

The reliability of standard seawater as an electrical conductivity standard

Standard seawater
Salinity
Conductivity
Chlorinity
Density
Eau de mer normale
Salinité
Conductivité
Chlorinité
Densité

Alain Poisson ^a, Tim Dauphinee ^b, Charles K. Ross ^c, Fred Culkin ^d.

^a Laboratoire de Physique et Chimie Marines, Université Pierre-et-Marie-Curie, Tour 24, 4, place Jussieu, 75230 Paris Cedex 05.

^b National Research Council, Montreal Road, Ottawa 7, Ontario, K1A OR6, Canada.

^c Atlantic Oceanographic Laboratory, Bedford Institute of Oceanography, Dartmouth, Nova Scotia, Canada.

^d Institute of Oceanographic Sciences, Wormley, Godalming, Surrey GU8 5UB, England.

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ABSTRACT

Bench salinometers used to determine salinity of seawater are calibrated with standard seawater, although this latter is certified in chlorinity only. This procedure assumes that the chlorinity/conductivity relationship is the same for all the batches of standard seawater.

A comparison of different samples from 26 batches of standard seawater made by four laboratories strongly confirm Poisson's findings: the variability in the chlorinity/conductivity relationship for standard seawater is significant. The greatest discrepancy (batch P49) is equivalent to 0.008‰ in salinity, but the most positive fact of these four independent studies is that the relative conductivity salinities remain essentially the same within about ± 0.003 ‰ for all the batches of the 1969-1975 period which include the last batches prepared in Denmark and those prepared now in England. The measurements of density, pH, silicate and dissolved organic carbon do not suggest any clear explanation of measured discrepancy in the chlorinity/conductivity relationship.

In summary a recommendation is made: standard seawater should be calibrated as soon as possible in conductivity relative to a potassium chloride solution.

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RÉSUMÉ

Fiabilité de l'eau de mer normale en tant qu'étalon de conductivité électrique

Les salinomètres électriques utilisés pour déterminer la salinité de l'eau de mer sont étalonnés à l'aide de l'eau de mer normale, bien que celle-ci ne soit certifiée qu'en chlorinité. Ceci implique que la relation chlorinité/conductivité est la même pour tous les stocks d'eau de mer normale.

La comparaison de différentes ampoules provenant de 26 stocks d'eau de mer normale effectuée par quatre laboratoires a confirmé les résultats de Poisson : pour une même chlorinité, la conductivité de l'eau de mer normale de certains stocks étudiés varie dans des limites non négligeables. Le stock P49 présente la variation maximale, équivalente à environ 0,008 ‰ en salinité, mais le résultat le plus important de ces quatre études indépendantes est que les salinités relatives déduites de la conductivité restent pratiquement les mêmes à $\pm 0,003$ ‰ près, pour tous les stocks fabriqués entre 1969 et 1975 dans lesquels sont entre autre inclus les derniers stocks préparés au Danemark et ceux

préparés actuellement en Angleterre. La mesure de la densité des différents échantillons, ainsi que celle du pH et de la teneur en silicate ou en carbone organique dissous ne permet pas d'expliquer clairement les variations observées en conductivité.

On suggère en conclusion que l'eau de mer normale soit étalonnée le plus rapidement possible en conductivité par rapport à une solution de chlorure de potassium.

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For more than seventy years the standard generally adopted for the determination of salinity has been standard seawater. This standard is prepared from North Atlantic surface water and is supplied in sealed glass ampoules by the Standard Seawater Service which operated from Copenhagen, Denmark until 1975 and since then from IOS Wormley, England. Each batch is certified in chlorinity determined by a high precision gravimetric/potentiometric method, the standard deviation of which is 0.0003‰ in chlorinity. In the past 15-20 years salinity has been widely determined by measurement of electrical conductivity. The usual method consists of calibrating a salinometer with standard seawater by trimming the instrument to read the conductivity corresponding to the chlorinity of the standard, a procedure which assumes that the chlorinity/conductivity relationship is the same for all batches of the standard.

A comparison of the conductivities of seven batches of standard seawater, relative to 0.1 normal potassium chloride solution by Poisson (1975) revealed that the conductivity of some batches is higher than that calculated from the certified chlorinity. In the case of one batch (P49) this discrepancy was equivalent to almost 0.01‰ in salinity. These findings, which confirm the conductivity measurements of Park (1964), were viewed with concern by the Joint Panel on Oceanographic Tables and Standards who recommended that the measurements should be repeated by other laboratories. Consequently, samples from 26 batches of standard seawater prepared during the period 1962-1975 were distributed to 4 laboratories (only 21 batches to Dauphinee), with a request that the conductivity of each should be measured relative to batch P64. Two laboratories also measured density and two laboratories measured pH and silicate. This paper is an attempt to summarize the findings, and to propose some recommendations on the future standardisation of the standard seawater. The results of one laboratory have been published independently (Millero *et al.*, 1977).

METHODS

All the measurements made by the other three laboratories were carried out within a short time period using the following procedures:

Determination of conductivity ratios

Poisson measured the double conductivity ratio on a model 8400 Guidline "Autosal" salinometer at a nominal temperature of 24°C. One ampoule of batch P64 was used at the beginning of the run to calibrate the salinometer; during the run of measurements, no drift was observed. The sample was transferred directly from the ampoule *via* a teflon tube; three readings were made after rinsing the cell twice. The maximum difference between the three readings was 3×10^{-5} in the double conductivity ratio. The ampoules were immediately sealed with a "cork" of parafilm and stored in a vertical position to wait for the density measurements which were made during the afternoon of the same day.

Ross measured the conductivity ratios on a model 8400 Guidelines "Autosal" salinometer. The bath temperature was set at a nominal value of 21°C and measured before and after the determinations with Rosemount 162C platinum resistance thermometer (calibration traceable to National Bureau of Standards) and the value was 21.004°C. Previous experience with this instrument would lead us to expect that the temperature remained constant to within 1×10^{-3} degree. The ambient room temperature during the measurements was 20 ± 0.5 °C. The measuring bridge was left at settings found to be consistent, on the average, from previous usage.

