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NOAA Technical Report OTES 7

# **Intercomparison of Primary and Secondary Standard Seawater Samples**

Washington, D.C.  
March 1982

**U.S. DEPARTMENT OF COMMERCE**  
**National Oceanic and Atmospheric Administration**  
Ocean Technology and Engineering Services



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Michael A. Basileo  
Meteorology Division  
Engineering Support Office

Alisa F. Akimova  
Analytical Laboratory  
P. P. Shirshov Institute of Oceanology  
U.S.S.R. Academy of Sciences

U.S./U.S.S.R. Working Group of Experts  
on Intercalibration and Standardization  
of Oceanographic Instrumentation and  
Methods

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## FOREWORD

Recognizing the importance of more complete knowledge and rational use of the world oceans, the governments of the United States and the Union of Soviet Socialist Republics signed, on June 19, 1973, the US/USSR Agreement on Cooperation in Studies of the World Ocean. This agreement specified intercalibration and standardization of oceanographic instrumentation and methods as one area of cooperation. The US/USSR Working Group of Experts on Intercalibration and Standardization of Oceanographic Instrumentation and Methods was established during the February, 1974 US/USSR Joint Committee Meeting in Washington, DC. During subsequent meetings of this Working Group (May, 1975 and April, 1977), it was decided to focus on three major marine parameters -- salinity/conductivity, temperature, and current velocity -- in order to establish the level of measurement comparability. Initial efforts have involved investigations of laboratory standards, facilities, and methods used in the two countries as reference for their field measurement programs.

Dr. J. L. Solomon  
Director, Engineering Support Office  
Office of Ocean Technology and Engineering Services  
National Oceanic and Atmospheric Administration

Dr. M. P. Nesterova  
Head of Analytical Laboratory  
P. P. Shirshov Institute of Oceanology  
USSR Academy of Sciences

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# INTERCOMPARISON OF PRIMARY AND SECONDARY STANDARD SEAWATER SAMPLES

Michael A. Basileo  
Meteorology Division  
Engineering Support Office  
and

Alisa F. Akimova  
Analytical Laboratory  
P.P. Shirshov Institute of Oceanology  
USSR Academy of Sciences

**ABSTRACT.** A cooperative program for determining the comparability of laboratory salinity measurements was conducted by the U.S. and USSR. This intercomparison involved the exchange and joint measurements of secondary standard seawater samples at 12 nominal salinities ranging from 5 to 40 parts per 1,000. Described are the secondary seawater standards preparation, measurement results, and conclusions.

## INTRODUCTION

This report documents the results of a salinity measurement intercomparison conducted as part of the US/USSR Agreement on Cooperation in Studies of the World Ocean. The intercomparison involved the exchange and measurement of samples of primary and secondary seawater standards. Sample preparation and measurement in the United States was performed by the Test and Evaluation Laboratory (T&EL), which is a component of the National Oceanic and Atmospheric Administration under the National Ocean Survey<sup>1</sup>. Sample preparation and measurement in the Soviet Union were conducted by the Analytical Laboratory of the P. P. Shirshov Institute of Oceanology, USSR Academy of Sciences, Moscow.

Primary standards were included in the exchange since it has been demonstrated that batch-to-batch variations in these standards do exist at a level comparable to the accuracy levels of the intercomparison. The primary standards provided by T&EL were IAPSO standard seawater, prepared by the Standard Seawater Service at the Institute of Ocean Science, Wormley, Surrey, Great Britain. The USSR primary standards were prepared by the Analytical Laboratory.

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<sup>1</sup> In October, 1980, as part of a reorganization of ocean engineering activities in NOAA, T&EL became the Engineering Support Office under the Office of Ocean Technology and Engineering Services.



Secondary seawater standards cover a wide salinity range and are generally used to calibrate portable laboratory salinometers. The salinity values of the secondary standards are established with respect to primary standard seawater. In this intercomparison, each laboratory prepared secondary standards at nominal salinities of 5, 10, 15, 20, 25, 30, 32, 34, 35, 36, 38 and 40 parts/thousand (ppt). The values were selected to provide a wide salinity range and to also emphasize the typical oceanographic range of 30 to 40 ppt. Triplicate samples were provided by each laboratory for both the primary and secondary standards.

