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Results of an Oxygen/Salinity
Comparison Cruise on the R/V
Vernadsky

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Results of an Oxygen/Salinity Comparison Cruise on the R/V Vernadsky

June 27 to July 8, 1991

by

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Abstract

This report summarizes the work, under the auspices of the WOCE Hydrographic Programme (WHP), which took place on the R/V *Akademik Vernadsky* in June–July 1991. The goal of the exercise was an international comparison/training cruise to obtain comparisons of water sampling methods and analytical techniques employed by several groups for the oceanographic measurement of salinity and oxygen in seawater. The training aspect was formalized in a pre-cruise practicum held on board the vessel by Dr. Fred Culkin and Mr. Paul Ridout of Ocean Scientific International, the manufacturer of IAPSO Standard Seawater. At-sea comparisons of Russian Reference Water, manufactured in Moscow, were made with IAPSO water. Further work involved comparisons of a Guildline and a pair of SOKOL salinometers using reference water and natural seawater collected on the cruise. While the agreement among the salinometers was quite good and at the level of acceptability for the WHP, it was discovered that lack of thermal equilibration of the salinity samples run on the SOKOLs led to substantial “errors” at large depths (or for cold water samples). This could not have been anticipated before the cruise and would have been missed in a shore-based or laboratory exercise. All five groups making oxygen comparisons benefitted from the technical exchange afforded by the cruise and, as a result of reconciling inter-group differences, have identified procedural changes they will make in the future in order to achieve the high standards required by the WHP. The technical interaction, which amounted to “training” for all groups, was greatly facilitated by the cooperation of Captain Malinovsky, Chief Scientist Panteleyev, the scientists from MHI, Sevastopol, and the crew of the *Vernadsky*.

On the *Vernadsky* comparison cruise, a shore-based practicum was held prior to sailing in order to review the theory and measurement of salinity. The cruise itself, which took place between 27 June and 8 July 1991, was in the NE Atlantic to the west of Madeira. An international group of experts in salinity and oxygen measurements was drawn from the United Kingdom (UK), Spain, Russia, Ukraine, and the United States (US).

Except for one of the five groups, measured oxygen values in the range of 3–5 ml/l (concentration units are used throughout) agreed with one another within $\pm 1\%$, which exceeds the WOCE requirements by a factor of 2. Subsequent analyses of the differences by all five groups could account for much of the observed inter-group variations. Intra-group precision was generally in the range of 0.1–0.4%. As a result of a low oxygen sparging experiment in which sample oxygens < 1.2 ml/l were generated, substantial inter-group differences of ± 0.08 ml/l were found indicating that oxygen specifications for WOCE need to be expressed as both a percent “error” and a low oxygen bias.

The salinity comparison component of the cruise enabled comparison of various batches of Russian Reference Water (RRW) of various salinities (10, 20, 30, 35 and 40) against IAPSO Standard Seawater (SSW) of various salinities (10, 30, 35 and 38); inferences could then also be drawn on the relative performance of the two types of salinometer (Guildline Autosol 8400 and SOKOL 4602) used during the experiment. Under quasi-laboratory conditions, the machines produced mean results different by no more than 0.001 in salinity for salinity 35 RRW, standardizing against salinity 35 SSW. The other salinities produced less conclusive results, but the three salinometers deviated by no more than

0.003 from the expected value over a wide range of salinities. Under operational conditions (analysis of duplicate samples collected from CTD casts) a mean bias emerged between machines of approximately 0.005 in salinity (SOKOL fresher than Guildline). Subsequent investigations tentatively ascribed this bias to non-equilibration of deep (cold) samples in the Russian system.

1. Introduction

A joint agreement was signed by the directors of the Woods Hole Oceanographic Institution (WHOI) and the Marine Hydrophysics Institute (MHI) in Sevastopol in May, 1990, initiating the planning for an international comparison/training cruise to obtain comparisons of water sampling methods and analytical techniques employed by several groups for the oceanographic measurements of oxygen and salinity in sea water. The cruise was to be conducted aboard the Research Vessel *Akademik Vernadsky* under the auspices of the World Ocean Circulation Experiment (WOCE). Additional planning and coordination for the cruise was carried out by Dr. T. Joyce in his position as Director of the WOCE Hydrographic Programme Office (WHPO) in Woods Hole. Ten days of ship time were made available by MHI, and funds were provided by the National Science Foundation, the Intergovernmental Oceanographic Commission (IOC) and the Director of Woods Hole Oceanographic Institution (WHOI).

The cruise was staged out of Funchal, Madeira, and lasted from June 27 until July 8, 1991. The five participating groups included personnel from Woods Hole Oceanographic Institution (WHOI), USA; Institute of Oceanographic Sciences, James Rennell Centre (IOSJRC), UK; Marine Hydrophysics Institute (MHI), Sevastopol, Ukraine; State Oceanographic Institute (GOIN), Moscow, Russia; and Instituto Espanol de Oceanografia (IEO), Tenerife, Spain. Prior to the cruise, Dr. Fred Culkin and Mr. Paul Ridout from Ocean Scientific International in the UK conducted a lecture and practicum on the best methods to obtain high quality oceanographic salinity measurements. A description of this activity is presented in Appendix A.

The ship rendezvoused with the Research Vessel *Vladimir Parshin* about 200 nm west of Madeira on June 28. Dr. S. Lappo, Director of the State Oceanographic Institute (GOIN), Moscow, arranged for two technical specialists from the R/V *V. Parshin* to participate in the oxygen comparison aboard the R/V *Vernadsky*. The first station was occupied the evening of June 28th to test the operation of the CTD and rosette. During this test station all twelve of the 10-liter Niskin bottles were tripped at 1000 m and samples were collected for the measurement of salinity and dissolved oxygen. The results of the salinity and oxygen measurements indicated that the rosette and sampling bottles were operating satisfactorily.

Stations 2-4 and 6-8 consisted of two casts of twelve bottles each with oxygen samples drawn from every bottle by each group. Four replicate samples were also drawn from each cast by all the groups. Salinity samples were collected from all the bottles by the Institute of Oceanographic Sciences, Deacon Laboratory (IOSDL) and MHI groups. The first cast at each station was to 3000 m (limited by available wire) with 12 water samples collected between 1000-3000 m. During the second cast 12 water samples were collected from the surface to 1000 m.

During the first cast of station 5 Niskin bottles 1-5 were tripped near the oxygen minimum layer at about 850 m and bottles 6-10 were tripped at 60 m where the oxygen values were higher. In order to assess their precision at station 5, each group collected and analysed six samples from one of the low and one of the high oxygen Niskin bottles. To determine each group's ability to measure very low oxygen concentrations it was necessary to

artificially reduce the oxygen concentration in some of the sea water samples. To accomplish this, all of the bottles at the second cast of station 5 were tripped at 10 m. The water in these bottles was sparged with nitrogen for various periods to reduce the dissolved oxygen content to values from 0.2 to 1.2 ml/l. Each group collected and analysed samples from Niskin bottles 1–10. In order to assess the homogeneity of the sparged water within the Niskin bottles, the IOSDL group collected and analysed six samples from bottle 11 and the WHOI group did the same with bottle 12. The results of this experiment are described later in this report.

An Autosol salinometer was loaned to the *R/V Vernadsky* personnel at the end of the comparison cruise to enable them to acquire additional salinity data for comparison with the MHI salinometer measurements. Samples were collected at 11 stations between July 15 and August 2, 1991, during their work in the Control Volume II area (AR11) for WOCE.

1.1 Oceanographic environment

The comparison work on the *R/V Vernadsky* took place while the vessel was doing survey work in the region of WOCE Control Volume II (AR11), known in the USA as the Subduction Experiment. Consequently, the stations (shown as large dots in Fig. 1) are distributed along the cruise track of this broader program. The region of the NE Atlantic covered by the cruise was noted by Saunders (1986) for its uniform potential in temperature/salinity and potential temperature/oxygen below about 3000 m. Since this was the deepest level sampled, only our deep data can be expected to show any spatial uniformity. In Figure 2, the Θ/S (Fig. 2a) and Θ/O_2 (Fig. 2b) distributions are shown from the calibrated CTD data for stations 1–8. The Θ/S is uniform for $\Theta < 4^\circ \text{C}$ and $12^\circ \leq \Theta \leq 14^\circ \text{C}$. However, considerable structure exists near the surface and in the layer influenced by the Mediterranean water. The oxygen is less homogeneous than salinity and even the deepest levels sampled (~ 3000 m) have a range of dissolved oxygen of 0.1 ml/l, or about $4 \mu\text{mol/kg}$. Thus, while our water sample comparisons for salinity can be compared with one another and Saunders' results, we can make no direct comparison with Saunders' oxygen results without introduction of real oceanographic variability into the observed differences.

Figure 1: Station locations during the R/V *Vernadsky* comparison cruise. Large dots denote comparison stations, while open circles and squares denote CTD stations part of a spatial survey in the Control Volume II (AR11) made solely by MHI and are not part of this report.

Figure 2: (a) Potential temperature (1968 temperature scale) versus salinity (PSS-78) for Mark IIIb CTD/O₂ stations 1 through 8 that have used laboratory calibrations for temperature and pressure, and have been reconciled to water sample data for calibration of the salinity and dissolved oxygen data.

2. Oxygen Comparisons

All five groups participated in the oxygen comparison experiment, each using their own equipment, chemicals and methods. In this section we will describe the groups, document their methods, and present the results of the experiments.

2.1 Oxygen—Participants and Methods

Group 1 - IOSDL

Rodger Paylor
United Kingdom

Group 1 uses Carpenter's (1965a,b) whole bottle method to titrate a 120 ml sample collected in weight calibrated sample bottles. The thiosulfate is 0.2 N and the iodate standard solution is 0.0100 N. The thiosulfate is dispensed with a Dosimat (± 1 microliter) under the control of an automated, photometric oxygen titration system, (Sensoren Instrumente Systeme - Kiel, Germany). The end point is calculated to better than ± 1 microliter. For example, 0.1 microliter is equivalent to about 0.008 ml/l dissolved oxygen.

