_ _	37.9403	1.1
X02_ _	36.6508	1.1
X03_ _	35.0549	0.8
X04_ _	33.5099	0.6
X05_ _	31.9754	1.0
X06_ _	36.5244	1.1
Y07_ _	38.0475	1.4
Y08_ _	36.6826	1.2
Y09_ _	35.0227	1.5
Y10_ _	33.5631	1.0
Y11_ _	32.0616	0.9
Y12_ _	33.5235	0.9

TABLE 6. Salinity differences between NOIC's PCC and other laboratories

SALINITY DIFFERENCES (ppm)

Nominal Salinity (ppt)	32.0		33.5			35.0		36.5			38.0	
Sample Group Number	X05	Y11	X04	Y10	Y12	X03	Y09	X02	X06	Y08	X01	Y07
Data Code Identity												
611	0	-1	1	BB	1	2	1	0	0	1	1	1
615	0	2	1	1	0	1	3	0	1	3	1	3
616	12	11	10	20	12	8	11	6	9	11	6	9

Data Key: BB-Broken Sample Bottle; no data.

Simulated environmental tests were also performed on the samples to determine if any measurement degrading factors could be attributable to shipment by air or storage at sea. The samples were tested under assumed conditions most likely to occur during transportation and subsequently on-board a GATE vessel. Environmental temperature, pressure and vibration were the prime parameters.

The test samples were placed in an environmental test chamber where the ambient pressure was lowered and the temperature was made to range from 32°C to 10°C. A visual investigation of the samples in a bright light indicated no change or crystallization of the solution. The samples were then heated to, and maintained at a temperature of 50°C for 6 hours. This test was to simulate the samples being on a ship's deck in direct sunlight. The samples were cooled to 1°C for 3 hours. At this temperature the samples were allowed after the waiting period to drift overnight up to 16°C and then recooled to 10°C under an ambient pressure of 585 mmHg. The samples were also exposed to vibration over a frequency range of 20 to 58 hertz at a temperature of 50°C. This frequency range was selected to duplicate transportation vibration. Again, visual inspection of these sealed samples (similar to those delivered to the GATE vessels) indicated no discernible change.

All the test samples, following the environmental tests, were remeasured during November 1974 with the PCC to determine the degree of salinity change. The maximum difference in salinity was 4 ppm, but the average difference was less than 2 ppm.

IV. INTERCOMPARISON RESULTS

The total measurements from GATE vessels were 560 data points with approximately 57 percent of this data falling within the ± 10 ppm salinity goal of the intercomparison project. The average standard deviation for this group was 10.4 ppm. Table 7 is an analysis of the three types of measurements used from the GATE vessels. Data resulting from the titration of samples was done generally as referred to earlier in H. O. Publication 607, "Instruction Manual for Obtaining Oceanographic Data". The exact method used by each GATE participant was not requested and subsequently not detailed herein. The measurement differences experienced by titration was typically higher than those by other measurement techniques, as only 31 percent of the measurements were within the ± 10 ppm region. Other measurements (non-titration) were grouped into two categories: Measurement by thermostated salinometers and measurement by non-thermostated salinometers. It can be noted that 65 percent of the measurement differences from the non-titration group fell within the ± 10 ppm region.

Thermostated salinometers are those such as the Guildline 8400 and WHOI Model 3, that utilize a temperature controlled bath which maintains both the reference sample (standard sea water for example) and the unknown sample at the same temperature to measure the conductivity ratio. The data observed from these type devices, in general, showed a significantly smaller measurement difference and standard deviations as illustrated in the data of Table 7. In comparison, the non-thermostated salinometers showed measurement differences and standard deviations quite lower than that of titration, but somewhat higher than that of thermostated salinometers. The non-thermostated salinometer was observed to have 61 percent of its data with the ±10 ppm range as compared to 100 percent for thermostated salinometers. The non-thermostated salinometers (Plessey, Hydrometpribor GM-65, Auto Lab 60k, MK III and Beckman RS-7) measure the conductivity ratio between the unknown and reference sample which are not necessarily at the same temperature. To compensate for this temperature difference, an electronic temperature compensating circuit is utilized. All available data indicated that the Hydrometpribor GM-65 salinometer was of the non-thermostated type and, therefore its data was treated as such.

TABLE 7. Analysis of measurements from GATE vessels.

MEASUREMENT TYPE	QUANTITY OF MEASUREMENTS	DATA OBSERVED WITHIN ±10 ppm (PERCENT)	STANDARD DEVIATION OF TYPE (ppm)
Titration	143	31	23.3
Non-Thermostated	370	61	11.2
Thermostated	47	100	2.3

The data received from the GATE vessels has been compared to the project's standard, NOIC's PCC. The results are tabulated in Table 8. The measurement differences were formulated using the raw data contained in the data sheets from the GATE vessels. Nominal salinities are noted at the top of the table, in ascending order from left to right. Each horizontal data code shows the measurement differences in ppm between the (NOIC) PCC's established values and the GATE measurer's readings.

TABLE 8. Salinity differences between NOIC PCC and GATE vessels.

SALINITY DIFFERENCES (ppm)

NOMINAL SALINITY (ppt)	32.0		33.5			35.0		36.5			38.0	
SAMPLE GROUP NUMBER	X05	Y11	X04	Y10	Y12	X03	Y09	X02	X06	Y08	X01	Y07
DATA CODE IDENTITY												
617	7	-4	9	-9	-9	15	-14	14	5	-22	22	-17
618	-5	-4	-1	-4	ND	-9	-3	-9	-3	-3	-8	-4
619	-2	-1	-3	-1	-1	-3	0	-5	-1	0	-4	-1
620	-12	2	-13	0	-6	-35	-8	-38	-39	-18	-38	-20
621	28	25	27	16	17	12	-2	10	4	-13	-16	-20
622	6	9	6	8	8	3	2	3	-2	1	2	-2
623	6	9	1	7	6	-9	-1	-14	-12	-4	-19	-6
624	10	18	6	ND	7	-2	7	-3	-4	-2	-8	3
625	2	4	1	1	2	-1	1	-2	-5	0	-2	-1
626	3	2	2	2	0	0	-2	-2	-3	-2	-5	0
627	-1	-10	-5	-20	-23	-10	-14	-13	-12	-24	-23	-34
628	10	21	17	15	14	2	10	8	10	10	2	14
629	22	33	31	32	21	-7	18	19	10	21	11	14
630	-13	17	-26	5	5	-33	0	-7	-10	28	-18	21
631	-4	-10	-14	-13	-22	-19	-18	8	0	7	-1	-3
632	31	29	28	16	18	15	12	27	14	7	19	1
633	24	5	13	3	0	8	1	3	3	-9	2	-18
634	-24	-10	5	-21	-12	-24	1	-29	-21	-21	-27	-14
635	-85	-32	-30	-13	-13	-25	-13	-31	-74	-53	-20	-97
636	-15	-12	0	-33	-23	-5	-3	-31	-14	-43	-20	-27
637	-15	-12	0	7	-13	-25	7	19	-14	7	-20	-7
638	5	8	0	-13	-33	-5	7	19	6	7	-20	-27
639	-15	-12	0	-13	-13	-45	-13	-11	-14	-33	0	33
640	-10	2	-6	-27	*	-38	-3	-5	-18	-17	-3	23
641	-35	8	0	-53	27	-45	27	-51	-14	-33	-20	-7
642	-30	10	-7	-59	17	-36	31	-40	0	-17	-32	-3
643	-15	-62	0	-33	-13	-25	-13	-11	26	-13	50	33
644	-19	-51	-2	-44	-21	-19	-2	-14	26	3	43	27
645	9	23	18	32	34	-4	3	11	15	14	23	31
646	-13	23	20	31	27	-6	-11	8	15	3	17	16

TABLE 8. (Continued)

SALINITY DIFFERENCES (ppm)

NOMINAL SALINITY (ppt)	32.0		33.5			35.0		36.5			38.0	
SAMPLE GROUP NUMBER	X05	Y11	X04	Y10	Y12	X03	Y09	X02	X06	Y08	X01	Y07
DATA CODE IDENTITY												
647	-15	28	20	7	27	-5	27	39	6	47	0	53
648	5	8	20	7	7	-25	-13	19	6	7	0	13
649	23	23	15	16	11	8	6	-3	-7	-2	-15	-17
650	21	19	14	13	10	9	3	-4	-13	-2	-14	-14
651	27	19	20	13	12	8	10	3	-9	-2	-12	-9
652	30	3	32	-3	-1	8	16	24	7	16	-6	-13
653	9	8	0	2	3	-5	2	-8	-7	-6	-10	-8
654	14	15	8	8	9	2	5	-5	-2	-1	-6	-7
655	16	6	12	13	2	6	0	*	4	2	-2	-2
656	6	-59	10	3	11	14	0	18	-8	9	10	-8
657	-5	0	1	-6	0	24	-15	3	8	-7	-3	-10
658	48	28	3	51	49	0	5	-2	45	-6	-5	-6
659	1	-2	2	-5	-4	1	-7	-5	-6	-8	-1	-9
660	3	-2	2	-2	-2	0	-1	1	0	-5	1	-7
661	2	3	-2	2	1	0	3	6	1	2	-1	1
662	4	2	1	2	1	1	2	-1	0	1	3	0
663	3	1	1	0	0	-3	0	-3	-5	-2	-5	-6

Data Key: ND - No data received for the sample
* - Unrealistic data; difference greater than 99 ppm

Each GATE vessel, that measured the X and Y samples, received an approximate repeated value in those groups. The nominal salinities of 33.5 ppt and 36.5 ppt were the repeated values. Also a nominal salinity value of 35.0 was provided in each X and Y sample group. It was assumed that the GATE vessels would exercise generally accepted operational practice with their equipment by standardizing at the standard of 35 ppt. This action, therefore, would have the effect of repeating the 35 ppt value when measuring the X and Y samples.