The Precision Conductivity Comparator (PCC)<sup>2</sup> was used as reference standard for the measurements performed at T&EL. The Analytical Laboratory (AL) used an inductive salinometer produced by Industria Manufacturing Engineers Pty., Ltd., of Australia. Both laboratories utilized the UNESCO tables<sup>3</sup> to convert conductivity ratio and temperature to salinity of the unknown samples.

#### PREPARATION OF SECONDARY SEAWATER STANDARDS

##### A. Test and Evaluation Laboratory

Secondary seawater standards are prepared utilizing open ocean water, typically 34 to 36 ppt, as a base. The water is collected by means of a submersible pump, normally from depths of 5 to 8 m, and transported back to the laboratory in 60 liter polypropylene containers. The preparation and bottling operations are done in a batch mode -- i.e., water of a particular salinity is prepared, then immediately bottled and sealed before preparation of the next salinity value is started. This method has demonstrated acceptable within-batch uniformity. The desired nominal salinity is achieved either by dilution with deionized water or by concentration utilizing low temperature (40°C) evaporation. The seawater is then filtered by pumping through a 0.3  $\mu$ m cold sterilizing filter. Glass bottles, which have been acid soaked prior to washing to remove residual salts, are used as sample containers; sample size is approximately 350 ml. The bottles are sealed with a thermoplastic film, aluminum foil and a bottle cap.

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<sup>2</sup> Sprenke, J.J., "Precision Conductivity Measurements," Proceedings of the Fourth STD/Ocean Systems Conference, Plessey Environmental Systems Inc., San Diego CA, January 1977.

<sup>3</sup> UNESCO 1971 International Oceanographic Tables, Volume 1, National Institute of Oceanography of Great Britain and UNESCO.



Determination of actual batch salinity and within-batch uniformity is made by measurements with the PCC. The first two and last two samples bottled in each batch are measured to verify acceptable uniformity. These measurements are averaged with three more samples from within the batch to establish the actual batch salinity value. In addition to these initial measurements, samples from each batch are reserved to allow for periodic measurements which verify the long-term stability of the bottled samples.

Analysis of the preparation and measurement process uncertainties indicates that the stated batch salinity values are accurate to within  $\pm 2$  ppm ( $3\sigma$ ) relative to IAPSO standard seawater. Long-term stability measurements have indicated within-batch drifts of less than 0.5 ppm per year.

#### B. Analytical Laboratory

Secondary seawater standards are prepared from ocean waters with salinity exceeding 35 ppt. Water is collected in the north-eastern Atlantic from areas not subjected to ice formation and free from the influence of river waters. A pump is used to collect the seawater from depths of 1-2 m. Following filtration through a 20-25  $\mu$ m glass filter under laboratory conditions, water is adjusted to the required salinity value either by dilution with distilled water, or by evaporation at 20-25°C.

After salinity adjustment, the seawater is flooded into a clean container and then distributed into ampoules. The ampoules are made of a special glass similar to that used for producing working series of primary standard seawater. The glass was chosen in accordance with requirements relating to non-contamination and stability, based on the results of studies of its physio-chemical properties. Water is discharged simultaneously into 60 ampoules, each containing about 350 ml. The ampoules are sealed immediately after filling.

The batch salinity and within-batch uniformity is determined by measurement of samples prepared at the beginning, the middle and final stages of the ampoule filling process. In addition, a number of samples from each series are stored away for subsequent periodic inspection and measurement. The salinity of the prepared water is determined by means of: the Guildline AUTOSAL model 8400; the inductive salinometer produced by the Australian firm Industria Manufacturing Engineers Pty., Ltd.; the inductive Soviet-made salinometers model GM-65; and in some cases, by using argentometric titration (using silver) -- Van Landingham's method.