Group 2 - MHI

Alexander Romanov and Evgeny Ovsjany
Ukraine

Group 2 determined dissolved oxygen in seawater using a modification of Carpenter's (1965a,b) whole bottle method and weight calibrated bottles with volumes between 110-140 ml. The thiosulfate is 0.02 N and the standard iodate solutions is 0.0200 N. A calibrated automatic burette, with scale divisions every 0.02 ml, is used to dispense the thiosulfate, and starch is used to determine the endpoint to ± 10 microliters, roughly equivalent to about ± 0.010 ml/l dissolved oxygen.

Group 3 - IEO-Tenerife

Jose Escañez
Spain

Group 3 used a modification of Strickland's and Parson's (1972) method for determining dissolved oxygen in sea water. Samples are collected in 130 ml weight calibrated flasks in which the iodine is liberated. After transfer to a 300 ml Erlenmyer flask, the iodine solution is titrated with 0.01 N thiosulfate. The potassium biiodate standard solution is 0.0100 N. A Dosimat is used to dispense the thiosulfate to ± 0.010 ml and starch to determine the endpoint to ± 10 microliters, or equivalent to about ± 0.006 ml/l dissolved oxygen.

Group 4 – GOIN

Boris Treskunov and Alexei Leibov
Ukraine and Russia

Group 4 used a modified Winkler method in which the contents of weight calibrated, 110 ml sample bottles are transferred to a 250 ml flask for titration. The thiosulfate is 0.02 N, and its normality is determined by adding 1 g dry potassium iodate to acidified distilled water. A burette with scale divisions every 0.05 ml is used to dispense the thiosulfate, and the endpoint is visually determined using starch to about ± 20 microliters, which is equivalent to about ± 0.025 ml/l dissolved oxygen.

Group 5 – WHOI

Marvel Stalcup
United States of America

Group 5 used a modified Winkler method in which a 50 ml aliquot is collected from a 150 ml sample bottle and titrated with 0.01N thiosulfate, the potassium iodate standard solution is 0.0100N. The thiosulfate is dispensed with a Dosimat (± 1 microliter) under control of an automated amperometric detection system. The endpoint is calculated to better than 1 microliter which is roughly equivalent to 0.001 ml/l dissolved oxygen.

2.2 Oxygen water sampling

Sea water samples were collected by each group from twelve, 10-liter Niskin bottles attached to a 24-place General Oceanic Rosette. An EG&G Mark IIIb CTD equipped with a second platinum temperature sensor, a new titanium pressure sensor and a pumped oxygen sensor was used to measure pressure, conductivity and oxygen concentration continuously during each cast. All stations were occupied in the evening to avoid the higher daytime temperatures and the attendant rapid warming of the water in the Niskin sampling bottles. Although samples were drawn on the open fore-deck of the vessel, weather conditions were favorable and salt spray was not a problem, nor did rain hamper the sampling.

The order in which each group drew samples and replicates from the Niskin bottles was carefully orchestrated to eliminate possible sampling-order bias. After everyone had collected samples from all 12 Niskin bottles, four replicate samples were collected from four different bottles by each group. Each group stored their reagents in their respective labs and brought them on deck just prior to sampling. The reagents used by each group are summarized in Table 1. Although each group's sampling technique varied slightly, everyone used a sampling tube that reached to the bottom of the sample bottle, rinsed each bottle at least once, and carefully filled and overflowed the bottle by at least 2–3 volumes. The manganese chloride (sulfate) and sodium (potassium) hydroxide-iodide reagents were then immediately added and the bottles shaken. Reagents, dispensers, standards, and blanks used by each group are summarized in Tables 1 and 2 and described in detail in Appendix B. Approximately 2–3 liters of water remained in each Niskin bottle after all of the samples had been drawn.

Table 1: An abbreviated description for the preparation of reagents used during the comparison. The normality and concentration of the acid, thiosulfate and standard solutions are also shown.

Group		MnCl ₂ (SO ₄) g	(K)NaOH-I g	H ₂ SO ₄	Thiosulfate	Standard	
1	IOSDL*	600MnCl ₂ /l	600NaI/1000 ml 320NaOH/400ml	10N	0.20N	KIO ₃	0.0100N
2	MHI*	500MnCl ₂ /l	300 KI/450ml 700KOH/700ml	20%	0.02N	KIO ₃	0.0200N
3	IEO ⁺⁺	365MnSO ₄ /l ⁺⁺	300KI/450ml 500NaOH/500ml ⁺⁺	100%	0.01N	KH(IO ₃) ₂	0.0100N
4	GOIN ⁺	500MnCl ₂ /l	392NaI/300ml 490KOH/360ml ⁺	20%	0.02N	KIO ₃	0.0200N
5	WHOI*	600MnCl ₂ /l	600NaI + 320NaOH 1000 ml	10N	0.01N	KH(IO ₃) ₂	0.0100N

* The MHI, IOSDL and WHOI groups filter their MnCl₂ and NaOH-I reagents through glass fiber filters.

+ The GOIN group filters only their MnCl₂ reagent.

++ The IEO-Tenerife group did not filter their reagents.

Table 2: The results of a comparison of blank and standardization (in ml/l of equivalent O₂) samples analysed by each group with the WHOI equipment and thiosulfate.

GROUP	AFFIL	BLANK	STANDARD	pH
1	IOSDL	0.005	5.804	1.75
2	MHI	0.005	5.796	2.01
3	IEO	0.022*	5.795	1.05
4	GOIN	0.004	5.774	1.48
5	WHOI	0.005	5.805	2.17

* The reagents and concentrations used by IEO are different from those used by the other Groups (see Table 1). This difference may result in the relatively large blank measured here. The low pH measured for Group 3 may also be responsible for the large value of their reagent blank since a low pH accelerates the atmospheric oxidation of iodide to iodine.

2.3 Oxygen reagents

Each group mixed their own reagents for use during the cruise and wrote a description of their techniques for preparing reagents, standardizing, blank determination, calculating dissolved oxygen, etc. (see Appendix B). A brief description of the reagents used by each group is presented in Table 1. The following procedure was used to directly compare the various reagents used during the cruise.

Using their own reagents and glassware, each group prepared several samples for the determination of their reagent blank value and several to measure the normality of their thiosulfate. They analysed these samples in WHOI's temperature-controlled, portable laboratory using the titration apparatus and thiosulfate used by the WHOI group. The results of these measurements are presented in Table 2 where the units are the amount of thiosulfate used for each titration. Table 2 also lists the pH (measured by MHI) of a typical acidified sample solution prepared by each group.

The reagent blanks for Groups 1, 2, 4, and 5 are satisfactorily low and probably reflect the fact that these groups use essentially the same reagents and, after preparation, filter them through glass fiber filters. The relatively high blank measured by Group 3 is possibly due to their use of manganese sulfate instead of the manganese chloride used by the other groups, or from using unfiltered reagents, or could be related to the low pH of their acidified sample. In future work this group plans to use the reagents described by Carpenter (1965a,b).

Table 3: Summary of algorithms used by the various groups to calibrate dissolved oxygen

Group		Algorithm used
1	IOSDL	Culberson's whole bottle formula ⁺
2	MHI*	$O_2 \text{ ml/l} = (111.97nK)/(V - 2)$
3	IEO	$O_2 \text{ ml/l} = (56nK)/(V - 2)$
4	GOIN*	$O_2 \text{ ml/l} = (111.96nK)/(V - 2)$
5	WHOI	Culberson's aliquot formula ⁺⁺
where:		
n	=	Thiosulfate (ml) used for titration
K	=	Calibration factor for thiosulfate normality
V	=	Volume of the sampling flask (ml)

* The normality of the thiosulfate used by these groups is 0.02N; IOSDL uses 0.2N thiosulfate and the other groups use 0.01N thiosulfate. These groups report oxygen concentrations to 0.01 ml/l; the other groups report to 0.001 ml/l.

⁺ Culberson's formula for calculating dissolved oxygen in sea water using Carpenter's (1965) whole bottle method is presented in WHPO publication 91-2.

⁺⁺ Culberson's formula for calculating dissolved oxygen using the aliquot version of Winkler method is given in WHPO publication 91-2.

As shown in Table 2, there is close agreement in the concentration of the standard solutions used by Groups 1 and 5 and Groups 2 and 3. The difference between Groups 1-5 and 2-3 is equivalent to about 0.01 - 0.03 ml/l as shown in Figure 3.

2.4 Algorithms

Algorithms used by the various groups are given in Table 3. The effects of the differences (relative to Group 1) in the reagents and the algorithms used to calculate dissolved oxygen are given in Table 4. The differences resulting from the algorithms used by Groups 2, 4 and 5 are nil and for Group 3 results from the use of 56 instead of 111.96/2 in the formula. Groups 2, 3 and 4 did not account for the oxygen added with their reagents nor for the effect of their reagent blanks as shown in Table 2. The result of differences in measured oxygen due to the algorithms, the various standard solutions and the totals are given here at concentrations of 1 and 5 ml/l.

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Oxygen Differences (rel to gp. 3)

Figure 3: Oxygen differences (relative to group 3) for samples analysed by Groups 1,2,4 and 5 plotted versus cast and bottle number for stations 1-8.

Table 4: Differences in the oxygen measurements (ml/l) made by Groups 2-5 relative to Group 1, (Groups 2-5 - Group 1)

Group Number	Algorithm		Oxy. in Reagents	Reagent Blank	Standard Conc.		Total	
	@ 1ml/l	@ 5ml/l			@ 1ml/l	@ 5ml/l	@ 1ml/l	@ 5ml/l
2	0.000	0.000	0.014	0.000	0.001	0.007	0.015	0.021
3	0.000	0.002	0.014	0.017	0.001	0.007	0.032	0.040
4	0.000	0.000	0.014	-0.001	0.005	0.026	0.018	0.039
5	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

2.5 Water sample comparisons

During the course of the cruise, comparison plots were prepared to show the reproducibility of the results by showing a running comparison with one of the 5 groups (group 3 was chosen initially because it seemed to be in the middle of the range). Bottle oxygen values from group 3 were subtracted from individual bottle results for the other four groups and plotted against station/cast number; the first bottle for each cast was the deepest one. After the first station, oxygen differences for the groups settled down to show consistent inter-group differences. Some samples are shifted vertically about local mean values for all groups because of the use of group 3 as a reference for data in Figure 3. Except for station 5, which was a low oxygen sparging experiment described below, it can be seen that, on average, the Groups measuring highest oxygen concentration, in decreasing order, were groups 2, 3, 1, 5, and 4.