Table 9 is an analysis of these repeated measurements. The amount of measurement differences from the PCC reference standard to be within ±10 ppm is shown in percent.

TABLE 9. Analysis of the repeated sample values measured by the GATE vessels.

OBSERVATIONS WITHIN ±10 ppm
(Percent)

NOMINAL SALINITIES REPEATED (ppt)	33.5	35.0[1]	36.5
EQUIPMENT			
Titration	17	25/25	21
Guildline	100	100/100	100
WHOI	100	100/100	100
Plessey	86	86/100	85
Beckman	85	57/71	64
Auto Lab	50	100/75	63
GM 65	27	69/62	62

1. Percentages represent X/Y sample groups; no repeat samples for this value were provided; it was assumed that the GATE vessels standardize their equipment at 35 ppt with standard water.

All comparisons, which include the GATE vessels, other laboratories and the quality control checks on the PCC, are graphically shown in Figures 1 through 13. The curves for each plot represent data received from measurements on the X and Y sets of samples. The hatched area is the ±10 ppm salinity tolerance level desired for all the GATE salinity data. The graphs have been grouped in accordance with the method used and the instrument: Titration; electrode salinometer (Guildline and WHOI); and inductive salinometer (PCC, Plessey, Beckman, Auto Lab and GM65).

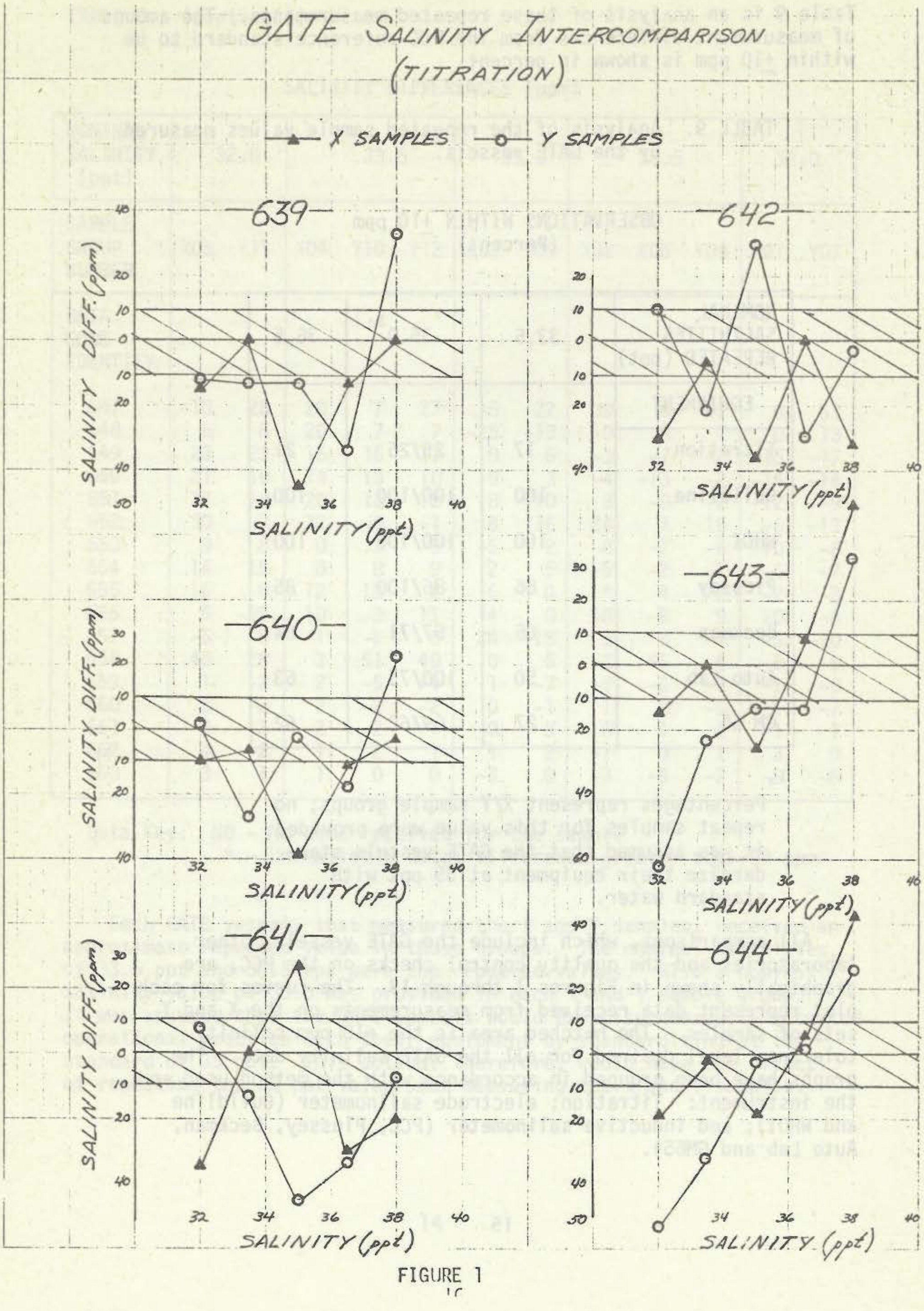

GATE SALINITY INTERCOMPARISON
(TITRATION)
X SAMPLES
Y SAMPLES
-639-
-640-
-641-
-642-
-643-
-644-
SALINITY DIFF. (ppm)
SALINITY (ppt)