All determinations were completed within a period of five hours. The sequence of the conductivity ratios of P64 were determined as the 1st, 2nd, 12th, 22nd and 30th samples.

Each sample was flushed through the cell twice and readings were taken on the 3rd, 4th and 5th fillings.

The maximum difference amongst the three readings was 4×10^{-5} in the double conductivity ratio.

All the measurements made by Dauphinee were taken at 24°C on the original NRC design (Dauphinee *et al.*, 1975) salinometer (a predecessor of the Guidline commercial models) using the same suppression setting throughout and reading differences from the digital voltmeter readout. The 2.000 00 reading for 35 ‰ seawater was adjusted some days earlier using samples of P69 and was left untouched throughout the measurements. All the readings were carried out in a 4 hours period one afternoon after a fairly extensive preliminary checkout of the salinometer. Each measurement represents the average of all of four or more readings of samples from the same ampoule.

Determination of relative densities

Poisson measured the relative densities of the different batches with a vibrating densimeter (Sodev, model 01D) by comparing the resonance frequency of a tube containing successively a reference liquid and the sample liquid. This apparatus is described elsewhere (Picker *et al.*, 1974); the temperature of the cell was stabilised at $24.985 \pm 0.001^\circ\text{C}$ with a closed-loop water temperature controller (Sodev, model CT-B) and measured with a platinum resistance thermometer and a precision AC double bridge (ASL, model H7).

The constant of the apparatus was determined with doubly distilled water of known density provided by the Bureau International des Poids et Mesures, Paris, and with one ampoule of standard seawater (P64-F). The Table of absolute density of Smow and the value given by the Bipm were used to obtain the density of water at the temperature of measurements. Knudsen's (1901) equation was used to calculate the density of the reference ampoule of seawater (P64-F). The variation of the relative density of the other batches relative to this ampoule was determined by using the relation:

$$d - d_0 = k(\tau^2 - \tau_0^2),$$

where k is the constant of the densimeter, d , the density of seawater; d_0 , the density of pure water and τ the corresponding period of the natural oscillation of the tube. The rest of the samples were immediately stored in PVC flasks after each measurement of density.

Determination of pH

The pH of the samples was measured by Poisson the next day with a Radiometer PHM 64 digital pH meter using a combined pH electrode. Two buffers were used to calibrate the pH meter: Radiometer type 1336 (pH = 9.18) and type 1316 (pH = 4.01). The samples were immersed in an open thermostat at 24.0°C, then stirred with a magnetic stirrer. The temperature of the samples was measured during the pH measurement.

Ross measured the pH of the standard seawater samples with an Orion 801 digital pH meter using a glass/calomel electrode system. The measurements were taken at 25°C

in a thermostatted cell. The pH meter was calibrated against a 7.415 buffer solution. The samples were stirred with a magnetic stirrer and the measurements were made after 2 minutes.

Determination of silicate

Poisson used the method described by Strickland and Parsons (1968) to determine the concentration of silicate in the different standard seawater samples. A Beckman DU-2 spectrophotometer was used to measure the extinction. The samples with a concentration greater than $50 \mu\text{g at.l}^{-1}$ were diluted 5 to 1 using a synthetic seawater. Two standard solutions of 44.5 and $17.8 \mu\text{g at.l}^{-1}$, prepared from a standard solution of silicate (Merck, titresol 9947), were used to calibrate the spectrophotometer.

Ross determined the silicate concentrations with a Technicon Auto Analyzer II based on the reduction of silicomolybdate in acidic solution to "molybdenum blue" by ascorbic acid (Industrial Method No. 186-72 W, March 1973, Technicon Industrial Systems, Tarrytown, NY). Standard solutions used were obtained from Sagami Chemical Research Centre in concentrations of 5.0, 10.0 and $25.0 \mu\text{g at.l}^{-1}$. A straight line passing through the origin was fitted to the standardization. Substandard solutions with nominal concentrations of 4.0, 20.0 and $50.0 \mu\text{g at.l}^{-1}$ were determined at the beginning and end of each set of determinations. Standard seawater samples with concentration greater than $66.5 \mu\text{g at.l}^{-1}$ were diluted 10 to 1 with synthetic seawater and re-analyzed the next day.

Determination of dissolved organic carbon

Dissolved organic carbon was determined by R. J. Moore, Department of Oceanography, Southampton University, using a modification of the automated method described by Collins and Williams (1977) which involves photochemical oxidation of the sample followed by infrared determination of the CO_2 produced.

RESULTS AND DISCUSSION

All the conductivity measurements are adjusted so that the mean value of P64 for each set has a double conductivity ratio of 2.000 37. The conductivity salinity (S_{cond}) derived from the International Oceanographic Tables (Unesco, 1966) and the chlorinity salinity (S_{Cl}) derived from the expression $S = 1.80655 \text{ Cl}$ and labelled chlorinity are given in Table 1 with date of preparation and the values of chlorinity determined by the Standard Seawater Service. To compare these data with each other and with the data of Park, Poisson and Millero, the differences between the conductivity salinity and the chlorinity salinity are calculated and presented in Tables 2 and 3. The results of Park are adjusted by taking the mean value of the difference $S_{\text{cond}} - S_{\text{Cl}}$ of batch P37 of the other measurements as reference.

Table 1
Conductivity salinity and chlorinity salinity of different batches of standard seawaters, taking P64 as reference.