2.6 Low oxygen concentration sparging experiment

The water in the Niskin bottles tripped at station 5, cast 2 were sparged with nitrogen to reduce the concentration of dissolved oxygen to values less than 1.2 ml/l. Each group drew samples from bottles 1-10 to determine their ability to measure low concentrations of dissolved oxygen. In order to assess the homogeneity of the water samples collected from the sparged bottles, groups 1 and 5 drew six samples from bottles 11 and 12 respectively. The average oxygen concentration and standard deviation for bottles 11 and 12 were respectively 0.856 and 0.004 ml/l and 0.222 and 0.006 ml/l. When compared with the precision measurements described above (at 3.5 and 5.4 ml/l), these results indicate that the water in the sparged Niskin bottles was as well mixed. The low oxygen concentrations shown later in Figure 5 were obtained during this experiment.

Table 5: A summary of pooled replicate comparisons of the oxygen measurements (ml/l) made by each group at all stations. 1-8.

Group Number	Mean Diff.	Standard Deviation	Standard Error $\sigma/\sqrt{2}$
1	- 0.004	0.006	0.004
2	0.001	0.011	0.008
3	- 0.012	0.043	0.030
4	0.007	0.020	0.014
5	- 0.001	0.013	0.009

Table 6: The average and standard deviation of six samples drawn by each group from Niskin bottles tripped at 50 and 850 m on station 5, cast 1.

Group Number	50m Average	50m Std. Deviation	850m Average	850m Std. Deviation
1	5.416	0.003	3.579	0.005
2	5.440	0.009	3.600	0.006
3	5.444	0.023	3.586	0.007
4	5.311	0.015	3.492	0.015
5	5.379	0.007	3.545	0.003

2.7 Replicate comparisons

Replicate samples were differenced (first—second sample) for each of the casts (15 in all) and used to calculate a running standard deviation (Fig. 4). As one might expect, the standard deviations of the early casts were larger than the later ones up to station 5. After station 5, the standard deviations of replicate samples became nearly constant. The most significant decrease in sampling error with time was that of group 3, with more than a factor of three improvement in precision with time. By pooling the variances of the 15 replicate comparisons, a table showing the experimental error was constructed (Table 5). The table includes the mean (1st-2nd) replicate differences, standard deviation of the differences and the standard error (standard deviation divided by $\sqrt{2}$) of each individual oxygen measurement. All oxygen units are in ml/l.

On station 5, five Niskin bottles were tripped at about 850 m ($O_2 = 3.5$ ml/l) and five were tripped at 50 m ($O_2 = 5.4$ ml/l). In order to assess their precision, each group drew six samples from one of the bottles tripped at 850 m and six samples from one tripped at 50 m. These samples were analysed in the usual fashion and the average and standard deviations are presented below in Table 6.

Figure 4: The standard deviation of replicate oxygen measurements made by groups 1-5 plotted versus station/cast number.

2.8 Discussion

Data from station 5 onward were edited to remove individual outliers and plotted against oxygen concentration (Fig. 5). Because we required that valid values be present from all five groups for this comparison, 71 out of a possible 82 comparisons were used. In this comparison, we used group 1 as a reference because its precision was the best. Results include the low oxygen sparging experiment and clearly show that trends in the measured differences exist that would have been difficult to discern from the naturally observed oxygen values in the water column (3.5-6 ml/l). While it is clear that a straight line fit to the differences versus oxygen does not capture all of the structure, it does show the observed trends and permits a concise summary of all the observed differences (using all groups as references) for the comparison experiment (Fig. 6). All possible differences can be generated by reflection of the linear least square fit about the horizontal oxygen axis. It is clear from this summary, that both an inter-group bias exists as well as an error proportional to oxygen concentration. We note that over most of the high oxygen end of the range, comparisons involving group 4 had the largest differences. For the remaining groups, the range in oxygen difference was ± 0.05 ml/l.

An experiment performed by group 2, subsequent to the comparison cruise described in this report, revealed that their method of standardizing (described in Appendix B) resulted in a loss of iodine equivalent to 0.09 ml/l dissolved oxygen. The over-estimation of the normality of their thiosulfate resulted in calculated oxygen values about 0.05 ml/l too high at concentrations of about 5 ml/l. If this correction is added to that shown in Table 4 the difference with group 5 is small, (see Figs. 5 and 6). Comparison oxygen datas for all stations are contained in Table 7. Presumably due to sampling mix-ups, the oxygen values for group 1 in Table 7 are suspect for station 2, cast 1, bottles 2 and 12; station 2, cast 2, bottles 2 and 12; and station 3, cast 1, bottles 2 and 12.

As a result of the comparison experiment, the following issues were addressed by each group:

Group 1 – IOSDL: The Sensoren Instrumente Systeme (SIS) program used to measure the endpoint during titration does not provide sufficient time to thoroughly mix the sample. At iodine concentrations equivalent to O_2 concentrations of less than about 1 ml/l, the titration takes only about 10–15 seconds and unreacted iodine is still present in the flask at the time the program has determined the endpoint has been reached. Since the algorithm used by the SIS program to calculate dissolved oxygen is not the one recommended by the WHP Office, all of the oxygen concentrations reported by this group were calculated separately. These problems have been reported to SIS.

Group 2 – MHI: This group has adjusted their blank determination procedure to measure both negative and positive reagent blanks and plans to perform standardization procedures following Carpenter's method.

Group 3 – IEO: This analyst plans to replace the manganese sulfate reagent used during the intercomparison with manganese chloride, adjust the concentration of the sulphuric acid to yield a sample with a pH near 2 and filter the potassium iodide and manganese

Figure 5: Oxygen differences (relative to group 1) for samples analyzed by groups 2-5 plotted versus oxygen concentration.

Figure 6: Linear least squares fits to oxygen differences between indicated pairs of groups plotted versus oxygen concentration.

chloride reagents. He will also measure the reagent blank and apply it to the calculation of dissolved oxygen.

Group 4 – GOIN: As a result of the oxygen comparison experiment, this group determined that their dissolved oxygen measurements were low by 0.036 ml/l at concentrations near 1 ml/l and low by 0.046 ml/l at concentrations of 6 ml/l. They attribute these differences to a variety of factors including contaminated potassium iodide. To address the problems they have replaced their titration flasks and burettes and modified their method of standardization to add 1 ml each of the potassium iodide and manganese chloride solutions to the standard. They also now measure and apply the reagent blank correction and account for the dissolved oxygen in the reagents. The potassium iodide and manganese chloride reagents are mixed and double filtered through glass filters in the shore laboratory where their purity is assessed.

Group 5 – WHOI: This group has modified their sample collection procedure by filling their sample bottles with water when not in use. Small bubbles were sometimes observed to adhere to the inside of the collection tube when collecting oxygen samples, and it is likely they contaminate the oxygen sample. To maintain a wetter surface within the tube, it is now stored in water when not in use.

Table 7: *Vernadsky* Oxygen Comparison Data (units are in ml/l)

Station	Cast	Bottle	Group 1	Group 2	Group 3	Group 4	Group 5
1	1	1	4.184	4.21	4.176	4.3	4.157
1	1	2	4.183	4.19	4.162	4.36	4.129
1	1	3	4.161	4.2	4.18	4.36	4.142
1	1	4	4.169	4.2	4.149	4.23	4.139
1	1	5	4.17	4.2	4.172	4.2	4.145
1	1	6	4.166	4.21	4.162	4.23	4.144
1	1	7	4.168	4.19	4.16	4.34	4.146
1	1	8	4.172	4.21	4.168	4.31	4.148
1	1	9	4.181	4.2	4.174	4.36	4.153
1	1	10	4.171	4.21	4.183	4.17	4.142
1	1	11	4.182	4.22	4.182	4.15	4.151
1	1	12	4.165	4.22	4.173	4.33	4.139
2	1	1	4.16	4.21	4.195	4.14	
2	1	2	4.172	5.77	5.712	5.1	5.684
2	1	3	5.767	5.82	5.244	5.25	5.739
2	1	4	5.817	5.87	5.87	5.24	5.817
2	1	5	5.822	5.87	5.818	5.83	5.797
2	1	6	5.461	5.51	5.461	5.4	5.455
2	1	7	5.7	5.72	5.673	5.57	5.634
2	1	8	5.663	5.71	5.659	5.6	5.641
2	1	9	5.481	5.55	5.508	5.4	5.491
2	1	10	5.071	5.13	5.086	4.98	5.06
2	1	11	4.622	4.68	4.868	4.5	4.61
2	1	12	5.655	4.21	4.195	4.08	4.169
2	2	1	4.17	4.225	4.208	4.11	4.268
2	2	2	5.197	4.16	4.136	4.45	4.113
2	2	3	4.217	4.265	4.235	4.14	4.215
2	2	4	4.356	4.41	4.38	4.22	4.362
2	2	5	4.591	4.63	4.611	4.51	4.589
2	2	6	4.539	4.585	4.558	4.45	4.538
2	2	7	4.111	4.57	4.587	4.43	4.512
2	2	8	4.61	4.65	4.63	4.55	4.599
2	2	9	4.907	4.93	4.901	4.8	4.889
2	2	10	5.329	5.33	5.316	5.26	5.325
2	2	11	5.401	5.44	5.415	5.27	5.451
2	2	12	4.534	5.21	5.217	4.59	5.248
3	1	1	5.704	5.76	5.708	5.63	5.684
3	1	2	4.064	5.8	5.78	5.65	5.738
3	1	3	5.818	5.87	5.836	5.74	5.811
3	1	4	5.88	5.93	5.88	5.88	5.866