FIGURE 1

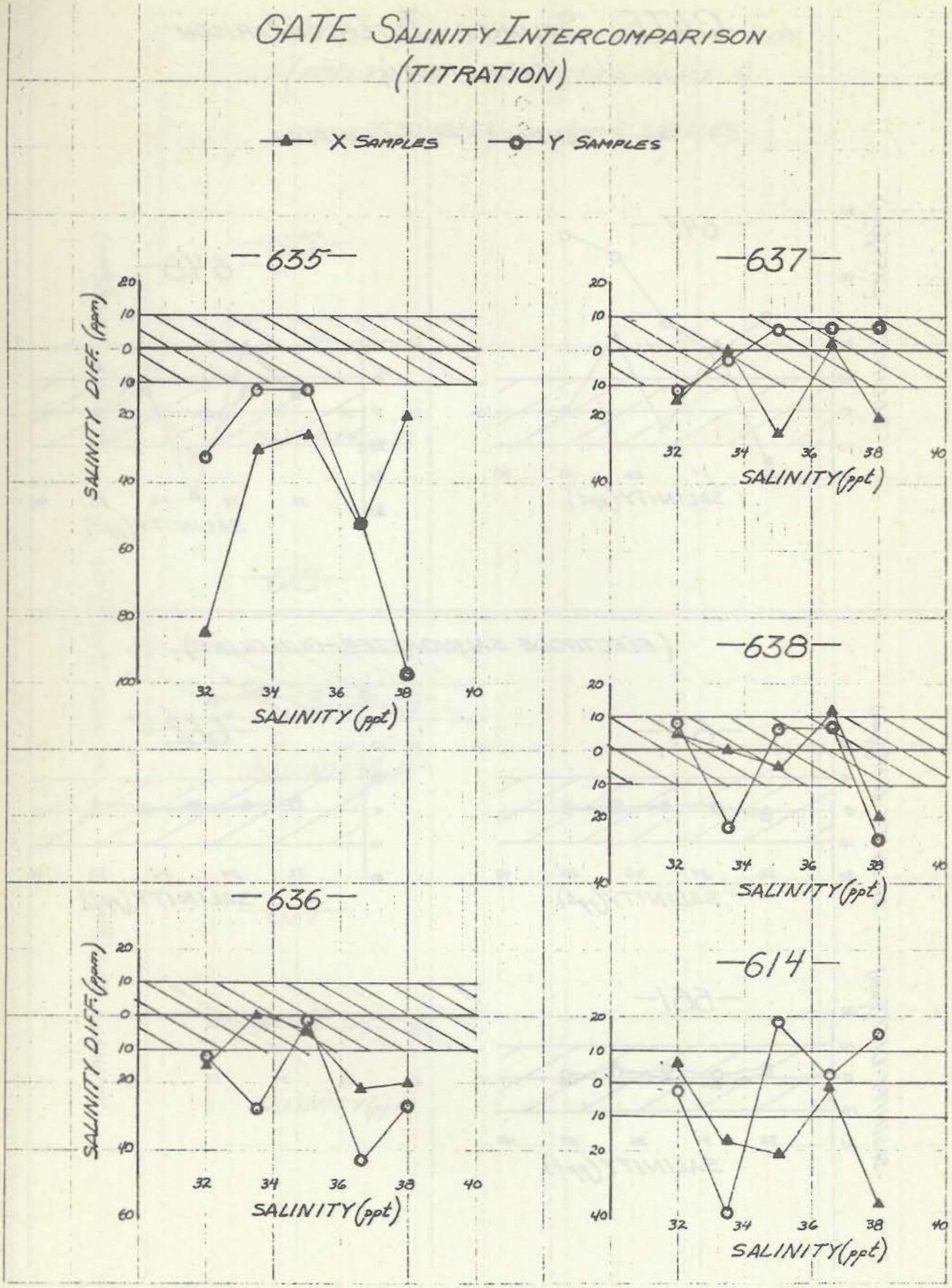
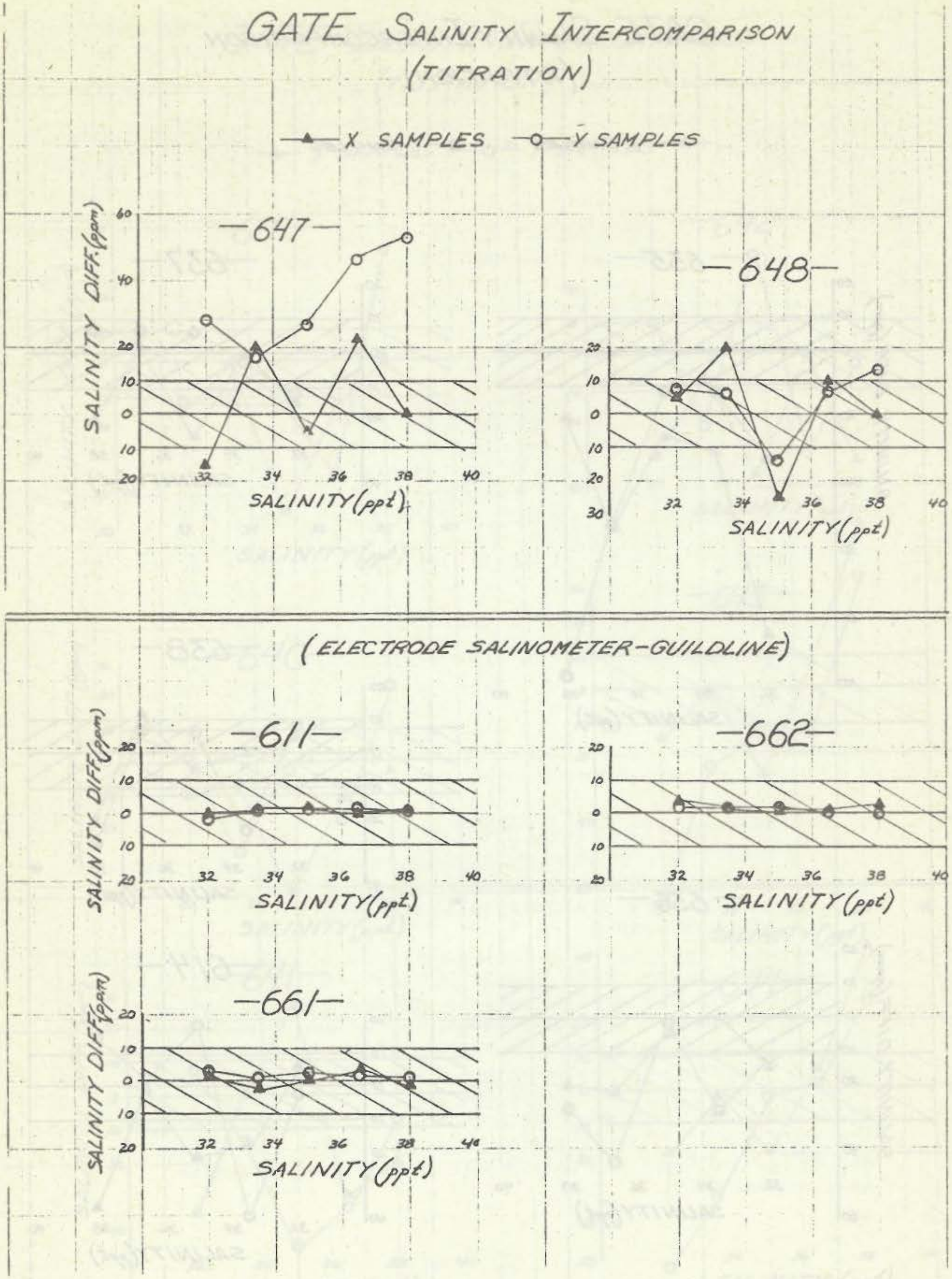

GATE SALINITY INTERCOMPARISON
(TITRATION)
X SAMPLES
Y SAMPLES
-635-
-637-
-638-
-636-
-614-
SALINITY DIFF. (ppm)
SALINITY (ppt)

FIGURE 2


GATE SALINITY INTERCOMPARISON
(TITRATION)
X SAMPLES
Y SAMPLES
-647-
-648-
SALINITY DIFF. (ppm)
SALINITY (ppt)
(ELECTRODE SALINOMETER-GUILDLINE)
-611-
-662-
-661-
SALINITY DIFF (ppm)
SALINITY (ppt)

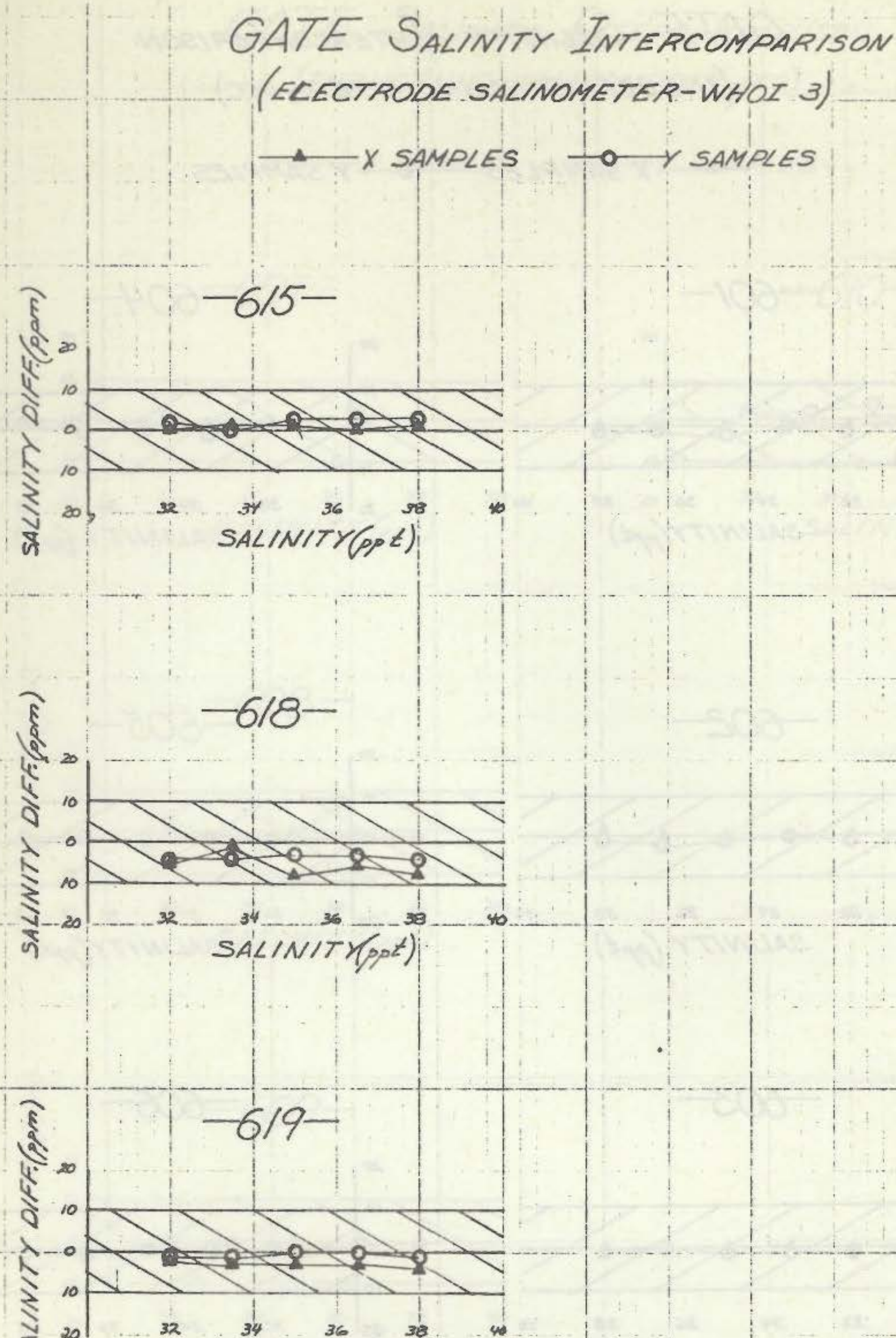

GATE SALINITY INTERCOMPARISON
(ELECTRODE SALINOMETER-WHOI 3)
X SAMPLES
Y SAMPLES
—615—
SALINITY DIFF.(ppm)
20
10
0
10
20
32
34
36
38
40
SALINITY(ppt)
—618—
SALINITY DIFF.(ppm)
20
10
0
10
20
32
34
36
38
40
SALINITY(ppt)
—619—
SALINITY DIFF.(ppm)
20
10
0
10
20
32
34
36
38
40
SALINITY(ppt)