Batch	Date of preparation	Chlorinity	S _{Cl}	Conductivity reading (offset from 2.000 00 × 10 ⁴)			S _{cond}			Average (g)
				Poisson	Dauphinee	Ross	Poisson	Dauphinee	Ross	
P37	16-12-62	19.368 6	34.990 3	- 51	- 44	- 45	34.990 0	34.991 4	34.991 2	34.990 9
P38	17-12-62	19.372 6	34.997 6	- 7	- 11	- 6	34.998 6	34.997 8	34.998 8	34.998 4
P39	07-04-63	19.371 9	34.996 3	- 15	- 18	- 11	34.997 1	34.996 5	34.997 8	34.997 1
P40	27-10-63	19.375 4	35.002 6	20		22	35.003 9		35.004 3	35.004 1
P41	7/8-11-63	19.373 0	34.998 3	6	8	10	35.001 2	35.001 6	35.002 0	35.001 6
P44	13-02-66	19.373 8	34.999 7	19		22	35.003 7		35.004 3	35.004 0
P46	04-12-66	19.376 8	35.005 2	26	31	31	35.005 1	35.006 1	35.006 1	35.005 8
P47	16-04-67	19.374 2	35.000 5	1		20	35.000 2		35.003 9	35.002 0
P48	16-04-67	19.375 3	35.002 4	5	20	22	35.001 0	35.003 9	35.004 3	35.003 1
P49	12-11-67	19.374 0	35.000 1		34	39		35.006 7	35.007 6	35.007 1
P50	6/7-4-68	19.375 3	35.002 4	39	36	30	35.007 6	35.007 1	35.005 9	35.006 9
P51	15/16-2-69	19.374 5	35.001 0	38	35	36	35.007 4	35.006 9	35.007 1	35.007 1
P52	18/19-10-69	19.370 6	34.994 0	- 15	- 18	- 10	34.997 1	34.996 5	34.998 0	34.997 2
P53	02-03-70	19.375 3	35.002 4	13		13	35.002 5		35.002 5	35.002 5
P54	22-11-70	19.380 0	35.010 9	50	48	49	35.009 8	35.009 4	35.009 6	35.009 6
P55	28-11-70	19.378 2	35.007 7	32	33	36	35.006 3	35.006 5	35.007 1	35.006 6
P56	12/13-6-71	19.375 1	35.002 1	17			35.003 3			35.003 3
P59	06-08-72	19.377 0	35.005 5	42	36	37	35.008 2	35.007 1	35.007 2	35.007 5
P60	25-11-72	19.376 5	35.004 6	19	25	20	35.003 7	35.004 9	35.003 9	35.004 2
P61	26-11-72	19.378 5	35.008 2	43	{ 45 } (a)	48	35.008 4	35.008 8	35.009 4	35.008 9
P62	27-05-73	19.377 6	35.006 6	32	32	32	35.006 3	35.006 3	35.006 3	35.006 3
P64	01-12-73	19.378 0	35.007 3	{ 37 } (b)	{ 37 } (c)	{ 37 } (f)	35.007 3	35.007 3	35.007 3	35.007 3
P66	27-07-74	19.367 6	34.988 5	- 55		- 42	34.989 2		34.991 8	34.990 5
P67	10-08-74	19.373 5	34.999 2	2	3	9	35.000 4	35.000 6	35.001 8	35.000 9
P68	08-03-75	19.371 8	34.996 1	- 15	- 15	- 9	34.997 1	34.997 1	34.998 2	34.997 5
P69	27-03-75	19.371 3	34.995 2	- 19	{ - 17 } (e)	- 12	34.996 3	34.996 7	34.997 6	34.996 9
P70	18-09-75	19.374 8	35.001 5	20	19	{ 23 } (f)	35.003 9	35.003 7	35.004 5	35.004 0
P71	11-10-75	19.374 1	35.000 3	14	11	15	35.002 7	35.002 2	35.002 9	35.002 6

(a) Average of 4 measurements. (c) Average of 4 measurements. (e) Average of 6 measurements. (g) Including the results of
(b) Average of 6 measurements. (d) Average of 5 measurements. (f) Average of 4 measurements. Millero *et al.*

Table 2
Differences between conductivity salinity and chlorinity salinity of different batches of standard seawaters taking P64 as reference.

Batch	(S _{cond} - S _{Cl}) × 10 ⁴							
	Poisson	Dauphinee	Ross	Millero (1977)	Park (1964)	Poisson (1975)	Average	Range
P37	- 3	11	9	- 1	4	3	4	14
P38	10	2	12	6			7	10
P39	8	2	15	13			9	13
P40	13		17	10			13	7
P41	29	33	37	37			34	8
P44	40		46	40			42	6
P46	- 1	9	9	14			8	15
P47	- 3		34	24			18	37
P48	- 14	15	19	19			10	33
P49		66	75	72		88	75	22
P50	52	47	35	48		59	48	24
P51	64	59	61	61			61	5
P52	31	25	40	24			30	16
P53	1		1	11		29	10	28
P54	- 11	- 15	- 13	- 13			- 13	4
P55	- 14	- 12	- 6	- 5			- 9	9
P56	12					36	24	24
P59	27	16	17	19			20	11
P60	- 9	3	- 7	9			- 1	18
P61	2	6	12	16			9	14
P62	- 3	- 3	- 3	0		- 11	- 4	11
P64	0	0	0	0		0	0	0
P66	7		33	17			19	26
P67	12	14	26	28			20	16
P68	10	10	21	9			12	12
P69	11	15	24	12			15	13
P70	24	22	30	27			26	8
P71	24	19	26	17			21	9

Table 3

Differences between conductivity salinity and chlorinity salinity of earlier batches of seawaters measured by Park, taking P64 as reference.

Batch	Date	Chlorinity	S_{Cl}	S_{cond}	$(S_{cond} - S_{Cl}) \times 10^3$
P15	30-06-37	19.393	35.034	35.032	- 2
P18	04-12-49	19.376	35.004	35.016	12
P24	06-05-56	19.378	35.007	35.011	4
P25	06-01-57	19.378	35.007	35.007	0
P26	08-12-57	19.367	34.987	34.990	3
P29	27-09-59	19.370	34.993	35.010	17
P30	28-02-60	19.370 0	34.992 8	34.995	2
P31	28-08-60	19.374 7	35.001 4	35.002	1
P32	08-01-61	19.376 2	35.004 1	35.006	2
P35	04/05-03-61	19.373 0	34.998 3	35.004	6
P36	17/18-09-62	19.375 1	35.002 1	35.004	2
P37	16-12-62	19.368 6	34.990 3	34.991	1

During Poisson's measurements, one ampoule of the batch P62 had a difference of $746 \times 10^{-4} \text{‰}$ in salinity and a difference of 57 ppm in density; its pH was 8.04 and its silicate concentration $39.4 \mu\text{g at.l}^{-1}$. This was probably a faulty ampoule and these results are not included in the Tables.