Van Landingham's modified method, used mainly for certifying the primary seawater standards, is based on the use of phenosafranine (3,6-diaminophenylphenacynchloride) as an adsorptive indicator. This indicator provides a distinct and fast color change near the steriometric point, a high-contrast and stepwise color transition from bright rosy to light blue. In the course of the titration, AgCl suspended in the solution adsorbs seawater  $\text{Cl}^-$  ions and undergoes negative charging. At the equivalent point, some of the excess  $\text{Ag}^+$  ions are absorbed by AgCl particles and become positively charged; the particles will attract anions of the adsorptive indicator causing the change in color. Chlorinity of the unknown samples is determined by a comparative volume-weighing method according to the difference of consumed  $\text{AgNO}_3$  solutions used on the titration of standard seawater and the tested sample.

Two spherical weight burettes of approximately 80 ml volume are simultaneously filled to the upper mark. One is filled with standard seawater, the other with the unknown sample. Two other weight burettes of similar volume are filled with a strong  $\text{AgNO}_3$  solution (prepared such that 1 kg of the solution contains an amount of silver equivalent to the halogen content of 1 kg of seawater with a chlorinity of about 19.45 ppt). Next, two weight burettes are filled with a weak  $\text{AgNO}_3$  solution, prepared by diluting the strong solution in a 1:10 ratio (weak  $\text{AgNO}_3$  solutions cannot be stored for long without degradation; the solution must be freshly prepared prior to each series of seawater analyses). The total weight of each burette is determined by weighing with an accuracy of 0.1 mg. The seawater burette is drained to its lower mark into the titration container. Titration, at a slow mixing rate (about 300 rotations per minute, using an electromagnetic mixer), is started by adding the strong  $\text{AgNO}_3$  solution. The burette contents are added slowly so that the change of color at the pouring site is distinctly visible. At this point, the mixing rate is increased to the maximum, and titration is continued in a drop-by-drop manner until the coloration instantly changes from rosy-blue to blue. Next, 1 or 2 drops of the seawater is added to the titration container from the burette, resulting in a color change back to rosy-blue. Titration is resumed using the weak  $\text{AgNO}_3$  solution at the maximum mixing rate until the abrupt color change of the titrated solution occurs. This completes the titration process; the burettes with remaining seawater and  $\text{AgNO}_3$  solutions are now weighed.



Table 1 provides comparative chlorinity data for titrations of standard seawater samples according to Van Landingham's method, measurement of relative electroconductivity, and computed differences between the two methods.

TABLE 1.  
Chlorinity Measurement Results by Two Methods

Sample Number	Chlorinity by Titration (1) ppt	Chlorinity by Electroconductivity (2) ppt	Difference (1) - (2) ppt
1.	19.387	19.388	-0.001
2.	19.381	19.379	+0.002
3.	19.378	19.381	-0.003
4.	19.374	19.376	-0.002
5.	19.371	19.369	+0.002
6.	19.366	19.364	+0.002

The electroconductivity measurements were made with an inductive salinometer produced by Industria Manufacturing Engineers Pty. Ltd. The salinometer was calibrated using IAPSO standard seawater. As indicated in Table 1, the two different measurement methods provide quite comparable results for the determination of seawater chlorinity.

#### MEASUREMENT RESULTS

##### A. Test and Evaluation Laboratory

In June 1978, 36 samples of secondary standard seawater and 3 samples of primary standard seawater provided by the Analytical Laboratory were measured with the PCC at T&EL. The reference standard used was Batch P75 (prepared March 1977) of IAPSO standard seawater. Table 2 gives the average salinity of each triplicate set, along with the sample standard deviation.

TABLE 2.  
T&EL Measurement Results for AL Samples  
(IAPSO Batch P75 used as reference)

Batch Number	Average Salinity ppt	Std. Dev. (3 samples) ppm	Batch Number	Average Salinity ppt	Std. Dev. (3 samples) ppm
C1	4.9836	0.06	C8	33.9990	0.15
C2	9.9895	0.29	C9	35.0050	0.21
C3	14.9667	0.21	C10	36.0099	0.72
C4	19.9987	0.46	C11	38.0181	0.52
C5	24.9932	0.15	C12	40.0310	0.15
C6	29.9966	0.31			
C7	32.0057	0.49	C86	34.9937	0.40

Previously, Batch P66 (prepared July 1974) of IAPSO standard seawater was used as the salinity reference at T&EL. The salinity values of secondary standards provided to the Analytical Laboratory were defined with respect to Batch P66; three samples of Batch P66 were provided to AL. T&EL's supply of Batch P66 has since been depleted, necessitating the use of Batch P75 as the reference for the measurements shown in Table 2.