FIGURE 4

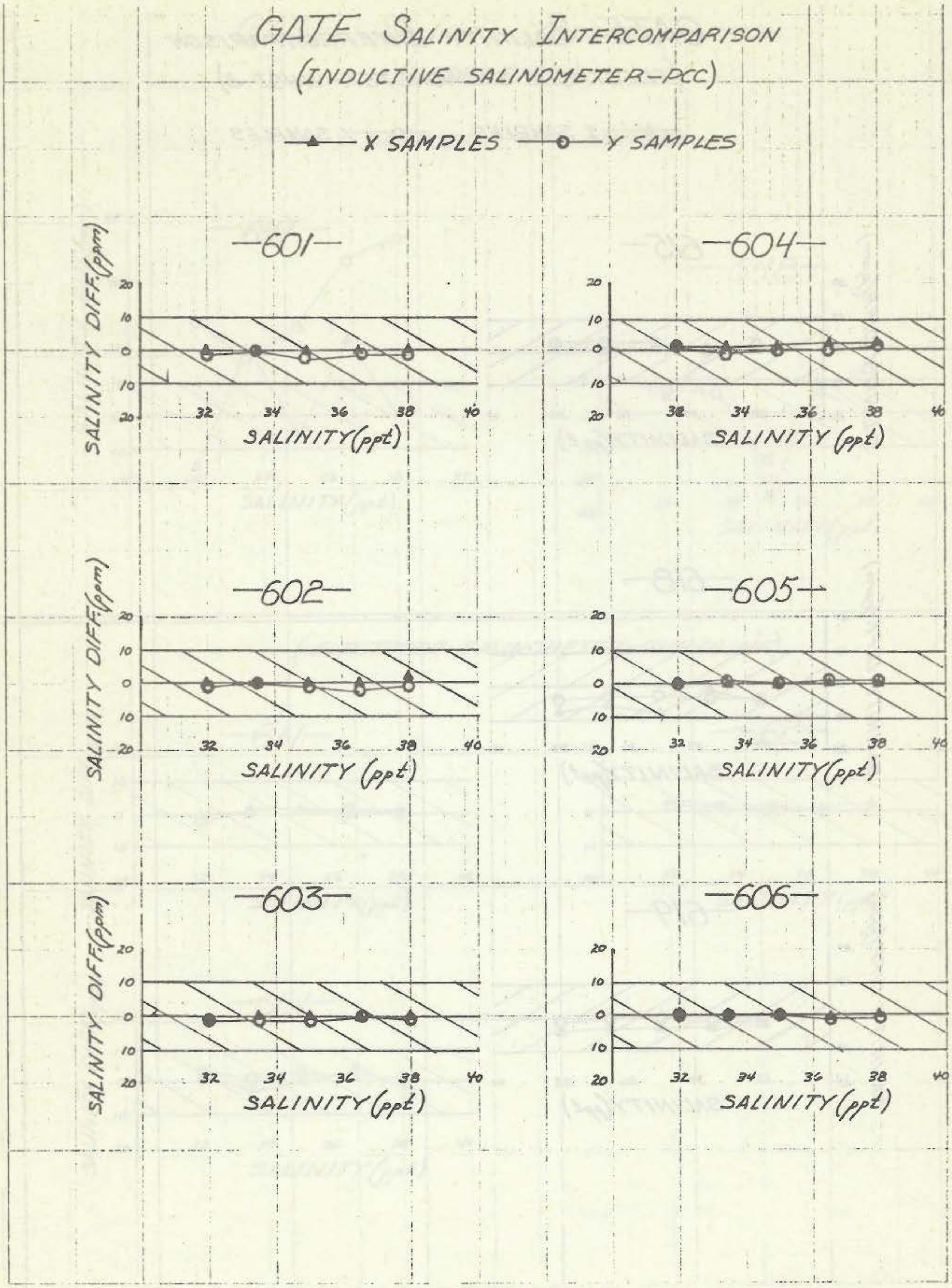

GATE SALINITY INTERCOMPARISON
(INDUCTIVE SALINOMETER–PCC)
X SAMPLES
Y SAMPLES
–601–
–602–
–603–
–604–
–605–
–606–
SALINITY DIFF. (ppm)
SALINITY (ppt)
20
10
0
10
20
32
34
36
38
40

FIGURE 5

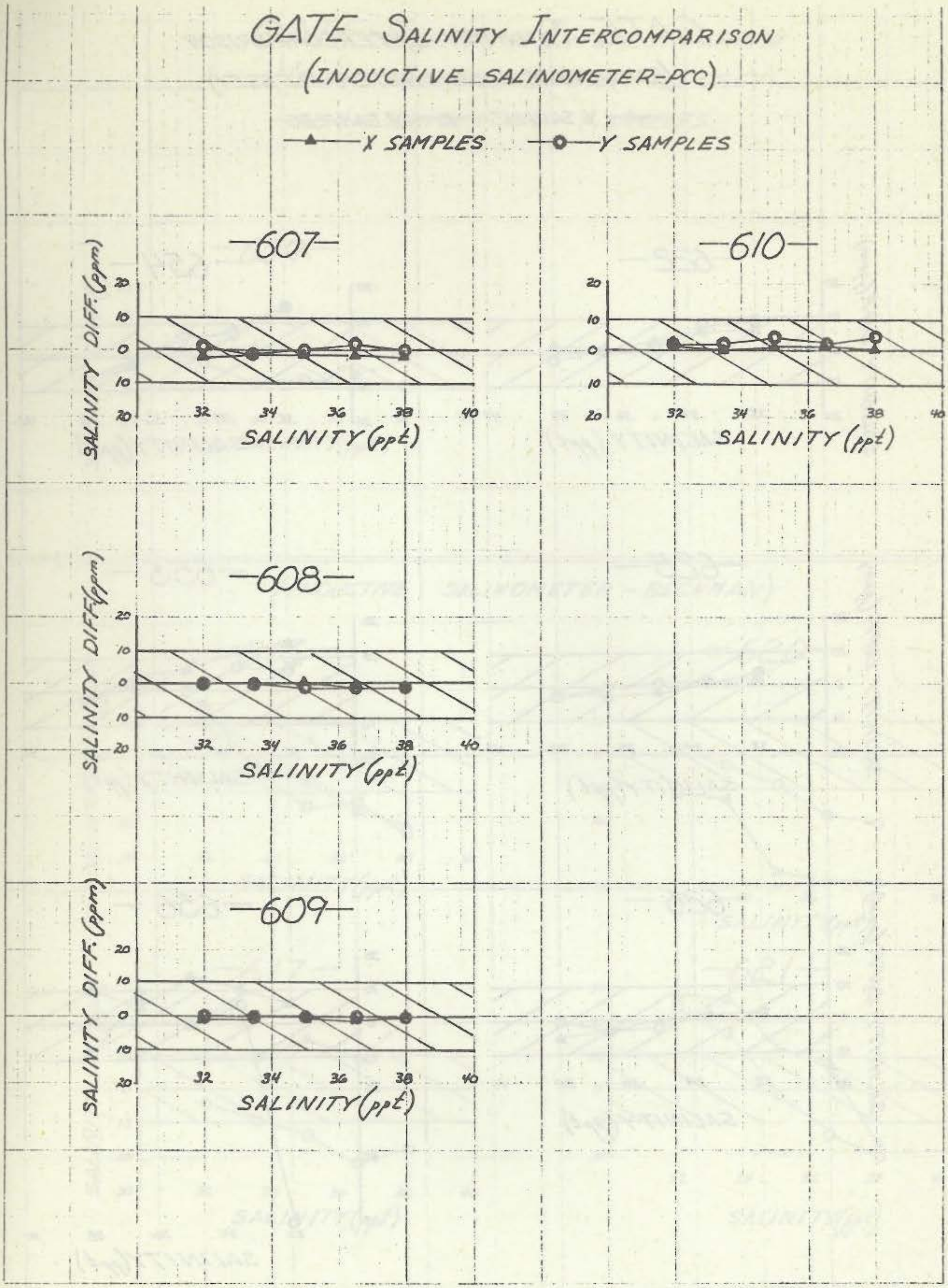
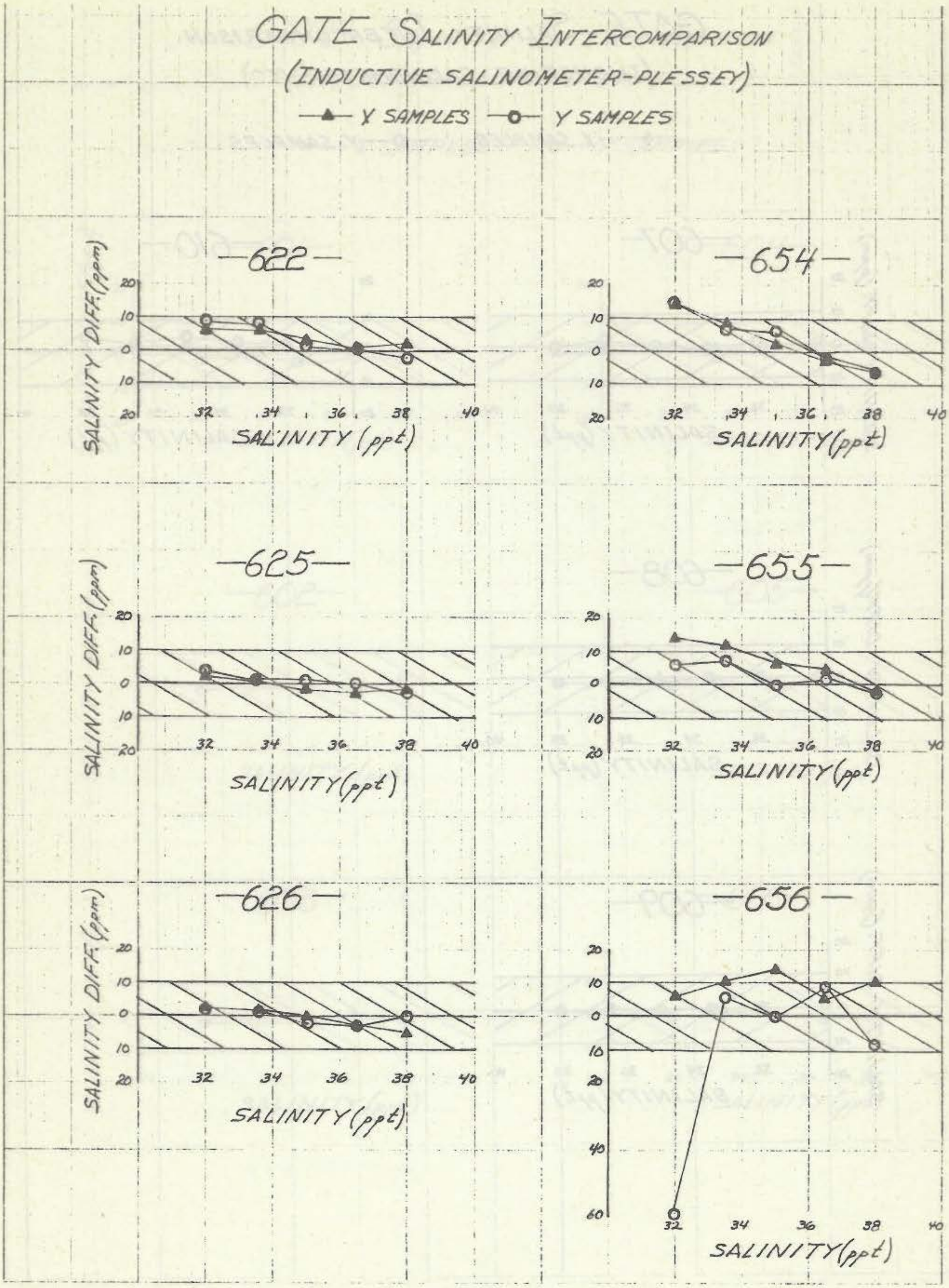