All sets of determinations strongly confirm the original findings of Park and Poisson that there is considerable variability in the chlorinity/conductivity relationship for standard seawater. The salinity difference ($S_{cond} - S_{Cl}$) has a range of $88 \times 10^{-4} \text{‰}$ over the analyzed batches prepared between 1962 and 1975 (Fig. 1). Within a given batch the average range of salinity difference values is $12 \times 10^{-4} \text{‰}$ over 20 batches for which a complete set of determinations were made by all four investigators using the same technique. This average is consistent with the average range found by each investigator performing replicate determinations on the same batch. It is not possible to determine how much of this variation

is due to errors in measuring the conductivity salinity and how much is due to real difference between ampoules from the same batch of standard seawater.

The choice of P64 as the comparison standard is arbitrary and means that the origin of the salinity difference scale is undetermined. However, it is readily apparent that for batches P49, P50 and P51 the conductivity salinity is considerably higher than the chlorinity salinity relative to the average of the other batches. The salinity discrepancy is slightly less but still greater than desirable for batches P44, P54, P41 and P55. All other batches analyzed remain within $20 \times 10^{-4} \text{‰}$ of the average salinity difference. No correlation was found between the salinity difference and the age of the standard seawater.

The two sets of measurements of pH and silicate concentration are shown in Table 4. The agreement between the 2 sets of pH measurements is very good except for P50 (pH = 7.82 and 8.33). For this batch, silicate

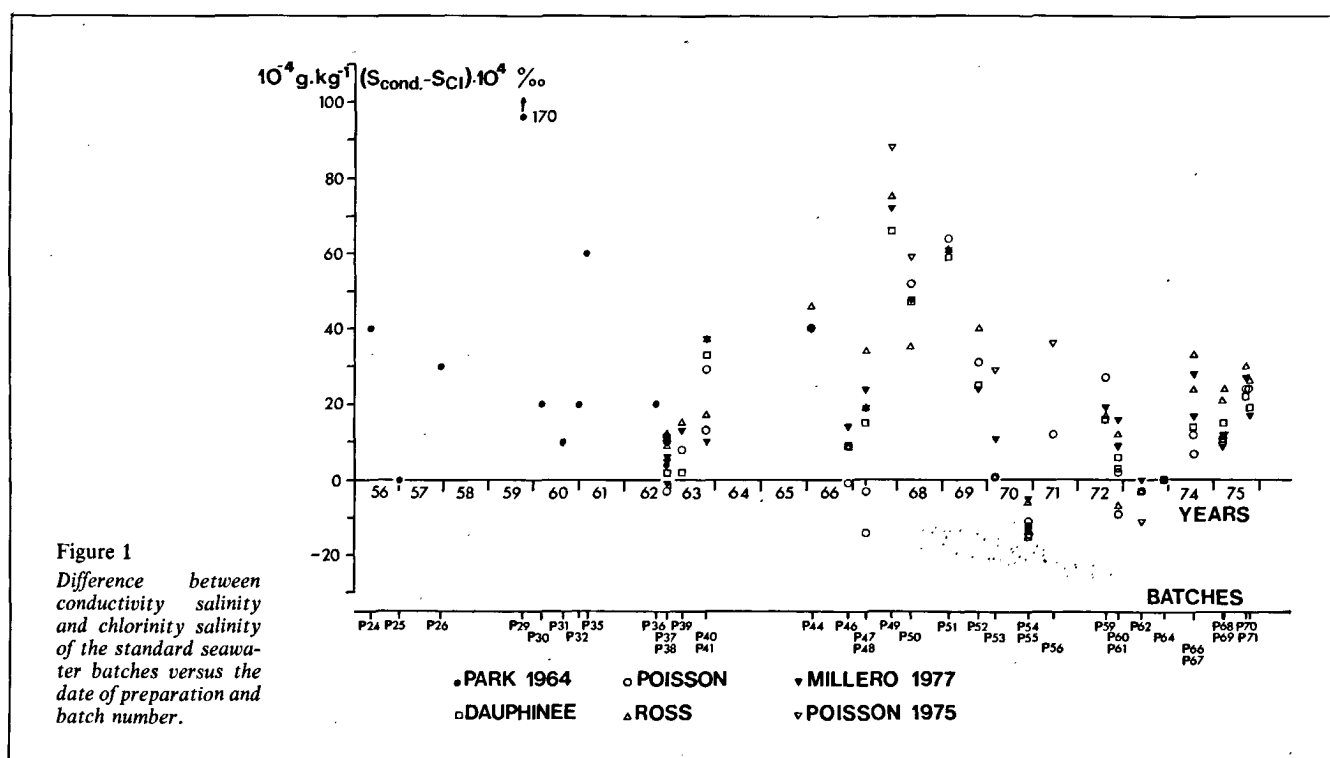


Table 4
pH, S_i concentration and dissolved organic carbon content of different batches of standard seawater.