Table 7: Continued

Station	Cast	Bottle	Group 1	Group 2	Group 3	Group 4	Group 5
3	1	5	5.926	5.96	5.92	5.84	5.893
3	1	6	5.829	5.89	5.851	5.74	5.819
3	1	7	5.773	5.7	5.674	5.61	5.652
3	1	8	5.485	5.53	5.485	5.41	5.486
3	1	9	5.145	5.22	5.193	5.1	5.165
3	1	10	4.691	4.74	4.715	4.63	4.683
3	1	11	4.17	4.2	4.684	4.1	4.164
3	1	12	5.645	4.11	4.089	4.05	4.061
3	2	1	4.331	4.36	4.351	4.38	4.325
3	2	2	4.128	4.16	4.259	4.09	4.127
3	2	3	4.16	4.23	4.182	4.1	4.151
3	2	4	4.298	4.38	4.319	4.27	4.287
3	2	5	4.539	4.58	4.557	4.45	4.524
3	2	6	4.7	4.76	4.712	4.65	4.687
3	2	7	4.744	4.77	4.755	4.68	4.729
3	2	8	4.729	4.8	4.743	4.71	4.724
3	2	9	4.786	4.8	4.783	4.72	4.763
3	2	10	5.229	5.26	5.217	5.18	5.226
3	2	11	5.611	5.62	5.648	5.5	5.596
3	2	12	5.209	5.2	5.24	5.14	5.206
4	1	1	5.656	5.74	5.701	5.62	5.69
4	1	2	5.696	5.74	5.701	5.62	5.69
4	1	3	5.742	5.79	5.759	5.67	5.728
4	1	4	5.781	5.83	5.722	5.72	5.771
4	1	5	5.682	5.73	5.686	5.61	5.678
4	1	6	5.477	5.49	4.986	5.37	5.487
4	1	7	5.432	5.47	5.479	5.32	5.454
4	1	8	4.893	4.93	4.909	4.82	4.892
4	1	9	4.772	4.8	4.779	4.69	4.75
4	1	10	4.277	4.29	4.282	4.28	4.244
4	1	11	3.837	3.86	3.843	3.73	3.807
4	1	12	3.802	3.83	3.8	3.72	3.778
4	2	1	3.878	3.9	3.875	3.77	3.868
4	2	2	3.751	3.78	3.767	3.68	3.73
4	2	3	3.692	3.71	3.76	3.6	3.691
4	2	4	3.834	3.87	3.853	3.74	3.83
4	2	5	4.299	4.33	4.307	4.17	4.267
4	2	6	4.413	4.44	4.418	4.33	4.448
4	2	7	4.475	4.5	4.469	4.36	4.459
4	2	8	4.5	4.53	4.512	4.4	4.492

Table 7: Continued

Station	Cast	Bottle	Group 1	Group 2	Group 3	Group 4	Group 5
4	2	9	4.736	4.77	4.737	4.63	4.708
4	2	10	5.326	5.34	5.316	5.21	5.313
4	2	11	5.414	5.44	5.4	5.3	5.428
4	2	12	5.204	5.2	5.181	5.08	5.23
5	2	1	0.175	0.2	0.226	0.14	0.27
5	2	2	0.152	0.19	0.185	0.12	0.222
5	2	3	0.137	0.18	0.183	0.15	0.207
5	2	4	0.135	0.15	0.196	0.11	0.188
5	2	5	0.122	0.15	0.166	0.12	0.186
5	2	6	0.334	0.37	0.373	0.32	0.428
5	2	7	0.287	0.34	0.329	0.24	0.384
5	2	8	0.286	0.31	0.358	0.28	0.355
5	2	9	1.063	1.08	1.11	1.12	1.184
5	2	10	0.815	0.81	0.835	0.76	0.9
6	1	1	5.722	5.75	5.7	5.59	5.715
6	1	2	5.741	5.77	5.724	5.63	5.723
6	1	3	5.796	5.83	5.785	5.7	5.76
6	1	4	5.799	5.83	6.022	5.7	5.763
6	1	5	5.773	5.82	5.264	5.69	5.767
6	1	6	5.697	5.74	5.676	5.57	5.676
6	1	7	5.637	5.67	5.617	5.54	5.673
6	1	8	5.462	5.49	5.45	5.4	5.436
6	1	9	5.166	5.21	5.214	5.1	5.152
6	1	10	4.633	4.67	4.622	4.54	4.6
6	1	11	4.174	4.2	4.173	4.09	4.152
6	1	12		4.24	4.214	4.13	4.179
6	2	1	4.182	4.21	4.182	4.1	4.17
6	2	2	4.263	4.29	4.273	4.29	4.241
6	2	3	4.162	4.2	4.157	4.07	4.136
6	2	4	4.238	4.27	4.256	4.17	4.212
6	2	5	4.477	4.51	4.474	4.4	4.45
6	2	6	4.565	4.6	4.574	4.48	4.542
6	2	7	4.681	4.71	4.669	4.57	4.648
6	2	8	4.654	4.68	4.636	4.57	4.623
6	2	9	4.662	4.7	4.656	4.55	4.628
6	2	10	5.264	5.29	5.258	5.16	5.233
6	2	11	5.494	5.5	5.512	5.36	5.454
6	2	12	5.01	4.98	4.989	4.86	5.068

Table 7: Continued

Station	Cast	Bottle	Group 1	Group 2	Group 3	Group 4	Group 5
7	1	1	5.69	5.74	5.681	5.59	5.655
7	1	2	5.712	5.73	5.799	5.66	5.688
7	1	3	5.718	5.77	5.704	5.62	5.708
7	1	4	5.703	5.75	5.697	5.6	5.681
7	1	5	5.631	5.71	5.627	5.55	5.634
7	1	6	5.441	5.48	5.426	5.37	5.422
7	1	7	5.211	5.25	5.216	5.19	5.199
7	1	8	4.942	4.99	4.952	4.84	4.932
7	1	9	4.62	4.69	4.618	4.53	4.596
7	1	10	4.289	4.34	4.296	4.2	4.283
7	1	11	3.88	3.92	4.324	3.8	3.877
7	1	12	3.803	3.85	3.982	3.77	3.799
7	2	1	3.859	3.9	3.86	3.79	3.854
7	2	2	3.807	3.85	3.997	3.72	3.792
7	2	3	3.799	3.84	3.815	3.7	3.797
7	2	4	3.957	3.99	3.966	3.88	3.942
7	2	5	4.276	4.31	4.276	4.17	4.268
7	2	6	4.467	4.49	4.463	4.32	4.449
7	2	7	4.487	4.52	4.036	4.37	4.469
7	2	8	4.561	4.6	4.556	4.43	4.542
7	2	9	4.817	4.84	4.816	4.69	4.785
7	2	10	5.187	5.22	5.2	5.11	5.175
7	2	11	5.112	5.14	5.14	5.01	5.152
7	2	12	5.09	5.12	4.684	4.99	5.112
8	1	1		5.74	5.813	5.61	5.688
8	1	2	5.724	5.75	5.726	5.59	5.71
8	1	3	5.728	5.77	5.713	5.64	5.699
8	1	4	5.675	5.71	5.671	5.59	5.661
8	1	5	5.498	5.53	5.483	5.37	5.481
8	1	6	5.402	5.43	5.385	5.3	5.384
8	1	7	5.268	5.31	5.264	5.18	5.249
8	1	8	4.972	5.01	4.974	4.87	4.959
8	1	9	4.575	4.61	4.593	4.5	4.564
8	1	10	4.192	4.23	4.203	4.12	4.182
8	1	11	3.789	3.82	3.807	3.73	3.771
8	1	12	3.678	3.71	3.687	3.58	3.658
8	2	1	3.727	3.76	3.848	3.6	3.704
8	2	2	3.864	3.89	3.882	3.68	3.848
8	2	3	4.127	4.16	4.13	4.04	4.106
8	2	4	4.234	4.25	4.245	4.11	4.204

Table 7: Continued

Station	Cast	Bottle	Group 1	Group 2	Group 3	Group 4	Group 5
8	2	5	4.327	4.34	4.256	4.21	4.307
8	2	6	4.58	4.61	4.573	4.48	4.574
8	2	7	4.924	4.96	4.929	4.76	4.915
8	2	8	5.358	5.39	5.356	5.27	5.337
8	2	9	5.252	5.28	5.282	5.16	5.234
8	2	10	5.177	5.19	5.193	5.0	5.15
8	2	11	1.468	1.45		1.4	1.464
8	2	12	0.776	0.8	0.776	0.75	0.732

3. Salinity Comparisons

The program of work for the salinity component of the intercomparison experiment was determined on board ship at the start of the cruise, subject to the constraint of limited supplies of IAPSO Standard Seawater. It was decided that the program would consist of four components, each of which would be carried out on the both the Guildline 9 and one or both of the SOKOL salinometers:

- (i) Comparison of IAPSO Standard Seawater (SSW) with Russian Reference Water (RRW). The latter is made in the Analytical Laboratory of the Institute of Oceanology of the Russian Academy of Sciences (Moscow) as a secondary standard of seawater;
- (ii) Determination of the linearity of the salinometers over the machines' full working range, with reference to IAPSO low and high salinity standard seawaters;
- (iii) Measurement of salinity of Russian low and high salinity reference waters; and
- (iv) Comparison of the operational performance of SOKOL and Guildline salinometers through parallel analysis of duplicate samples collected during CTD casts.

Additionally, during the first three sections, the salinometers themselves were further compared. The results of this work program are reported in the sections following.

The following individuals participated in the comparison of salinometers, standard seawater and salinity measurements during the R/V *Vernadsky* Cruise 43 from June 27 to July 8, 1991.

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Three salinometers were used during these experiments: (i) a Guildline Autosol salinometer model 8400A number 9 owned by Woods Hole Oceanographic Institution (WHOI), operated at 110 volts 50 Hz (stepped down from the ship's 220 volt supply) in the WHOI container lab on the aft deck of the ship; and (ii) two Russian salinometers model SOKOL 4602, numbers 1 and 3, run in the ship's salinity laboratory from the ship's power supply, 220 Volts 50 Hz. These salinometers will be referred to in this text as the Guildline 9 and the SOKOL 1 and 3.

It was noted soon after the start of the cruise that the actual power supply in the container lab was delivering nearer 106 Volts, which did not appear to affect noticeably the performance of the Guildline 9. However, it was also noted that the Guildline 9's stability was considerably affected when the ship was steaming; whether this was due to mechanical effects (vibration of the fantail) or electrical (possible disturbance of the supply due to engagement of the power train) was not determined, but was nevertheless eliminated by only working the Guildline 9 when the ship was hove-to on station.