GATE SALINITY INTERCOMPARISON
(INDUCTIVE SALINOMETER-PCC)
X SAMPLES
Y SAMPLES
-607-
-610-
-608-
-609-
SALINITY DIFF. (ppm)
SALINITY (ppt)
20
10
0
10
20
32
34
36
38
40

FIGURE 6



GATE SALINITY INTERCOMPARISON
(INDUCTIVE SALINOMETER-PLESSEY)
X SAMPLES
Y SAMPLES
-622-
-654-
-625-
-655-
-626-
-656-
SALINITY DIFF. (ppm)
SALINITY (ppt)

FIGURE 7

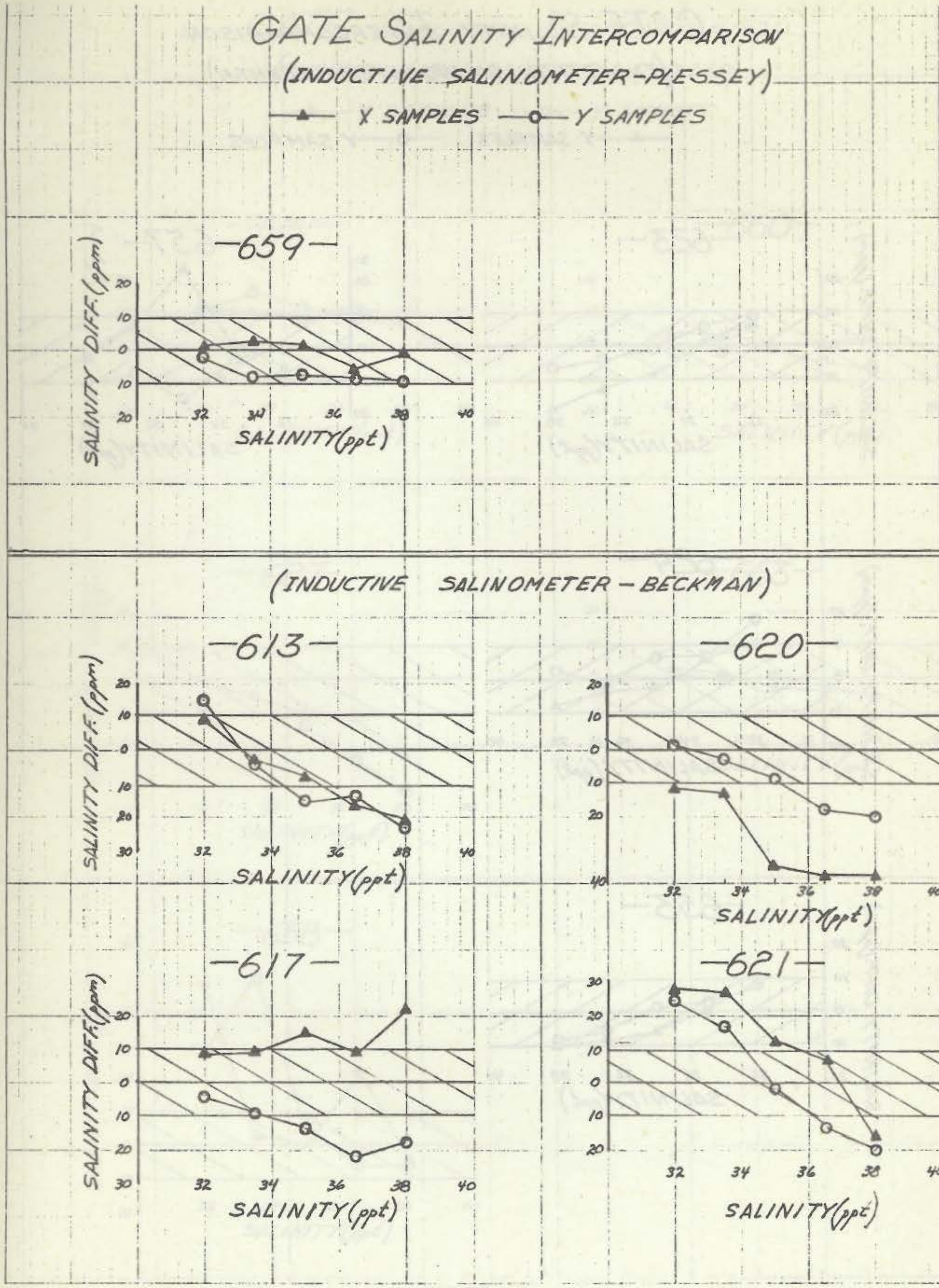

GATE SALINITY INTERCOMPARISON
(INDUCTIVE SALINOMETER-PLESSEY)
X SAMPLES
Y SAMPLES
-659-
SALINITY DIFF. (ppm)
SALINITY (ppt)
(INDUCTIVE SALINOMETER - BECKMAN)
-613-
-620-
-617-
-621-