Batch	pH				S_i ($\mu\text{g at.l}^{-1}$)				Dissolved organic carbon (mg.l^{-1}) Moore
	Poisson	Ross	Average	Range	Poisson	Ross	Average	Range	
P37	8.19	8.10	8.15	0.09	182.1	93.7	137.9	88.4	0.63
P38	7.95	8.03	7.99	0.08	97.2	158.6	127.9	61.4	0.60
P39	8.04	8.04	8.04	0.00	141.9	162.4	152.2	20.5	0.55
P40	8.09	8.04	8.07	0.05	177.1	146.6	161.9	30.5	-
P41	7.98	7.99	7.99	0.01	109.6	137.5	123.6	27.9	0.74
P44	7.92	7.89	7.91	0.03	127.5	137.5	132.5	10.0	0.76
P46	8.10	8.07	8.09	0.03	156.3	177.5	166.9	21.2	-
P47	7.90	7.87	7.89	0.03	57.5	66.5	62.0	9.0	-
P48	7.92	7.87	7.90	0.05	104.7	90.7	97.7	14.0	-
P49	-	7.69	7.69	-	-	297.6	297.6	-	1.28
P50	7.82	8.33	8.08	0.51	65.0	636.8	350.9	571.8	0.88
P51	7.77	7.72	7.75	0.05	74.9	113.3	94.1	38.4	1.21
P52	8.03	7.95	7.99	0.08	200.9	153.4	177.2	47.5	1.07
P53	8.08	8.10	8.09	0.02	67.0	108.8	87.9	41.8	-
P54	8.22	8.18	8.20	0.04	202.9	121.6	162.3	81.3	-
P55	8.17	8.14	8.16	0.03	173.1	134.5	153.8	38.6	-
P56	7.97	-	7.97	-	98.7	-	98.7	-	-
P59	7.81	7.74	7.78	0.07	44.3	43.8	44.1	0.5	-
P60	8.02	8.04	8.03	0.02	36.4	47.6	42.0	11.2	-
P61	7.98	7.98	7.98	0.00	38.1	43.8	41.0	5.7	-
P62	8.05	8.01	8.03	0.04	45.1	41.6	43.4	3.5	-
P64	8.05 (a)	8.04 (b)	8.05	0.01	38.1 (a)	36.3 (b)	37.2	1.8	-
P66	7.82	7.79	7.81	0.03	35.5	37.4	36.5	1.9	-
P67	7.86	7.91	7.89	0.05	31.7	45.8	38.8	14.1	-
P68	7.93	7.91	7.92	0.02	25.0	25.3	25.2	0.3	0.99
P69	7.88	7.84	7.86	0.04	25.8	28.1	27.0	2.3	1.07
P70	7.77	7.70 (c)	7.74	0.07	21.2	21.2 (c)	21.2	0.0	0.82
P71	7.73	7.71	7.72	0.02	25.1	23.8	24.5	1.3	1.03

(a) Average of 6 measurements (ranges: pH = 0.02; S_i = 5.5 $\mu\text{g at.l}^{-1}$).

(b) Average of 5 measurements (ranges: pH = 0.04; S_i = 5.7 $\mu\text{g at.l}^{-1}$).

(c) Average of 4 measurements (ranges: pH = 0.01; S_i = 1.6 $\mu\text{g at.l}^{-1}$).

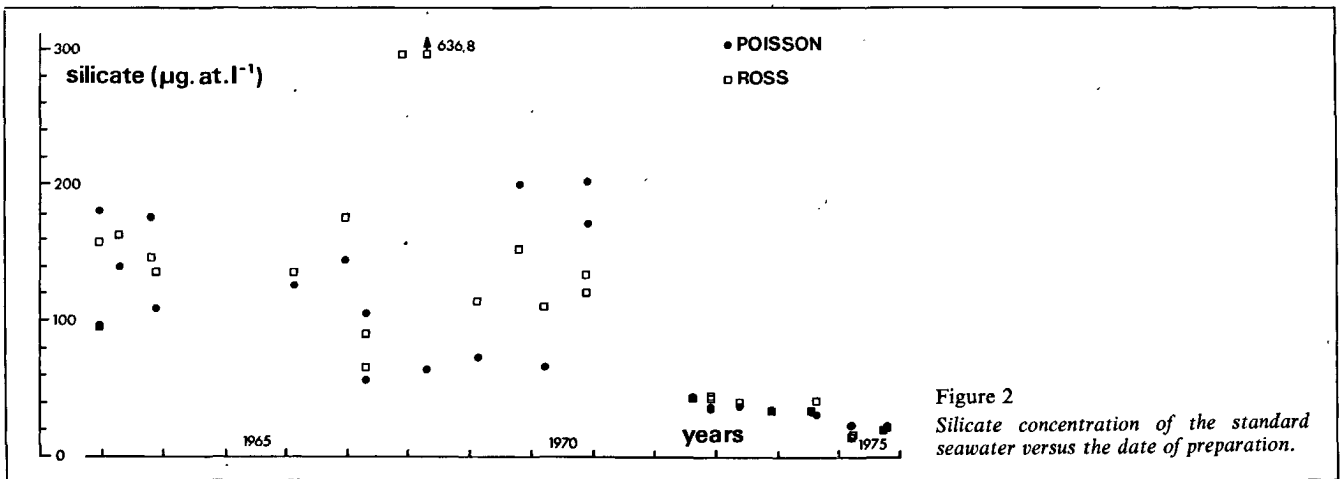


Figure 2
Silicate concentration of the standard seawater versus the date of preparation.

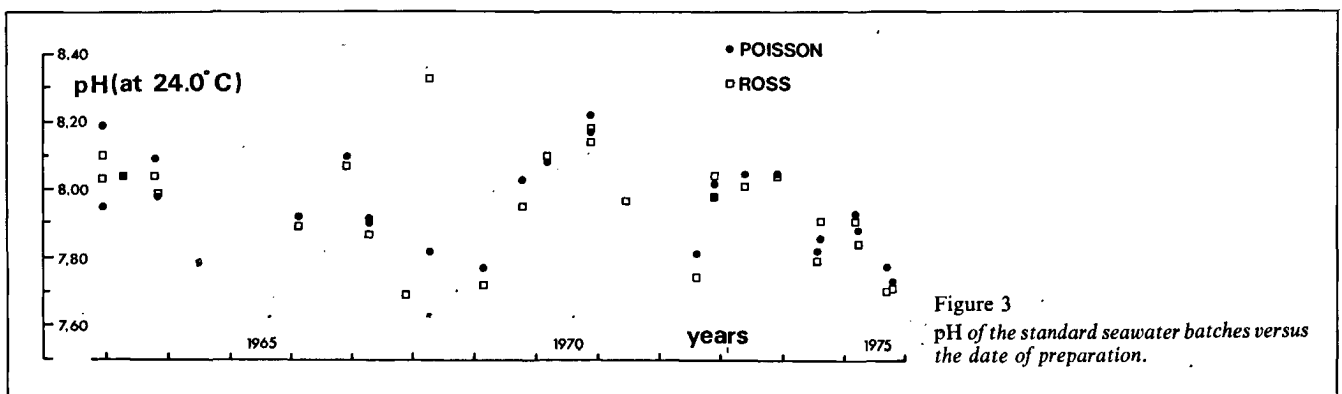


Figure 3
pH of the standard seawater batches versus the date of preparation.