Table 3 displays the comparison between the T&EL measurements and the AL reported values. It was first necessary, however, to convert the T&EL measurements reported in Table 2 to an IAPSO Batch P66 reference. Measurements were made with the PCC to compare Batch P75 to Batch P66. These measurements showed that the salinity of Batch P75 (based on conductivity ratio measurement with P66 as reference) was 1.3 ppm higher than indicated by the stated chlorinity value. This difference was applied to convert the measured values (Table 2) to a Batch P66 reference, which will provide consistency with the earlier measurements in this intercomparison.



TABLE 3.  
Comparison of T&EL Measurements with AL Reported Values  
(IAPSO Batch P66 used as reference)

Batch Number	T&EL Measured Salinity ppt	AL Reported Salinity ppt	Difference (AL)-(T&EL) ppm
C1	4.9838	4.984	0.2
C2	9.9899	9.991	1.1
C3	14.9673	14.967	-0.3
C4	19.9994	20.003	3.6
C5	24.9941	24.992	-2.1
C6	29.9977	29.999	1.3
C7	32.0069	32.008	1.1
C8	34.0003	34.004	3.7
C9	35.0018	35.004	2.2
C10	36.0112	36.012	0.8
C11	38.0195	38.021	1.5
C12	40.0325	40.036	3.5
C86	34.9950	34.9983*	3.3

\* Computed from (1.80655)(Chlorinity)

The difference indicated in Table 3 for the C86 primary standard seawater (3.3 ppm) is in excellent agreement with earlier measurements. In March 1977, five samples of Batch C86 were measured using Batch P66 as a reference; the resultant difference was 3.2 ppm.

## B. Analytical Laboratory

Thirty-six samples of secondary standard seawater prepared by T&EL were measured at the AL using the inductive salinometer produced by Industria Manufacturing Engineers Pty., Ltd. The IAPSO primary standard seawater (Batch P66) provided by T&EL was used as the reference. Table 4 displays the average salinity of each triplicate set of measurements, along with the sample standard deviation.

TABLE 4  
AL Measurement Results for T&EL Samples  
(IAPSO Batch P66 used as reference)

Batch Number	Average Salinity ppt	Std. Dev. (3 Samples) ppm	Batch Number	Average Salinity ppt	Std. Dev. (3 Samples) ppm
M2-01	5.064	2	M2-07	32.013	4
M2-02	10.058	5	M2-08	34.008	5
M2-03	15.337	4	M2-09	35.079	2
M2-04	20.050	5	M2-10	36.069	1
M2-05	25.275	0	M2-11	38.032	1
M2-06	29.951	5	M2-12	40.177	1

Table 5 presents the AL measured values compared to the T&EL reported values.



TABLE 5  
Comparison of AL Measurements with T&EL Reported Values  
(IAPSO Batch P66 used as reference)

Batch Number	AL Measured Salinity ppt	T&EL Reported Salinity ppt	Difference (AL)-(T&EL) ppm
M2-01	5.064	5.0631	0.9
M2-02	10.058	10.0589	-0.9
M2-03	15.337	15.3399	-2.9
M2-04	20.050	20.0496	0.4
M2-05	25.275	25.2780	-3.0
M2-06	29.951	29.9517	-0.7
M2-07	32.013	32.0131	-0.1
M2-08	34.008	34.0058	2.2
M2-09	35.079	35.0771	1.9
M2-10	36.069	36.0690	0.0
M2-11	38.032	38.0286	3.4
M2-12	40.117	40.1128	4.2

#### CONCLUSIONS

The difference observed between the primary standards used by the two laboratories are within levels that have been observed between separate batches of IAPSO standard seawater. Thus, it is concluded that there is not a significant systematic difference between the primary seawater standards used in the two countries.

The measurement differences for the secondary standard seawater samples (last columns of Tables 3 and 5) have been plotted in Figure 1. All measurement differences lie within the range of  $\pm 5$  ppm; thus, the salinity

differences observed in the measurement intercomparison seem acceptable and should not be a source of significant discrepancy in joint field experiments which involve salinity measurements made with salinometers. It should, however, be noted that uncertainties of field data acquired with in situ instrumentation are dependent on calibration procedures and instrument characteristics in addition to primary and secondary standards.