FIGURE 8

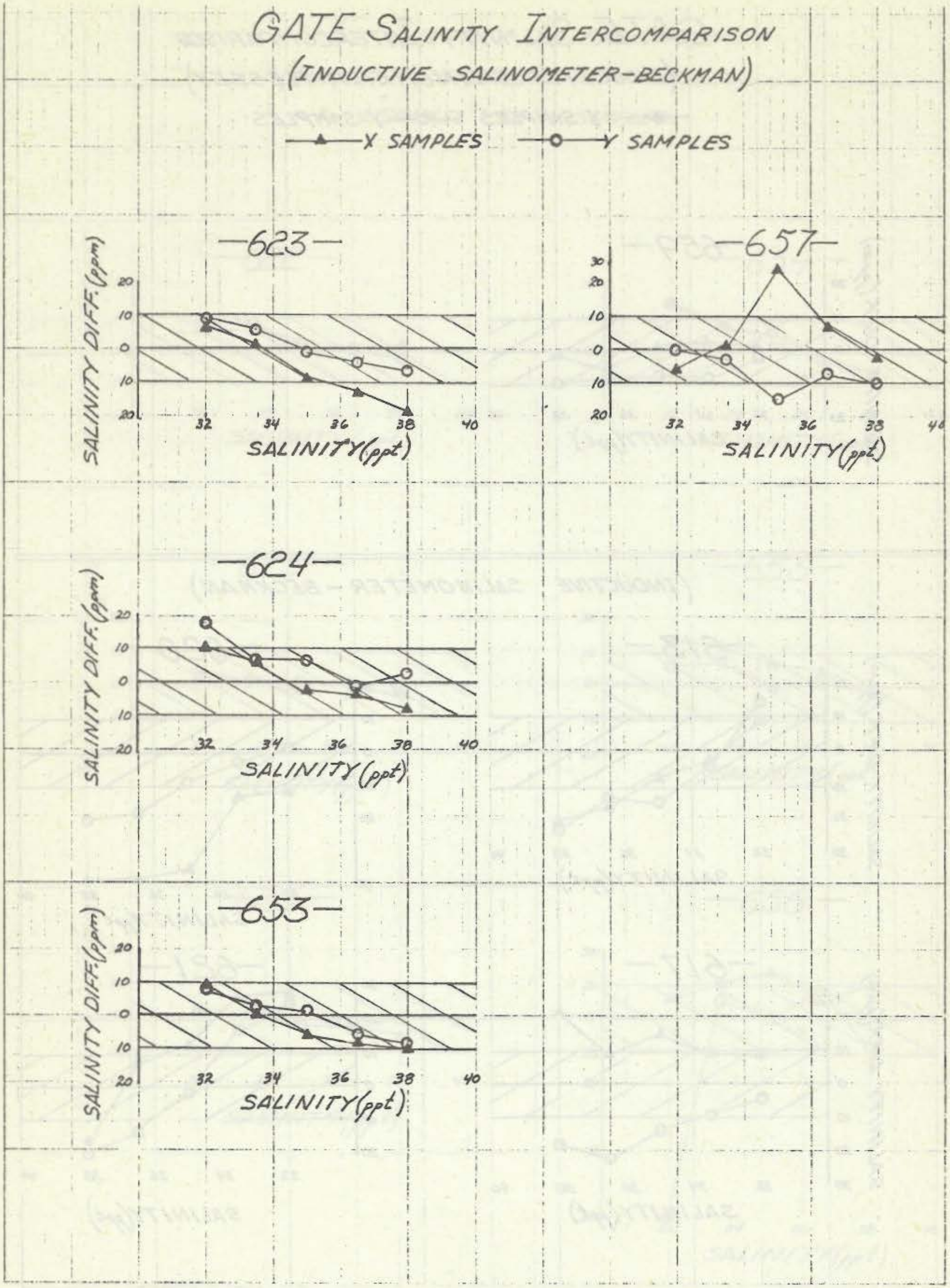

GATE SALINITY INTERCOMPARISON
(INDUCTIVE SALINOMETER-BECKMAN)
X SAMPLES
Y SAMPLES
-623-
-657-
-624-
-653-
SALINITY DIFF. (ppm)
SALINITY (ppt)
32
34
36
38
40

FIGURE 9

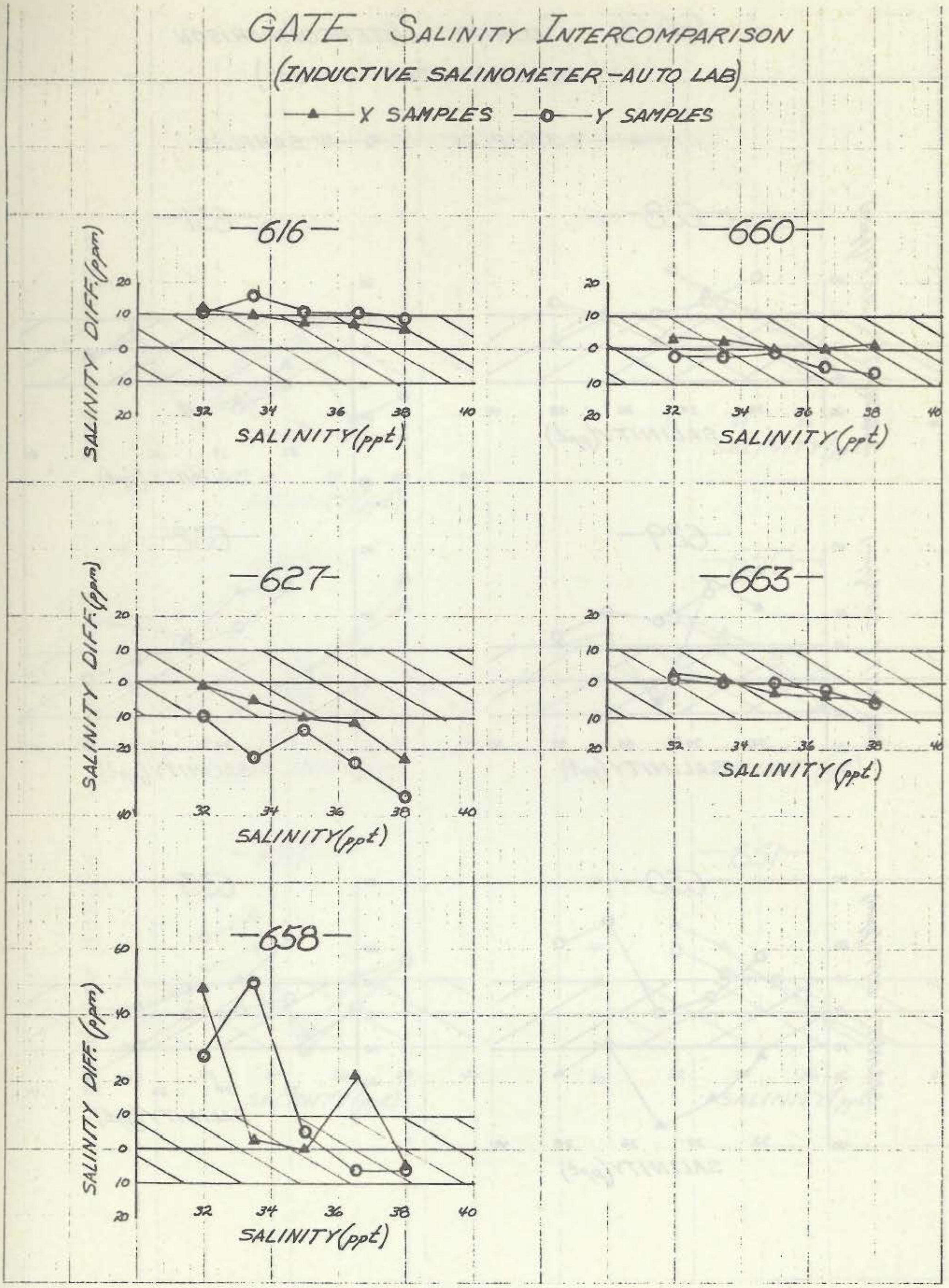

GATE SALINITY INTERCOMPARISON
(INDUCTIVE SALINOMETER - AUTO LAB)
X SAMPLES
Y SAMPLES
-616-
-660-
-627-
-663-
-658-
SALINITY DIFF. (ppm)
SALINITY (ppt)
32
34
36
38
40