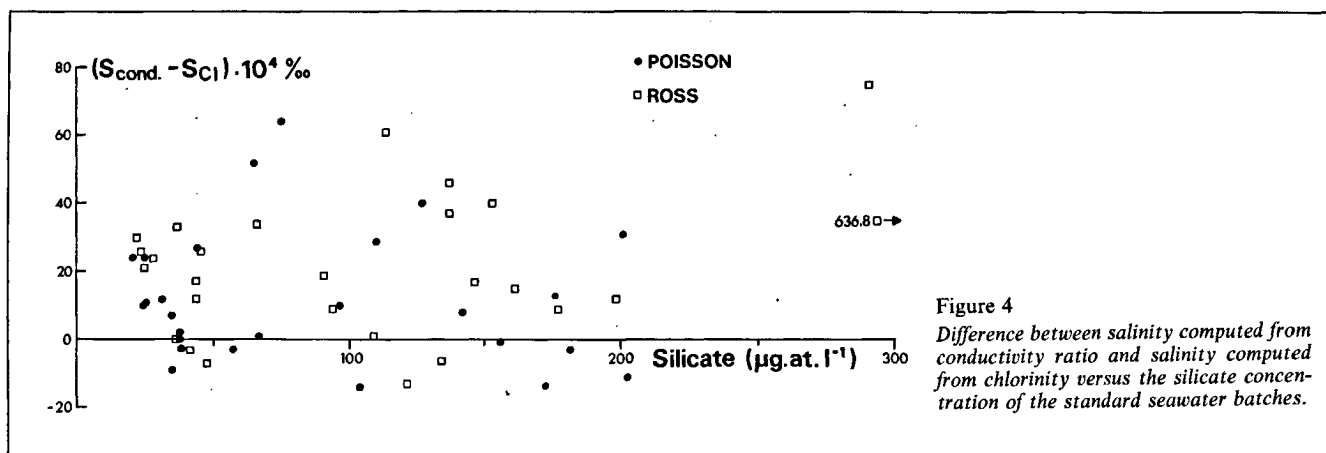


Figure 4
Difference between salinity computed from conductivity ratio and salinity computed from chlorinity versus the silicate concentration of the standard seawater batches.

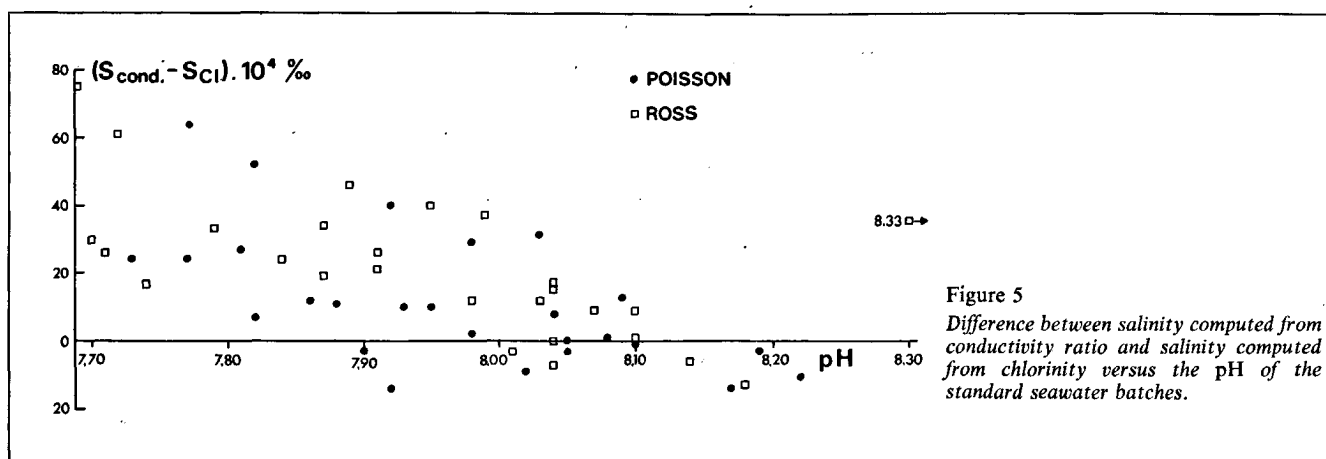


Figure 5
Difference between salinity computed from conductivity ratio and salinity computed from chlorinity versus the pH of the standard seawater batches.

Table 5
Comparison of Poisson's specific gravity anomalies measurements with the results of Millero et al.

Batch	σ_{25}			σ_{25} measured - σ_{25} Knudsen $\times 10^3$	
	Knudsen	Poisson	Millero	Poisson	Millero
P37	23.355	23.367	23.356	12	1
P38	360	368	364	8	4
P39	359	371	363	12	4
P40	364	376	369	12	5
P41	361	371	367	10	6
P44	362	374	368	12	6
P46	366	375	367	9	1
P47	363	367	363	4	0
P48	364	369	365	5	1
P49	368	-	405	-	37
P50	364	373	369	9	5
P51	363	378	366	15	3
P52	358	376	360	18	2
P53	364	367	364	3	0
P54	370	381	368	11	-2
P55	368	377	369	9	1
P56	364	375	-	11	-
P59	366	374	370	8	4
P60	366	368	371	2	5
P61	368	370	368	2	0
P62	367	369	372	2	5
P64	368	368	368	0	0
P66	354	356	356	2	2
P67	362	365	368	3	6
P68	359	361	362	2	3
P69	359	361	358	2	-1
P70	363	366	364	3	1
P71	362	365	363	3	1