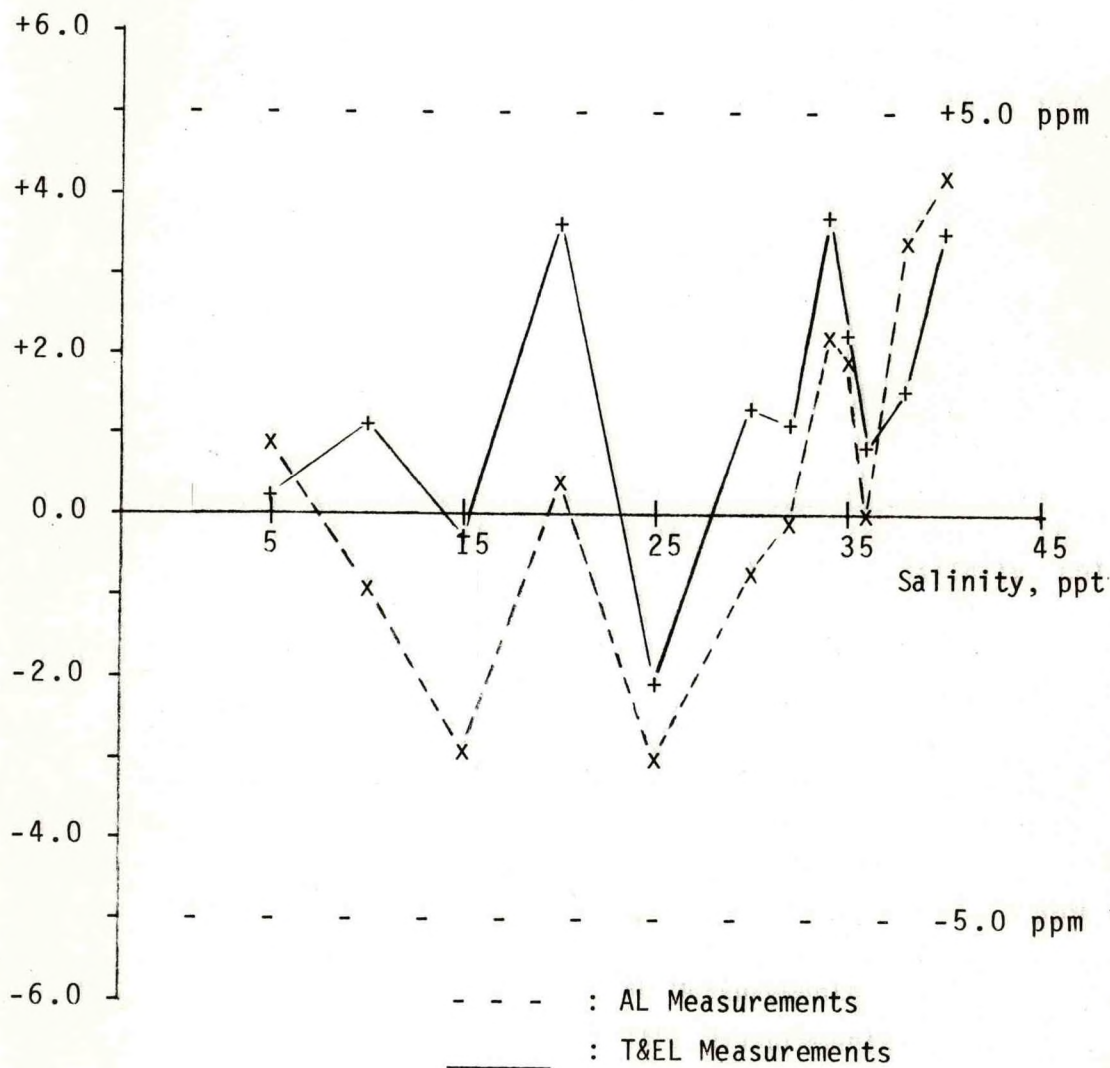


Figure 1. SALINITY MEASUREMENT DIFFERENCES



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