FIGURE 10

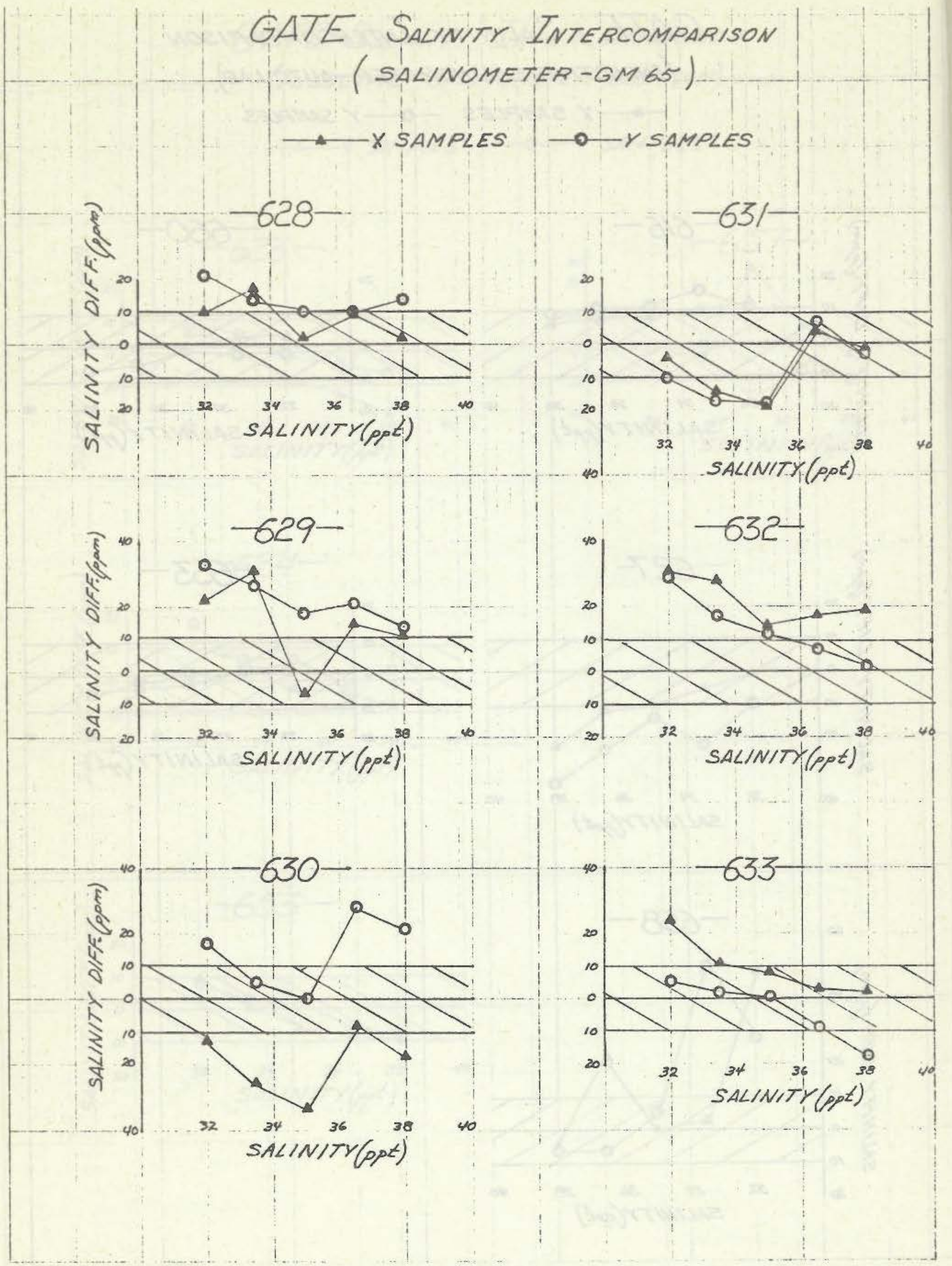
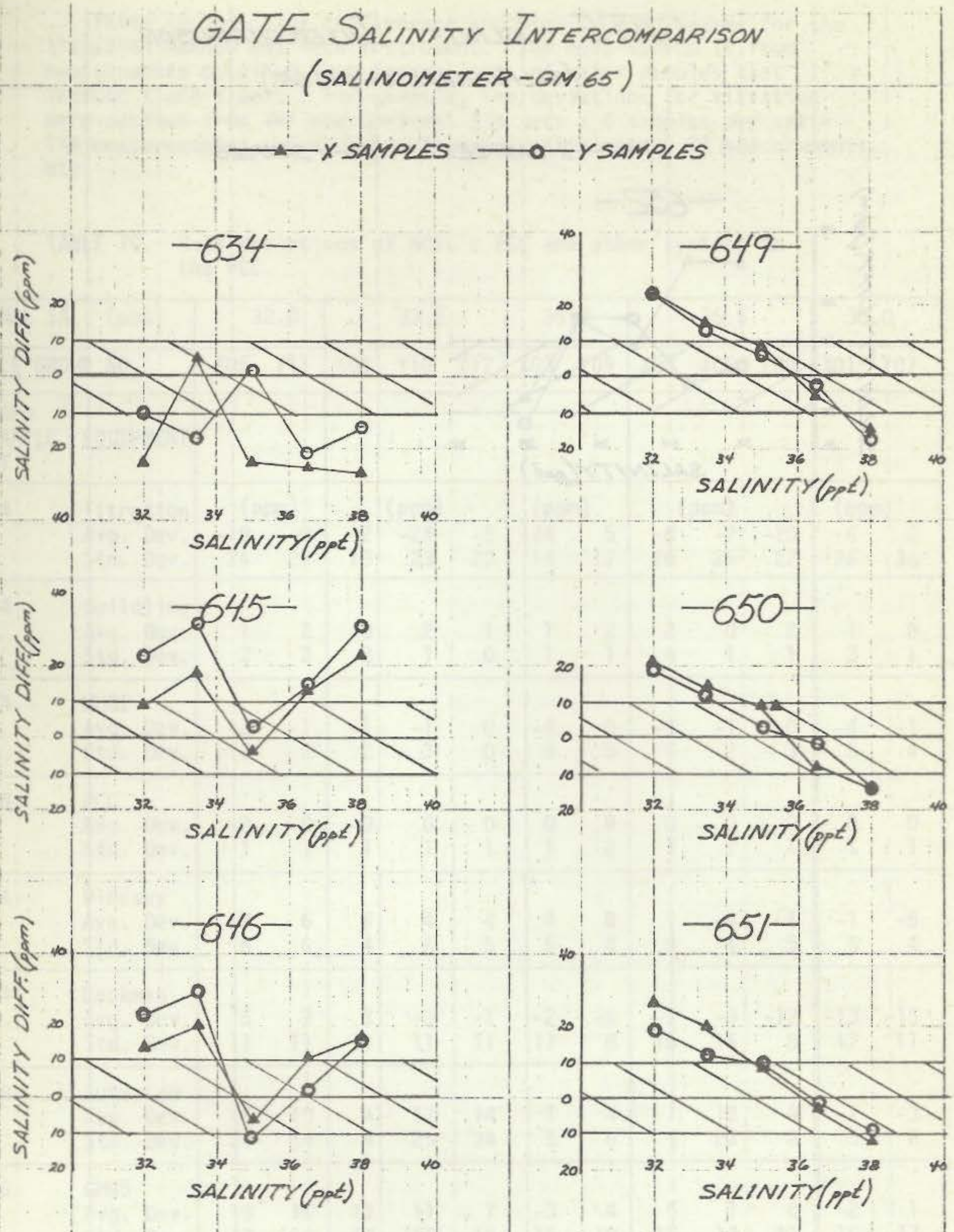

GATE SALINITY INTERCOMPARISON
(SALINOMETER - GM 65)
X SAMPLES
Y SAMPLES
628
631
629
632
630
633
SALINITY DIFF. (ppm)
SALINITY (ppt)

FIGURE 11



GATE SALINITY INTERCOMPARISON
(SALINOMETER - GM 65)
X SAMPLES
Y SAMPLES
-634-
-645-
-646-
-649-
-650-
-651-
SALINITY DIFF. (ppm)
SALINITY (ppt)

FIGURE 12

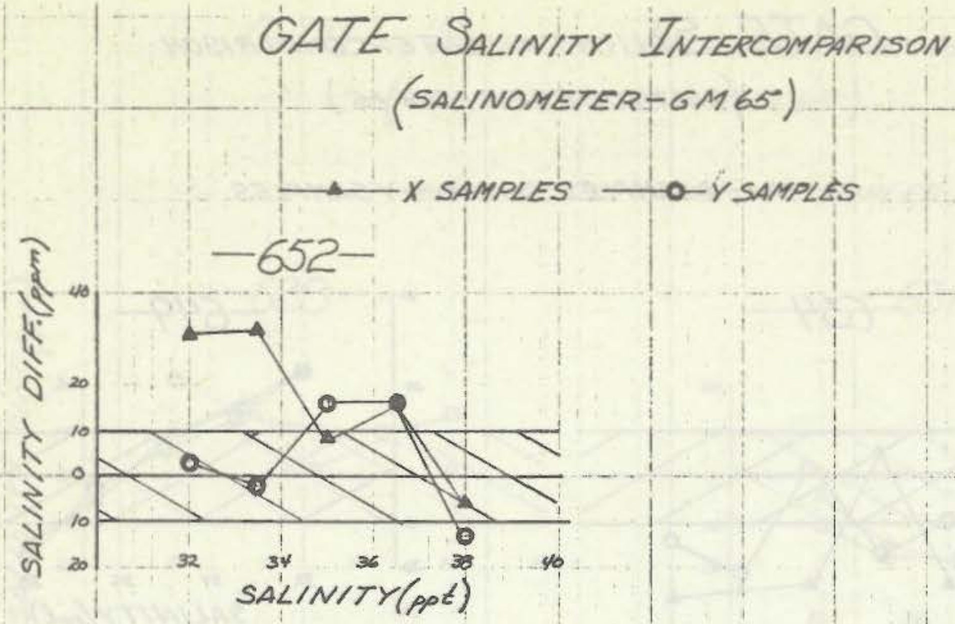

GATE Salinity Intercomparison
(SALINOMETER-GM 65)
X SAMPLES
Y SAMPLES
-652-
SALINITY DIFF.(ppm)
40
20
10
0
10
20
32
34
36
38
40
SALINITY(ppt)

FIGURE 13

Table 10 indicates the average and standard deviations for the titration method and each instrument. The data source is from measurements obtained from several sets of water samples that include X and Y sets. For example, the deviations for titration were derived from 144 measurements (24 sets x 6 samples per set = 144 measurements). Guildline electrode salinometer, 24 measurements, etc.

TABLE 10. Data deviations of NOIC's PCC and other systems to the PCC.

NOMINAL SAL. (ppt)		32.0		33.5			35.0		36.5			38.0	
SAMPLE GROUP NO.		X05	Y11	X04	Y10	Y12	X03	Y09	X02	X06	Y08	X01	Y07
NUMBER OF SAMPLE SET	EQUIPMENT												
24	Titration	(ppm)		(ppm)			(ppm)		(ppm)			(ppm)	
	Avg. Dev.	-19	-9	-2	-24	-5	-24	5	-8	-7	-10	-6	2
	Std. Dev.	24	26	13	23	20	14	17	26	25	27	26	38
4	Guildline												
	Avg. Dev.	1	2	0	2	1	1	2	2	0	2	1	0
	Std. Dev.	2	2	2	1	0	1	1	4	1	1	2	1
4	WHOI												
	Avg. Dev.	-3	-1	-1	-1	0	-4	0	-4	-1	0	-4	-1
	Std. Dev.	3	3	2	3	0	5	3	5	2	3	5	4
18	PCC												
	Avg. Dev.	0	0	0	0	0	0	0	0	0	0	0	0
	Std. Dev.	1	1	1	1	1	1	2	1	1	1	1	1
14	Plessey												
	Avg. Dev.	7	6	6	4	4	4	0	1	-4	1	-1	-5
	Std. Dev.	6	6	4	6	5	5	4	9	4	5	5	4
14	Beckman												
	Avg. Dev.	5	7	3	-3	-1	-2	-6	-7	-9	-12	-13	-15
	Std. Dev.	11	11	11	11	11	17	8	16	15	8	17	11
8	Auto Lab												
	Avg. Dev.	16	10	4	17	14	1	4	1	12	0	-1	-3
	Std. Dev.	21	14	4	25	24	5	6	4	23	8	5	8
26	GM65												
	Avg. Dev.	13	15	13	11	7	-3	4	5	1	6	-2	1
	Std. Dev.	17	14	17	16	16	15	10	15	12	13	16	17

The 108 measurements taken by NOIC on its PCC before, during and after the GATE project had a standard deviation of 1.1 ppm as shown in Table 11. The randomly selected samples, tested by other laboratories with similiar thermostated equipment, had a standard deviation of 1.1 ppm. The collaborative measurements by other laboratories with titration and with the use of non-thermostated equipment served the purpose of demonstrating a typical performance for those measurement types.