concentrations were also in complete disagreement (65.0 and 636.8 $\mu\text{g at.l}^{-1}$). The pH of the different batches varies significantly within the range 8.20-7.69. The two sets of silicate measurements agree fairly well for recent batches; but the concentrations found were higher than would be expected in the North Atlantic surface water from which standard seawater is prepared. This suggests that some silicate has leached from the ampoule glass. The highest silicate concentrations are found in the older batches (P37-P55) and, for these batches there is considerable disagreement between the two sets of data which is unlikely to be due to analytical error. There is some indication of an increase in silicate content with age (Fig. 2) but there is no correlation between pH and age of the batches (Fig. 3). The difference $S_{\text{cond}} - S_{\text{Cl}}$ is not correlated with silicate concentrations (Fig. 4) and seems to be correlated with pH (Fig. 5) but this correlation is poor ($r = 0.60$). A least squares fit of salinity difference as a function of pH gives a slope of $8.3 \times 10^{-3} \text{‰/pH unit}$.

Poisson's density measurements are compared with Millero's data. The two sets of measurements (Table 5) are in good agreement for the recent batches but some disagreement appears in earlier batches. This disagreement could be due to the different methods of measurements: Poisson made his measurements directly with standard seawater whereas Millero filtered the seawater before making his measurements. One part of the differ-

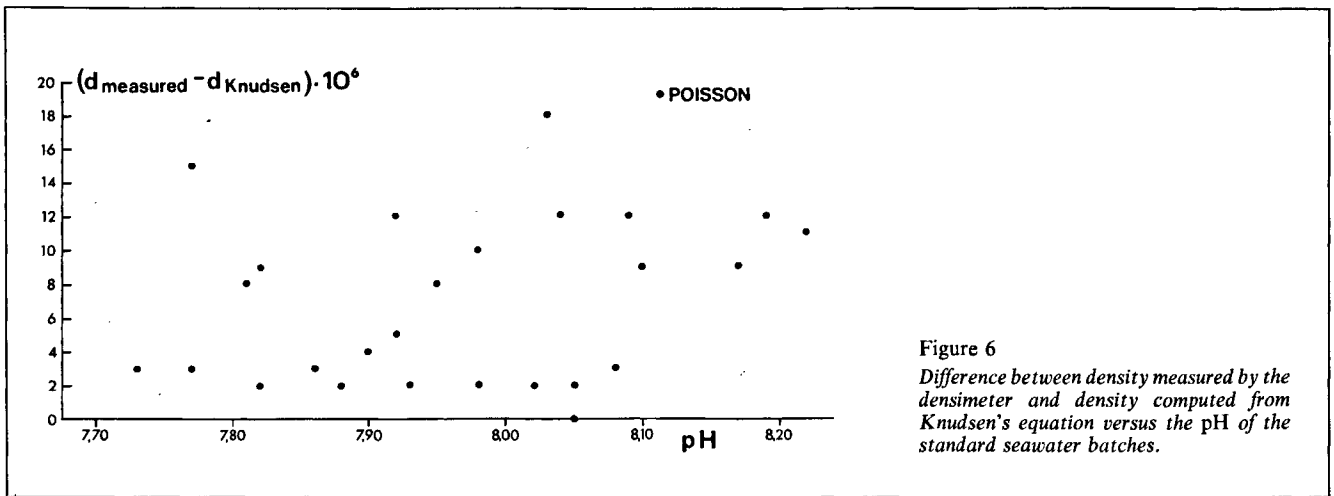


Figure 6
Difference between density measured by the densimeter and density computed from Knudsen's equation versus the pH of the standard seawater batches.

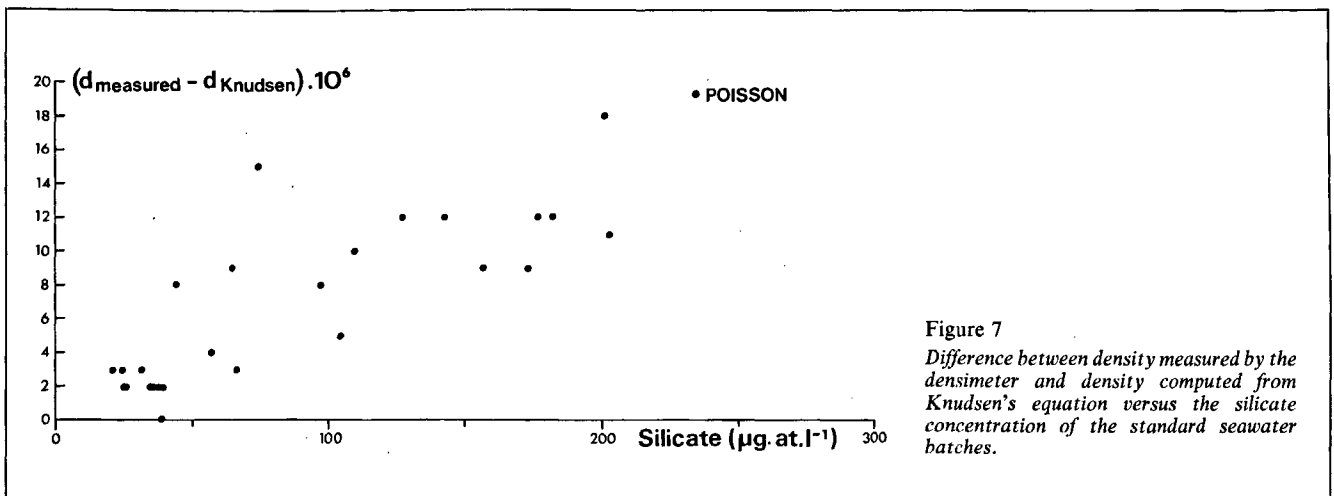


Figure 7
Difference between density measured by the densimeter and density computed from Knudsen's equation versus the silicate concentration of the standard seawater batches.