With regard to operational accuracies of the salinometers, the absolute accuracy of the Guildline Autosol machines is stated by the manufacturers to be 0.003 in salinity, but following the most careful operational procedures, this is improved to 0.001. The accuracy of the SOKOL 4602 machines is stated as 0.005 in salinity in routine operation, and 0.003 with careful operation. Both types of machine are read to a precision of 1 part in 10^5 ; for the SOKOLs, in conductivity ratio; for the Guildline, in 2x conductivity ratio.

The SOKOLs determine conductivity ratio with a two-cell conductivity measurement system; one cell holds the standard or reference water, while the other is filled with the sample to be measured. Therefore, since the measured value of conductivity ratio is determined by direct reference to a standard, no calibration correction is required, as is with the Guildline which measures sample conductivity with respect to an internal resistance. The cell volumes of 100 ml are considerably larger than that of the Guildline (<10 ml). The value of conductivity ratio measured by the SOKOLs is the value quoted as such in the text following. The SOKOL cells are surrounded by an oil bath intended to maintain the cells at the same temperature; the temperature of the oil bath (generally 20-22°C, and measured to 0.01°C) is the quoted value of temperature associated with SOKOL conductivity ratio in the text following.

The Guildline Autosol machines determine conductivity ratio by reference to an internal resistance which is (usually) set to produce values correct to approximately 1 part in 10^4 . The correct conductivity ratio for a sample is then determined by applying a single-point calibration correction (using IAPSO Standard Seawater, salinity 35) derived for each sample measurement run. Quoted values of conductivity ratio for the Guildline 9 in the following have been corrected according to the reference standard appropriate to each run. During this cruise, the Guildline 9 would have been standardized at the start and end of each run (or once per hour, whichever is the lesser) in accordance with normal IOSDL practice; the available quantity of Standard Seawater did not permit this, however, so the machine was generally standardized only once per run, at the beginning. The standardization history of the machine during the cruise is given in Appendix C. The Guildline 9 was run throughout the cruise at 24°C.

Table 8: IAPSO Standard Seawater (P-series) and Russian Reference Water (C-series) batch specifications

Batch	Production Date	Conductivity Ratio	Salinity S(Label)
P-113	Feb.90	0.99984	34.9937
P-114	Jul.90	0.99986	34.9945
C-141	Dec.87	1.00009	35.0035
C-145	Feb.89	1.00010	35.0039
C-149	Apr.90	1.00011	35.0043

Duplicate samples were drawn from the Multisampler rosette bottle into 0.1 liter WHOI sample bottles with screw caps and plastic sealing inserts, for analysis by the Guildline 9; for the SOKOLs, with higher sample volume requirement, two types of bottle were used: Russian medical bottles of 0.4 liter capacity with rubber stoppers, and bottles of 0.5 liter capacity with plastic stoppers.

3.1 Comparison of IAPSO Standard Sea Water (SSW) and Russian Reference Water (RRW)

IAPSO Standard Seawater Batch No. P-114 was used for all standardizations during this section; some ampoules of P-113 were also used, in the course of the work reported below. The work was conducted using the SOKOL 3 and the Guildline 9. The work using the latter machine was conducted over two days (29-30 June 91) in order to identify any possible day-to-day variations in results. The specifications of the IAPSO SSW (P-series) and the RRW (C-series) are given in Table 8. Note that S(Label) stands for the salinity value specified on the ampoule label for each batch.

The results of the measurements of the salinity of the RRW C-series are given in Tables 9A, 9B and 9C. Note that for each batch analyzed by the Guildline 9, ampoules 1-3 were analyzed on day 1, ampoules 4-6 on day 2. The Guildline 9 was standardized before and after each measurement run. Note that S(Measured) stands for the measured value of salinity. The last column in Tables 9A and 9B contains, for each batch, the batch number, the overall measured mean salinity S(Measured), the standard deviation (std. dev.) of the values of S(Measured), the salinity of each batch as specified on the ampoule labels S(Label), and the difference $S(L) - S(M)$.

It can be seen from Table 9A that there are small differences between the measurements of salinity made over the two days by the Guildline 9, but these differences are within the stated accuracy of the machine (0.001 in salinity). The Russian Reference Water appears consistent in salinity within batches; the standard deviations of the measured salinities for each batch are all within 0.001. Batch C-141 registers 0.0009 low in salinity, C-145

Table 9: (A) Measurements of Russian Reference Water Salinities by Guildline No. 9

Batch number	Temp °C	Conduc- tivity Ratio	Salinity S(Measured)	Mean (day) values and std. dev.	Overall mean, std. dev., S(Label), S(L)-S(M)
C-141-1	24	1.000035	35.0014	Of 1,2,3:	C-141:
C-141-2	24	1.000055	35.0022	35.0018	35.0026
C-141-3	24	1.000045	35.0018	0.0004	0.0009
C-141-4	24	1.00010	35.0039	Of 4,5,6:	35.0035
C-141-5	24	1.000085	35.0033	35.0033	0.0009
C-141-6	24	1.00007	35.0028	0.0006	
C-145-1	24	1.00006	35.0024	Of 1,2,3:	C-145:
C-145-2	24	1.000065	35.0026	35.0025	35.0032
C-145-3	24	1.000065	35.0026	0.0006	0.0010
C-145-4	24	1.000085	35.0033	Of 4,5,6:	35.0039
C-145-5	24	1.000125	35.0049	35.0038	0.0007
C-145-6	24	1.000085	35.0033	0.0010	
C-149-1	24	1.000065	35.0026	Of 1,2,3:	C-149:
C-149-2	24	1.000065	35.0026	35.0026	35.0027
C-149-3	24	1.000065	35.0026	0.0000	0.0006
C-149-4	24	1.000085	35.0033	Of 4,5,6:	35.0043
C-149-5	24	1.000065	35.0026	35.0027	0.0016
C-149-6	24	1.00006	35.0024	0.0003	

Table 9: (B) Measurements of Russian Reference Water Salinities by the SOKOL 3

Batch and number	Temp °C	Conduc- tivity Ratio	Salinity S(Measured)	Overall mean, std. dev., S(Label), S(L)-S(M)
C-141-1	22.85	1.00007	35.0025	C-141:
C-141-2	22.75	1.00010	35.0037	35.0030
C-141-3	22.76	1.00008	35.0029	0.0006
				35.0035
				0.0005
C-145-1	23.01	1.00006	35.0023	C-145:
C-145-2	23.05	1.00006	35.0023	35.0019
C-145-3	22.91	1.00003	35.0010	0.0008
				35.0039
				0.0020
C-149-1	23.15	1.00005	35.0019	C-149:
C-149-2	23.07	1.00004	35.0016	35.0023
C-149-3	22.91	1.00009	35.0034	0.0010
				35.0043
				0.0020

Table 9: (C) Summary of differences in overall mean salinity

<u>RRW Batch:</u>	<u>Salinity Difference</u>		
	C-141	C-145	C-149
SOKOL 3—Guildline 9:	0.0004	– 0.0013	– 0.0004

Table 10: IAPSO low and high SSW specifications

Batch Number	Temp °C	Conductivity Ratio	Salinity
10L2	24	0.32452	10.1311
30L2	24	0.87187	30.0132
38H1	24	1.07518	37.9791

0.0007 low and C-149 0.0016 low. Thus a consistent negative offset is noted, of Russian Reference Water relative to IAPSO Standard Sea Water. The first two offsets (C-141 and C-145) are within one standard deviation of measured values and may not be statistically significant. The last offset (C-149) is more than two standard deviations low and probably is significant.

From Table 9B, it can be seen that the measurements made by the SOKOL 3 are similar to those of the Guildline 9, with standard deviations of approximately 0.001 (based on a sample of only three values, however), and similar negative offsets to those measured by the Guildline. C-141 is measured 0.0005 low, and C-145 and C-149 are both 0.0020 low.

Some satisfactory comments can be made here on the relative performance of the two salinometers SOKOL 3 and Guildline 9. Both machines used SSW of one batch (P114) as standard. Both machines then analyzed quantities of RRW from each of three batches. Under these controlled conditions, using only water "samples" taken from sealed ampoules stored on board ship at near-laboratory-ambient temperatures, the two machines produced mean salinities within 0.001 or better of one another (see Table 9C).

3.2 Linearity Checks on Guildline No. 9 and SOKOL No. 1 and No. 3 Salinometers

This experiment was intended to determine the Guildline 9 and SOKOL 1 and 3 salinity offsets outside their normal working ranges, taken to be about Salinity=35. IAPSO SSW Batch P114 was used for all tests during this section. Two batches of "low" salinity SSW (salinities $\sim S=10$ and $\sim S=30$) and one of "high" salinity SSW (salinity $\sim S=38$) produced by the IAPSO Standard Seawater Service were used: 10L2 ($S=10$), 30L2 ($S=30$) and 38H1 ($S=38$). Sample specifications (at one temperature) of these batches are given in Table 10. The ampoule labels quote conductivities measured at six temperatures (15 to 30°C, in steps of 3°C), so that salinities determined by the Guildline 9 made reference to the standard conductivity as quoted on the ampoule label for 24°C, the same as the operating temperature for the Guildline 9. Those salinities determined by the SOKOL salinometers used conductivities appropriate to the measured bath temperature determined by linear interpolation between relevant quoted standard conductivities. The measurements were made during the analysis described in the following section, and the results are presented in Table 11. Note that salinity corrections are generated for the SOKOLs, but conductivity

Table 11: (A) Results of linearity checks for SOKOLs

Salino- meter	Batch Number	Temp °C	Conduct- ivity Ratio	Salinity S(M)	Difference S(L)-S(M)
SOKOL No.1	10L2	22.20	0.32419	10.1283	0.0027
	30L2	23.21	0.87173	30.0114	0.0019
	38H1	23.15	1.07524	37.9799	- 0.0009
SOKOL No. 3	10L2	23.89	0.32445	10.1339	- 0.0029
	30L2	22.90	0.87175	30.0129	0.0004
	38H1	22.88	1.07515	37.9761	0.0029

Table 11: (B) Results of linearity checks for Guildline No. 9

Batch Number	Measured Conduct- ivity Ratio	Conduct- ivity Ratio Correction	Salinity S(Measured)	Difference S(L) - S(M)
10L2	0.324545	- 0.000025	10.1321	- 0.0010
30L2	0.871875	- 0.000055	30.0154	- 0.0022
38H1	1.07517	+0.00001	37.9787	0.0004

ratio corrections for the Guildline 9; this latter is converted into an equivalent salinity correction for comparison with the SOKOLs.