TABLE 11. Analysis of the quality control data.

MEASUREMENT GROUP	QUANTITY OF MEASUREMENTS	DATA OBSERVED WITHIN ±10 ppm	STANDARD DEVIATION OF GROUP (ppm)
NOIC Inhouse Control	108	100	1.1
Collaborative Titration	12	50	18.6
Collaborative Non-Thermostated	24	46	13.0
Collaborative Thermostated	26	100	1.1

V. CONCLUSIONS

The GATE Salinity Intercomparison results from the field data indicates that:

(1) The titration method for measuring salinities within ±10 ppm is unreliable and probably beyond its capabilities. Many of the data points were very erratic and trends in the overall performances could not be calculated.

(2) The electrode-thermostated type salinometers performed superior to other types of methods and equipment in terms of data accuracy. Its maintainability is unknown at this time due to limited utilization among scientists.

(3) The conventional inductive-non-thermostated type salinometer exhibited performances that have become typical with this instrument, such as: generally satisfactory when used with salinities close to 35 ppt; a negative error slope through 35 ppt where positive differences occur at lower salinities than 35 ppt and negative differences at higher than 35 ppt salinities; and frequent standardization with standard seawater and adjustments can produce improved performances.

In review, the operational scheme for measuring the samples aboard the GATE vessels was to determine the salinity of the X set of samples before the start of a GATE phase and of the Y set at the conclusion of a phase. Hopefully, the resultant measurements would produce a stability and/or drift trend with the equipment. Discounting the titration method because of erratic data, 55 percent of the X and Y set measurements indicated equipment drift equal to or greater than 10 ppm for an approixmate time differential of 30 days.

It is not possible to extract meaningful conclusions about the equipment performance abroad the vessels. Information was not received or instructions given to the vessels pertaining to calibration procedures, operational instructions on the salinity measuring equipment, training of the operators, etc. The salinity sets were delivered to the vessels with minimal instructions: measure the samples, record the appropriate data on the data sheets and on completion, forward them to NOIC.

There is no reason to doubt the stability of the samples and the validity of their values obtained with the PCC. All quality control checks conducted on the PCC and the samples before, during and after the GATE exercise, including intercomparison measurements on similar type of equipment with reputable laboratories, resulted in approximately 1 ppm standard deviation. A report from one of the GATE vessels that a white, crystalline material appeared in the sample, could not be duplicated in NOIC's testing laboratory. Samples of the same solutions, that were forwarded to the GATE vessels, were exposed to a broad range of harsh environmental conditions with negative results. No white crystalline material or any other apparent deterioration of the water was observed during the tests.

ACKNOWLEDGEMENT

The author wishes to express his gratitude and special thanks to Edward Snead, James Sprenke and all those members of NOIC's Metrology Division for their generous support given in the carrying out of this GATE Salinity Intercomparison Project. The collaborative measurements performed by the U. S. Naval Oceanographic Office (J. Sullivan), Woods Hole Oceanographic Institution (K. Schleicker), Canada's Bedford Institute of Oceanography (J. Bedlem) and Institute of Oceanographic Sciences (F. Culkin) in support of this project are also greatly appreciated.

ATTAC

DATA CODE
601
602
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ATTACHMENT 1

DATA CODE KEY

DATA CODE	DATES OF MEASURE	COUNTRY	VESSEL	INSTRUMENT/METHOD
601	2 APR-5 APR	USA	NOIC (Wash)	PCC
602	2 APR-5 APR	USA	NOIC (Wash)	PCC
603	7 JUN-7 JUN	USA	NOIC (Wash)	PCC
604	15 JUL-16 JUL	USA	NOIC (Wash)	PCC
605	7 AUG-7 AUG	USA	NOIC (Wash)	PCC
606	20 AUG-20 AUG	USA	NOIC (Wash)	PCC (250)
607	28 AUG-28 AUG	USA	NOIC (Wash)	PCC (150)
608	17 SEP-17 SEP	USA	NOIC (Wash)	PCC (250)
609	1 OCT-4 OCT	USA	NOIC (Wash)	PCC
610	27 NOV-27 NOV	USA	NOIC (Wash)	PCC (ENV TEST)
611	11 JUN-11 JUN	CANADA	AOL (B10)	Guildline 8400
612	4 SEP-4 SEP	CANADA	AOL (B10)	Guildline 8400
613	26 JUN-27 JUN	USA	NAVOCEANO	Beckman RS-7B
614	27 JUN-27 JUN	USA	NAVOCEANO	Titration (Knudsen)
615	22 AUG-22 AUG	USA	WHOI (Schleicher)	WHOI #3
616	25 FEB-25 FEB	UK	IOS (F. Culkin)	Auto Lab 601MKIII
617	17 JUL-17 JUL	USA	DALLAS (716)	Beckman RS-7B
618	16 JUN-1 JUL	USA	ATLANTIS II	WHOI #2
619	12 JUL-29 JUL	USA	ATLANTIS II	WHOI #2
620	18 JUN-19 JUL	USA	GILLISS	Beckman RS-7C
621	8 AUG-18 AUG	USA	GILLISS	Beckman RS-7C
622	30 JUN-20 AUG	USA	TRIDENT	Plessey 6230N
623	0 JUN-27 JUL	USA	OCEANOGRAPHER	Beckman RS-7B
624	17 JUL-20 SEP	USA	OCEANOGRAPHER	Beckman RS-7B
625	1 JUL-23 JUL	USA	RESEARCHER	Plessey 6230
626	28 AUG-10 OCT	USA	RESEARCHER	Plessey 6230
627	18 AUG-22 AUG	USA	H.J.W. FAY	Auto Lab 601MKIII
628	26 AUG-22 SEP	USSR	PASSAT	GM-65
629	3 SEP-20 SEP	USSR	M. LOMOROSOV	GM-65
630	25 JUL-24 AUG	USSR	OCEAN	GM-65
631	29 AUG-21 SEP	USSR	OCEAN	GM-65
632	30 AUG-22 SEP	USSR	ADADEMIK KURCHATOV	GM-65
633	25 JUN-16 JUL	USSR	MUSSON	GM-65
634	17 AUG-19 SEP	USSR	MUSSON	GM-65
635	25 JUN-16 JUL	USSR	MUSSON	Titration
636	17 AUG-19 SEP	USSR	MUSSON	Titration
637	27 JUL-15 AUG	USSR	PRIBOY	Titration
638	28 AUG-19 SEP	USSR	PRIBOY	Titration
639	28 JUN-16 JUL	USSR	AKADEMIK KOROLOV	Titration
640	28 JUN-16 JUL	USSR	AKADEMIK KOROLOV	Auto-Titration

ATTACHMENT 1 (Continued)

DATA CODE KEY

DATA CODE	DATES OF MEASURE	COUNTRY	VESSEL	INSTRUMENT/METHOD
641	28 JUL-14 AUG	USSR	AKADEMIK KOROLOV	Titration
642	28 JUL-14 AUG	USSR	AKADEMIK KOROLOV	Auto-Titration
643	30 AUG-17 SEP	USSR	AKADEMIK KOROLOV	Titration
644	30 AUG-17 SEP	USSR	AKADEMIK KOROLOV	Auto-Titration
645	24 JUN-29 JUL	USSR	ERNST KRENKEL	GM-65
646	20 AUG-19 SEP	USSR	ERNST KRENKEL	GM-65
647	24 JUN-29 JUL	USSR	ERNST KRENKEL	Titration
648	20 AUG-19 SEP	USSR	ERNST KRENKEL	Titration
649	24 JUN-16 JUL	USSR	PORYV	GM-65
650	28 JUL-16 AUG	USSR	PORYV	GM-65
651	29 AUG-19 SEP	USSR	PORYV	GM-65
652	0 SEP-15 SEP	USSR	DEZHNEV	GM-65
653	29 JUN-15 JUL	FRANCE	JEAN CHARCOT	Beckman RS-7B
654	1 SEP-23 SEP	FRANCE	CAPRICORNE	Plessey 6230
655	26 JUN-19 SEP	BRAZIL	ALMIRANTE SALDANHA	Plessey 6230N
656	27 JUL-17 AUG	BRAZIL	ALMIRANTE SALDANHA	Plessey 6230N
657	31 JAN-31 JAN	FRG	METEOR PLANET DOHRN	Beckman RS-7B
658	28 JUN-17 SEP	NETHERLANDS	ONVERSAAGD	Auto Lab 601MKIII
659	2 SEP-17 SEP	UK	DISCOVERY	Plessey 6230
660	27 AUG-28 AUG	UK	DISCOVERY	Auto Lab 601MKIII
661	1 JUL-30 JUL	CANADA	QUADRA	Guildline 8400 #2
662	30 JUL-22 SEP	CANADA	QUADRA	Guildline 8400 #2
663	28 AUG-28 AUG	GDR	A.V. HUMBOLDT	Auto Lab 601MKIII