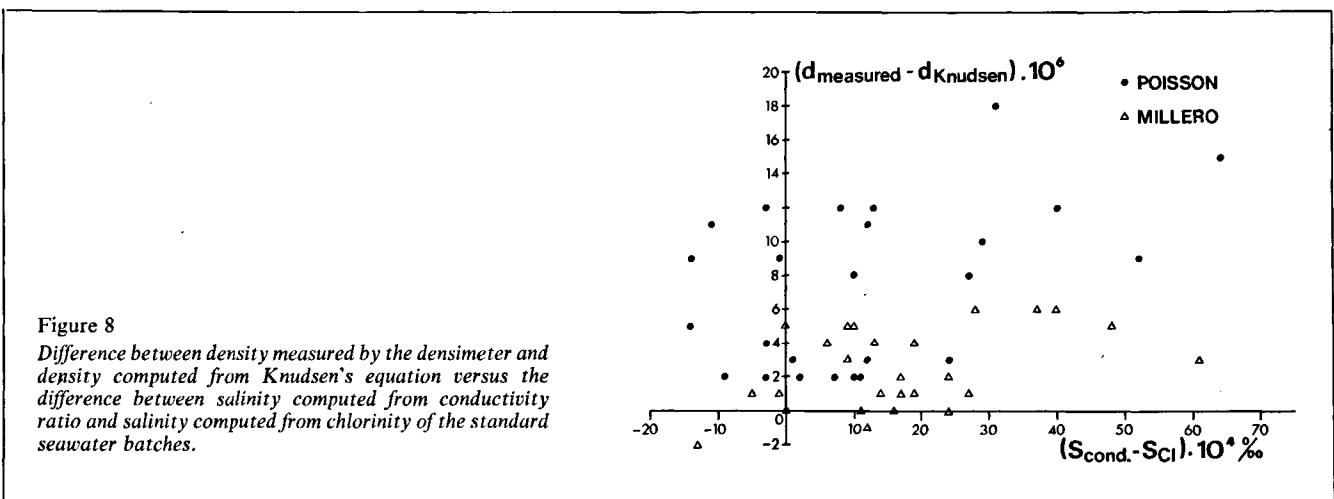


Figure 8
Difference between density measured by the densimeter and density computed from Knudsen's equation versus the difference between salinity computed from conductivity ratio and salinity computed from chlorinity of the standard seawater batches.

ences between the two sets of measurements can certainly be assigned to the influence of particulate material contained in the older samples, but the differences observed are too large to be entirely due to particulates. No correlation was found between the difference "density measured—density calculated from the labelled chlorinity using Knudsen equation" and the pH (Fig. 6) or the differences of salinities (Fig. 8). This difference of density seems to be correlated ($r = 0.80$) with silicate concentration (Fig. 7), but this correlation is not clear;

it is difficult to be sure of these correlations because of the small variations of salinity and density relative to the precision of their measurement. A least squares fit of density difference as a function of silicate concentration gives a slope of $6.4 \times 10^{-5} \sigma$, per $\mu\text{g at.l}^{-1}$, i. e. approximately 1.5 times the value quoted by Brewer and Bradshaw (1975).

Dissolved organic carbon was determined in thirteen batches of the standard. It should be pointed out that the distinction between dissolved and particulate matter

is an arbitrary one and refers to material which has passed through or been retained by a filter of a given pore size. The results of these determinations show (Table 4) that batches P49-P52 whose conductivities were high, contain higher levels ($0.88\text{-}1.28\text{ mgC.l}^{-1}$) than the earlier batches ($0.55\text{-}0.76\text{ mgC.l}^{-1}$), confirming Hermann's suggestion of contamination during the period 1967-1969 (see later). On the other hand, the more recent batches (P68-P71) which had been filtered through a membrane filter with a smaller pore size than the filter paper which was used earlier, also contained higher levels ($0.82\text{-}1.07\text{ mgC.l}^{-1}$).

It seems unlikely, therefore, that any useful conclusions can be drawn from these results as they all fall within the range of $0.5\text{-}2.0\text{ mgC.l}^{-1}$ usually quoted for dissolved organic carbon in seawater (Williams, 1975).

The investigations described in this paper confirm that the conductivity of some batches of standard seawater prepared in the earlier period investigated are now unacceptably high, although they were correct at the time these standards were prepared (F. Hermann, private communication). These high conductivities (relative to the mean) cannot be attributed to high silicate concentrations alone, because an increase in silicate produces a decrease in conductivity (Brewer, Bradshaw, 1975), although the possibility of other constituents of the glass dissolving in the seawater and slight chemical transformation of seawater cannot be ruled out.

Possibly more relevant is some information provided by F. Hermann (private communication) who was in charge of the Standard Seawater Service when the batches in question were prepared. The water from which batches P49-P51 were prepared was collected in the North Atlantic, west of longitude 15°W , and was filtered through filter paper only, before being transferred to the ampoules. Some time after its preparation, batch P51 was found to be contaminated by bacteria. Mr. Hermann has suggested that these seawaters may have had a higher organic content than usual, possibly oil contamination, and that this organic matter was oxidised to carbon dioxide by the bacteria, which would certainly increase the conductivity. It should be pointed out that since 1970 the seawater used for preparing the standard has been collected from a position much further east and that the filtration system used has included a membrane filter which should remove particulate material, including bacteria, down to a size of $0.3\text{ }\mu\text{m}$.

The main conclusion to be drawn from these investigations is similar to those reached by Park, Poisson, Millero *et al.*, viz. that each batch of standard seawater should be certified in conductivity as well as chlorinity as soon as possible. Discussion of these results at the 8th meeting of the Joint Panel on Oceanographic Tables and Standards (Unesco, 1977) led to the following recommendations.

The concentration of potassium chloride solution having the same conductivity as standard seawater of chlorinity $19.374\text{ }0\text{ }_{\text{oo}}$ (*i. e.*, salinity $35.000\text{ }0\text{ }_{\text{oo}}$) should be determined in four laboratories and the conductivity of all future batches of standard seawater should be measured, by the standard seawater Service, relative to the potassium chloride solution. Standard seawater will then be labelled with the appropriate value of R^{15} for calibrating salinometers.

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