The linearity check shows that none of the machines' responses deviate from the expected value by more than about 0.003 in salinity, indicating that all are "well-behaved" outside the most commonly used salinity range. The differences between the SOKOLs and the Guildline 9 are summarized in Table 11C, but no conclusions can be drawn with confidence on the machines' relative performance, since only one ampoule of each standard at each salinity was available for each machine.

3.3 Analysis of RRW Ampoules of Salinity=10,20,30 and 40

The Guildline 9 and SOKOL 1 and 3 salinometers were used to determine the salinities of Russian Reference Waters of salinities S=10, 20, 30 and 40. The measurements were performed as "blind" tests, with the label values of salinity erased. Measurements of

Table 11: (C) Summary of differences in linearity checks

<u>SSW Batch:</u>	10L2	30L2	38H1
Salinity difference:			
SOKOL 3 – Guildline 9:	– 0.0019	0.0027	0.0025
SOKOL 1 – Guildline 9:	0.0037	0.0041	– 0.0013

ampoules of RRW, and SSW as reported above in section 3, were made in the order:

- (1) SSW: P114; (2) SSW: 10L2; (3) RRW: S=10
 (4) SSW: 30L2; (5) RRW: S=30; (6) SSW: 38H1
 (7) RRW: S=40; (8) RRW: S=20; (9) SSW: P114.

The results of the measurements of RRW by the Guildline 9 are given in Table 12A, and those by SOKOL 1 and 3 in Tables 12B and 12C.

In order to apply a correction based on SSW to RRW of salinity for S=20, a correction was calculated by linear interpolation between the corrections for salinities at S=10 and S=30, based on the offset determined by use of SSW batches 10L2 and 30L2. As in the previous section, measured and corrected conductivity ratio are presented for the Guildline 9, but measured and corrected salinity for the SOKOLs.

The consistency of the values obtained from three ampoules at each salinity as measured by the Guildline 9 suggests that within batches, these normal waters are consistent in quality. All values at each salinity were within 0.001, except the S=30, the values of which covered a range of 0.004. The mean difference between the SOKOL 1 and Guildline from these data (Table 12 D) is not significantly different from zero. The mean difference for the SOKOL 3, however, is on average – .003 with the SOKOL 3 salinities higher than the Guildline at all but the lowest salinity reference water.

3.4 Comparison of Performance of Guildline 9 and SOKOL 1 Salinometers during Routine Sample Analysis

Duplicate salinity samples were drawn from Stations 2, 3 and 4 (both casts), station 5 (cast 1), and stations 6, 7 and 8 (both casts). These samples were analysed by both the Guildline 9 and SOKOL 1 salinometers. The results are given in Table 13, in which S=station, C=cast and B=bottle.

CR9 and Sal9 are the Guildline 9 and CR1 and Sal1 the SOKOL 1 conductivity ratio and salinity measurements respectively. T1 is the SOKOL 1 bath temperature (in °C). For each bottle firing, SalCTD is the uncalibrated salinity value and Θ the potential

Table 12: (A) Guildline No. 9 measurements

Nominal Salinity Batch number	Measured Conductivity Ratio	Corrected Conductivity Ratio	Salinity
10-1	0.32584	0.325815	10.1750
10-2	0.325845	0.32582	10.1752
10-3	0.32585	0.325825	10.1753
30-1	0.871125	0.87107	29.9843
30-2	0.87119	0.871135	29.9862
30-3	0.87124	0.871185	29.9887
40-1	1.12596	1.12597	40.0143
40-2	1.125965	1.125975	40.0145
40-3	1.12598	1.12599	40.0151
20-1	0.61043	0.61039	20.2130
20-2	0.61040	0.61036	20.2119
20-3	0.61043	0.61039	20.2130

Table 12: (B): SOKOL No. 1 measurements

Nominal Salinity Batch number	Temp °C	Conducti- vity Ratio	Measured Salinity	Corrected Salinity
10-1	23.30	0.32564	10.1722	10.1749
10-2	23.02	0.32560	10.1721	10.1748
30-1	23.26	0.87106	29.9856	29.9875
30-2	23.18	0.87105	29.9854	29.9873
40-1	23.08	1.12602	40.0137	40.0128
40-2	22.90	1.12604	40.0139	40.0130
40-3	23.04	1.12613	40.0183	40.0174
20-1	22.97	0.61025	20.2131	20.2151
20-2	23.06	0.61019	20.2103	20.2123

Table 12: (C) SOKOL No. 3 measurements

Nominal Salinity Batch number	Temp °C	Conducti- vity Ratio	Measured Salinity	Corrected Salinity
10-1	23.06	0.32575	10.1771	10.1742
10-2	22.69	0.32571	10.1774	10.1745
30-1	23.00	0.87127	29.9942	29.9946
30-2	22.88	0.87114	29.9895	29.9899
40-1	22.84	1.12614	40.0180	40.0209
40-2	22.61	1.12596	40.0100	40.0129
40-3	22.71	1.12612	40.0169	40.0198
20-1	22.77	0.61036	20.2178	20.2166
20-2	22.74	0.61028	20.2153	20.2141

Table 12: (D) Summary of mean values of measured salinity

Nominal Salinity	Mean salinity Guildline 9	measured by SOKOL 1	salinometer: SOKOL 3
10	10.1752	10.1749	10.1743
20	20.2126	20.2137	20.2153
30	29.9864	29.9874	29.9922
40	40.0146	40.0144	40.0179

temperature in °C obtained from the WHOI Neil Brown Mark IIb CTD. The Guildline 9 was standardized mainly using SSW batch P114, although some ampoules of P113 were also used; see Appendix C1 for details. The SOKOL 1 used RRW batch C-149 as standard for all casts except the last, when SSW P114 was used.

Note that, subsequent to this cruise, further salinity comparison data were gathered using samples drawn from a Russian water bottle rosette attached to the ISTOK-7 CTD system. A second WHOI salinometer, Guildline 10, was set up in the ship's salinity laboratory beside the SOKOLs. These data have not been included in this report because the Guildline data from WHOI Number 10 were noisy.

Table 13: Salinity measurements from CTD stations occupied during the Oxygen/Salinity comparison cruise

S	C	B	CR9	Sal9	T1	CR1	Sal1	SalCTD	Theta

2	1	1	1.013890	34.9427	22.49	1.01369	34.9418	34.9508	2.488
2	1	2	0.998545	34.9593	22.54	0.99852	34.9492	34.9633	2.642
2	1	3	0.998965	34.9703	22.62	0.99871	34.9642	34.9760	2.818
2	1	4	0.999245	34.9974	22.65	0.99909	34.9913	35.0038	3.110
2	1	5	0.999935	35.2836	22.63	0.99978	35.2707	35.0251	3.387
2	1	6	1.007200	35.1045	22.51	1.00688	35.0989	35.1092	3.902
2	1	7	1.002655	35.1589	22.45	1.00252	35.1593	35.1681	4.562
2	1	8	1.004035	35.2349	22.44	1.00406	35.2351	35.2382	5.157
2	1	9	1.005965	35.4036	22.44	1.00598	35.3956	35.4099	6.458
2	1	10	1.010245	35.5815	22.46	1.01006	35.5742	35.5888	7.858
2	1	11	1.014755	35.6100	22.48	1.01459	35.6079	35.6211	8.984
2	1	12	1.015475	35.5474	22.48	1.01544	35.5387	35.5498	9.330
2	2	1	1.015370	35.5948	22.63	1.01541	35.6068	35.6157	8.957
2	2	2	1.013690	35.5395	22.60	1.01355	35.5332	35.5481	9.395
2	2	3	1.012235	35.4821	22.57	1.01218	35.4791	35.4942	9.968
2	2	4	1.012900	35.5083	22.51	1.01291	35.5080	35.5179	10.774
2	2	5	1.015045	35.5930	22.49	1.01515	35.5965	35.6056	11.687
2	2	6	1.018225	35.7185	22.46	1.01802	35.7095	35.7222	12.612
2	2	7	1.022705	35.8791	22.43	1.02274	35.8956	35.8982	13.902
2	2	8	1.028320	36.1175	22.41	1.02831	36.1159	36.1288	15.232
2	2	9	1.038875	36.5355	22.40	1.03894	36.5365	36.5519	17.315
2	2	10	1.046265	36.8286	22.40	1.04633	36.8291	36.8341	18.753
2	2	11	1.048360	36.9117	22.41	1.04829	36.9072	36.9211	19.737
2	2	12	1.044475	36.7575	22.43	1.04456	36.7592	36.7711	21.464
3	1	1	0.998605	34.9451	22.64	0.99807	34.9241	34.9492	2.461
3	1	2	0.998740	34.9504	22.67	0.99864	34.9465	34.9620	2.611
3	1	3	0.998985	34.9601	22.63	0.99877	34.9516	34.9748	2.791
3	1	4	0.999595	34.9841	22.54	0.99924	34.9701	34.9895	3.013

3	1	5	1.000020	35.0008	22.47	0.99975	34.9901	35.0108	3.287
3	1	6	1.001465	35.0577	22.43	1.00127	35.0497	35.0708	3.795
3	1	7	1.003830	35.1508	22.45	1.00374	35.1469	35.1627	4.479
3	1	8	1.006140	35.2418	22.47	1.00600	35.2359	35.2502	5.189
3	1	9	1.009125	35.3595	22.50	1.00897	35.3529	35.3644	6.141
3	1	10	1.013490	35.5316	22.54	1.01340	35.5272	35.5407	7.621
3	1	11	1.015000	35.5912	22.62	1.01508	35.5936	35.6059	8.887
3	1	12	1.013785	35.5433	22.71	1.01376	35.5419	35.5534	9.326
3	2	1	1.014880	35.5865	22.69	1.01492	35.5877	35.6016	8.770
3	2	2	1.014215	35.5602	22.63	1.01430	35.5627	35.5725	9.404
3	2	3	1.012655	35.4987	22.57	1.01266	35.4984	35.5110	9.896
3	2	4	1.012580	35.4957	22.61	1.01244	35.4896	35.5074	10.551
3	2	5	1.013645	35.5377	22.67	1.01364	35.5371	35.5506	11.257
3	2	6	1.012240	35.4823	22.65	1.01735	35.6833	35.6984	12.456
3	2	7	1.021190	35.8356	22.65	1.02132	35.8397	35.8512	13.564
3	2	8	1.026230	36.0349	22.68	1.02638	36.0398	36.0439	14.830
3	2	9	1.034485	36.3615	22.62	1.03456	36.3632	36.3770	16.609
3	2	10	1.042180	36.6665	22.66	1.04230	36.6696	36.6878	18.113
3	2	11	1.043295	36.7107	22.68	1.04335	36.7114	36.7276	18.995
3	2	12	1.046960	36.8562	22.62	1.04709	36.8596	36.8714	21.363
4	1	1	0.998540	34.9425	22.55	0.99830	34.9331	34.9514	2.483
4	1	2	0.999050	34.9626	22.71	0.99873	34.9500	34.9662	2.648
4	1	3	0.999330	34.9736	22.72	0.99905	34.9626	34.9815	2.837
4	1	4	0.999845	34.9939	22.68	0.99970	34.9882	35.0058	3.114
4	1	5	1.001290	35.0508	22.67	1.00079	35.0309	35.0465	3.501
4	1	6	1.002875	35.1132	22.64	1.00255	35.1001	35.1138	4.064
4	1	7	1.004495	35.1770	22.63	1.00433	35.1702	35.1881	4.658
4	1	8	1.006360	35.2505	22.62	1.00609	35.2395	35.2583	5.322
4	1	9	1.009115	35.3591	22.57	1.00887	35.3486	35.3648	6.263
4	1	10	1.001410	35.0555	22.54	1.01120	35.4407	35.4594	7.349
4	1	11	1.011075	35.4364	22.54	1.01079	35.4244	35.4431	8.146
4	1	12	1.012595	35.4963	22.64	1.01237	35.4869	35.5075	8.959
4	2	1	1.010880	35.4287	22.88	1.01079	35.4245	35.4401	8.194
4	2	2	1.013335	35.5255	22.98	1.01318	35.5189	35.5414	9.206
4	2	3	1.013215	35.5208	22.89	1.01312	35.5165	35.5323	9.707
4	2	4	1.013180	35.5194	22.83	1.01305	35.5136	35.5269	10.244
4	2	5	1.013500	35.5320	22.68	1.01341	35.5280	35.5423	10.992
4	2	6	1.015665	35.6175	22.64	1.01561	35.6146	35.6260	11.803
4	2	7	1.019295	35.7608	22.63	1.01921	35.7568	35.7747	12.935
4	2	8	1.025040	35.9878	22.61	1.02501	35.9857	35.9876	14.404
4	2	9	1.035970	36.4204	22.59	1.03592	36.4149	36.4329	16.667
4	2	10	1.048340	36.9109	22.61	1.04829	36.9047	36.9255	18.878
4	2	11	1.049105	36.9413	22.59	1.04906	36.9377	36.9378	19.582
4	2	12	1.051305	37.0287	22.64	1.05138	37.0299	37.0425	21.096

5	1	1	1.011525	35.4541	22.49	1.01146	35.4509		
5	1	2	1.011575	35.4561	22.56	1.01151	35.4527		
5	1	3	1.011535	35.4545	22.62	1.01146	35.4510		
5	1	4	1.011510	35.4535	22.65	1.01146	35.4510		
5	1	5	1.011490	35.4527	22.67	1.01140	35.4486		
5	1	6	1.050340	36.9904	22.70	1.05011	36.9796		
5	1	7	1.050105	36.9810	22.66	1.05013	36.9803		
5	1	8	1.050095	36.9806	22.61	1.05019	36.9826		
5	1	9	1.050150	36.9828	22.57	1.05022	36.9838		
5	1	10	1.050160	36.9832	22.54	1.05022	36.9837		
6	1	1	0.998400	34.9370	22.25	0.99812	34.9260		
6	1	2	0.998590	34.9445	22.27	0.99850	34.9409	34.9555	2.542
6	1	3	0.999145	34.9663	22.29	0.99890	34.9567	34.9790	2.825
6	1	4	0.999655	34.9864	22.27	0.99954	34.9819	34.9980	3.045
6	1	5	1.000575	35.0226	22.28	1.00037	35.0141	35.0308	3.394
6	1	6	1.001620	35.0638	22.30	1.00134	35.0525	35.0754	3.779
6	1	7	1.003065	35.1207	22.29	1.00290	35.1137	35.1308	4.315
6	1	8	1.005000	35.1969	22.33	1.00347	35.1857	35.2081	4.994
6	1	9	1.007565	35.2980	22.33	1.00747	35.2934	35.3031	5.863
6	1	10	1.010315	35.4064	22.38	1.01019	35.4011	35.4201	7.125
6	1	11	1.010860	35.4279	22.44	1.01074	35.4227	35.4414	8.030
6	1	12	1.011200	35.4413	22.45	1.01109	35.4366	35.4547	8.805
6	2	1	1.010715	35.4222	22.44	1.01051	35.4136	35.4275	7.898
6	2	2	1.011490	35.4527	22.39	1.01134	35.4462	35.4610	8.826
6	2	3	1.010870	35.4283	22.40	1.01082	35.4256	35.4382	9.613
6	2	4	1.011625	35.4580	22.46	1.01151	35.4526	35.4709	10.478
6	2	5	1.014290	35.5632	22.50	1.01421	35.5591	35.5790	11.594
6	2	6	1.019155	35.7552	22.57	1.01883	35.7417	35.7569	12.964
6	2	7	1.024250	35.9566	22.47	1.02409	35.9492	35.9683	14.400
6	2	8	1.029890	36.1796	22.40	1.02985	36.1765	36.1925	15.795
6	2	9	1.037175	36.4681	22.34	1.03711	36.4638	36.4765	17.553
6	2	10	1.045540	36.7998	22.29	1.04539	36.7919	36.8098	19.476
6	2	11	1.044255	36.7488	22.27	1.04417	36.7438	36.7621	20.921
6	2	12	1.050795	37.0084	22.22	1.05077	37.0051	37.0261	24.000
7	1	1	0.998450	34.9390	22.39	0.99843	34.9382	34.9511	2.492
7	1	2	0.998915	34.9573	22.35	0.99880	34.9528	34.9680	2.677
7	1	3	0.999350	34.9744	22.34	0.99909	34.9642	34.9874	2.878
7	1	4	0.999990	34.9996	22.37	0.99987	34.9949	35.0099	3.134
7	1	5	1.000870	35.0342	22.39	1.00072	35.0281	35.0442	3.478
7	1	6	1.002860	35.1126	22.45	1.00200	35.0785	35.0984	3.987
7	1	7	1.003720	35.1465	22.50	1.00345	35.1354	35.1531	4.523
7	1	8	1.005050	35.1989	22.54	1.00500	35.1966	35.2097	5.129
7	1	9	1.006870	35.2706	22.55	1.00664	35.2611	35.2773	5.894
7	1	10	1.008095	35.3189	22.58	1.00803	35.3158	35.3313	6.759
7	1	11	1.007715	35.3039	22.60	1.00761	35.2995	35.3176	7.615

7	1	12	1.009425	35.3713	22.55	1.00923	35.3630	35.3858	8.432
7	2	1	1.007865	35.3098	22.49	1.00777	35.3055	35.3174	7.589
7	2	2	1.009770	35.3849	22.41	1.00938	35.3690	35.3866	8.472
7	2	3	1.011175	35.4403	22.34	1.01103	35.4339	35.4544	9.455
7	2	4	1.012755	35.5026	22.33	1.01257	35.4948	35.5119	10.468
7	2	5	1.014500	35.5715	22.39	1.01443	35.5682	35.5791	11.375
7	2	6	1.017900	35.7057	22.44	1.01755	35.6911	35.7132	12.537
7	2	7	1.021805	35.8599	22.46	1.02167	35.8537	35.8711	13.679
7	2	8	1.028000	36.1049	22.54	1.02780	36.0959	36.1168	15.216
7	2	9	1.039125	36.5454	22.54	1.03908	36.5422	36.5612	17.442
7	2	10	1.052140	37.0619	22.51	1.05200	37.0545	37.0728	20.008
7	2	11	1.057380	37.2701	22.53	1.05724	37.2623	37.2821	21.784
7	2	12	1.057325	37.2680	22.58	1.05730	37.2650	37.2847	22.078
8	1	1	0.998545	34.9427	22.38	0.99838	34.9363	34.9538	2.538
8	1	2	0.998935	34.9581	22.36	0.99885	34.9547	34.9697	2.693
8	1	3	0.999345	34.9742	22.36	0.99911	34.9649	34.9898	2.905
8	1	4	1.000155	35.0061	22.35	1.00005	35.0017	35.0195	3.216
8	1	5	1.001190	35.0468	22.35	1.00104	35.0405	35.0590	3.598
8	1	6	1.002480	35.0976	22.39	1.00229	35.0897	35.1079	4.028
8	1	7	1.004450	35.1752	22.43	1.00430	35.1689	35.1855	4.649
8	1	8	1.006655	35.2621	22.46	1.00659	35.2592	35.2732	5.418
8	1	9	1.009230	35.3636	22.43	1.00911	35.3582	35.3739	6.376
8	1	10	1.010195	35.4016	22.41	1.01012	35.3979	35.4148	7.251
8	1	11	1.010250	35.4038	22.40	1.01025	35.4035	35.4175	8.198
8	1	12	1.011650	35.4590	22.41	1.01131	35.4449	35.4595	8.910
8	2	1	1.012180	35.4799	22.46	1.01219	35.4798	35.4937	9.715
8	2	2	1.012915	35.5089	22.49	1.01288	35.5068	35.5235	10.485
8	2	3	1.014350	35.5656	22.56	1.01436	35.5651	35.5807	11.297
8	2	4	1.017055	35.6723	22.59	1.01709	35.6729	35.6932	12.323
8	2	5	1.020965	35.8267	22.56	1.02095	35.8852	35.8414	13.417
8	2	6	1.028675	36.1316	22.54	1.02869	36.1309	36.1468	15.319
8	2	7	1.041905	36.6556	22.51	1.04196	36.6563	36.6720	17.860
8	2	8	1.048720	36.9260	22.46	1.04863	36.9206	36.9420	19.130
8	2	9	1.051265	37.0271	22.48	1.05130	37.0266	37.0450	20.746
8	2	10	1.051540	37.0380	22.51	1.05139	37.0302	37.0488	21.336

The first-order results of the comparison of measured salinities Sal9, Sal1 and SalCTD are shown in Figure 7, in which are plotted the mean (by cast) salinity differences Sal1-Sal9, Sal9-SalCTD and Sal1-SalCTD, where SalCTD is the "uncalibrated" CTD salinity available on the ship.

From the data presented here, it can be seen that the SOKOL 1 salinities are ~ 0.005 fresh on average relative to the Guildline 9 values (and also that the CTD salinities settle to a mean offset of $\sim +0.01$ relative to the Guildline 9 values).

Figure 8 shows the standard deviation (about the mean by cast) of the above salinity differences, from which it is seen that all three standard deviations are similar and equal approximately 0.003–0.004. Thus, there is a bias of 0.005 with a std. dev. of 0.003 in the results of the two salinometers. Also, the fits of the salinity offset derived from each machine to the CTD salinity are seen to be statistically indistinguishable, so that no suggestion of the source of the bias is deduced from these data.

Some bad data values were excluded (8 out of a total possible 140) from the computations of the values presented in Figures 7 and 8; and since the statistics therein are of differences, each single bad value excludes two difference values from the computations for each station (if Sal9 is wrong, then so are both Sal1-Sal9 and SalCTD-Sal9). Note that a sample salinity which disagrees with the relevant CTD salinity (by reason of Niskin bottle leakage contamination, for example) is not necessarily automatically excluded, as the sample salinities Sal1 and Sal9 may still be comparable, so the CTD salinity is then identified as the 'bad' value. Bad data values (following) are identified as station-cast-bottle-variable, and were: 2-1-5-SalCTD; 3-2-6-Sal9; 4-1-5-Sal9; 4-1-10-Sal9; 4-2-8-SalCTD; 4-2-11-SalCTD; 7-1-6-Sal9; 8-2-5-Sal1.

Figure 9 shows salinity difference Sal1-Sal9 plotted against CTD potential temperature for each sample. Note that, at this stage, other available sample variables could have been used as the ordinate instead of potential temperature: pressure (depth), salinity (in this region of the North Atlantic), and bottle position on the rosette are all monotonically increasing or decreasing functions of depth and would thus produce results with similar trends. The functionality of the bias identified above emerges here: a linear regression on salinity difference versus potential temperature gives a line with slope:

$$(\text{Sal1} - \text{Sal9}) = -0.0084 + 0.00033\Theta \quad (1)$$

so that the bias is approximately 0.001–0.002 for 20 °C (surface water), and increases to 0.007 for 2–3 °C (3000 meter water). Note that the SOKOL 1 are somewhat fresher than Guildline 9 salinities. However, the source of the bias is not thus uniquely identified. Also three further values were excluded as outliers in the determination of (1) above: 2-2-1-Sal9; 2-2-7-Sal1; 3-1-1-Sal1 and Sal9.

Saunders (1986) describes the deep Θ -S relationship in the North Atlantic in the same region as this cruise and at depths below about 3000 meters as "remarkably uniform". He is able, using deep north-east Atlantic data from 1957 to 1983, to identify a straight-line relationship between salinity and potential temperature for sample data below about 3000 meters. Systematic salinity differences between "high-quality" data sets are of the order of 0.003. Figures 10a and 10b show the deepest sample salinities from this cruise derived

Figure 7: Mean salinity differences by cast: SOKOL 1, Guildline 9, and CTD

Figure 8: Standard deviation of salinity difference by cast: SOKOL 1, Guildline 9 and CTD

Figure 9: Salinity difference, SOKOL 1 - Guildline 9 versus CTD potential temperature

Salinity vs potential temperature

Figure 10: Salinity versus potential temperature

from both Guildline 9 and SOKOL 1, respectively, plotted against potential temperature, together with Saunders' line, given as

$$S = 34.698 + 0.098\Theta \quad (2)$$

From these figures it can be seen that the Guildline 9 salinity values coincide with Saunders' line, but that (for given potential temperature) the SOKOL 1 values are biased ~ 0.007 fresh, which corresponds to the mean bias at low temperatures resulting from the regression stated in equation (1) above.

3.5 Conclusions

In a preceding section, it was shown that the two types of salinometer are capable of working to comparable accuracy and precision under "laboratory" conditions: the analysis of RRW ampoules gave equivalent salinity values different between machines by 0.001 or better, on average for the Guildline 9 and SOKOL 1. However, an operational bias has been identified and tentatively ascribed to an as yet unidentified aspect of the operation of the SOKOL 1 machine. It is possible to advance the following hypothesis as a consistent explanation of the features described above. The Russian system requires water samples to be drawn from the rosette into large (~ 0.5 liter) capacity bottles. It is the deep, and therefore the coldest, samples which show the greatest salinity bias. If the water samples had not reached thermal equilibrium with the standard cell in the SOKOL salinometer at the time of analysis, they would, if anything, be colder than the cell, which would reduce the measured conductivity ratio below the value to be expected assuming thermal equilibrium at the measured bath temperature, and so reduce (i.e. freshen) the expected salinity. Test calculations show that a temperature difference between the cells in the SOKOL salinometer of up to $.01^\circ\text{C}$ could produce the observed bias. Therefore, it is recommended that Russian water samples be given time to thermally equalibrate (perhaps a water bath would accelerate this process) before they are analyzed in the SOKOL.

Appendix A

Pre-Cruise Salinity Measurement Training presented by Ocean Scientific International Godalming, Surrey, UK

A.1 Introduction

Pre-cruise training on the "Laboratory Measurement of Salinity" was provided by Ocean Scientific International Ltd., Wormley, UK. The course was run aboard the R/V *A. Vernadsky*, whilst in port at Funchal, Madiera, on 27th June 1991. Tutors for the course were Dr. Fred Culkin, and Paul Ridout. All lectures and discussions were aided by the services of the interpreter on the *Vernadsky*.

The opening lectures were carried out in the officers' saloon so that slides could be projected. Attendance at this time comprised approximately 25 personnel from the *Vernadsky* (some of whom were non-scientific) and scientists from WHOI and Tenerife.

Later in the morning the number of attendees reduced to those scientists who had a direct involvement in salinity measurement in the cruise. Each participant was provided with a full set of course notes, background papers and relevant UNESCO documents. Most of the participants had some first-hand knowledge of the Guildline Autosol. However, they had not used the instrument at sea.

A.2 Course Details

A.2.1 History and Definitions

After a brief welcome and introduction by Paul Ridout, a lecture was presented by Fred Culkin on the history and definitions of salinity in which he covered the development of salinity measurement methods from the early work to the present day internationally approved Practical Salinity Scale. Dr. Culkin stressed the importance of the current formula, that all measurements are conductivity based, and that salinity is dimensionless.

A.2.2 Standard Seawater

Following an open discussion period, Dr. Culkin described the development of the IAPSO Standard Seawater Service from the original work of Martin Knudsen to its modern day operation by Ocean Scientific International Ltd. at Wormley, UK. The importance of salinity standards was discussed and comparisons drawn with that of the Russian Standard Seawater Service, particularly with respect to the range of salinities available and accuracy

of label values. It was agreed, by all parties, that close collaboration between the IAPSO and Russian Standard Seawater Service should be actively encouraged. Ocean Scientific were presented with ampoules of Russian Standard Seawater and, in return gave 20 ampoules from their range of standards (35, 38, 30, and 10) for comparative measurement during the cruise.

A.2.3 Sampling and Sample Storage

Paul Ridout explained that high precision salinity measurement (to 0.001) required close attention to details, of which sample storage was important. His lecture provided information about suitable sample bottles and closures, preparation, filling and storage methods plus general precautions to eliminate evaporation or contamination of the water sample.

A.2.4 Data Processing and Reporting

This practical session was designed to highlight the importance of accurate and detailed data recording and processing. Discussion included use of raw data log sheets, *Unesco Technical Papers in Marine Science*, No. 39, (Unesco 1981) and computer software. The programs 'SALINITY' and 'CONDUCTIVITY' which calculate salinometer salinity and CTD salinity respectively, using approved algorithms, were demonstrated and then used by the participants. Prepared log sheets were provided for this exercise. At the end of this session the Russian scientists were presented with full working copies of the software for future use.

A.2.5 High Precision Measurement

Following a short introduction, this work took place in the WHOI container which was equipped with two operating Guildline Autosol salinometers (8400A). Procedures for standardization and measurement were demonstrated using the IAPSO Standard Seawater and samples provided. Detailed discussion with "hands-on" practice then followed. However, it was decided that due to the limitations on space, further practical sessions comparing individual measurements on different salinometers (Guildline and Russian) should continue during the cruise.

Most of the participants had some first-hand knowledge of the Guildline Autosol. However, they had not used the instrument at sea. Their Russian sea-going salinometers were demonstrated.

A.2.6 Salinometer Maintenance

Paul Ridout demonstrated the normal maintenance program as followed at Ocean Scientific. There was detailed discussion within the group on all aspects of maintenance to ensure maximum stability of the instrument. One Autosal was "opened up" for operational study.

A.3 Conclusion

The course was well received and the general feeling of the participants was that the exercise had been both informative and useful. Hope was expressed from all sides that there would continue to be close communication and cooperation in the future.

Appendix B

B.1 Institute of Oceanographic Sciences, James Rennell Centre (JRC)

Automated Oxygen Analysis Procedure for the R/V *Vernadsky* Intercalibration Cruise, June 1991

B.1.1 Overview

Recent purchase of an IBM PC controlled instrument by the Institute of Oceanographic Sciences (IOS), James Rennell Centre (JRC) from Sensoren Instrumente Systeme - Kiel, Germany, allows oxygen determinations based on the whole bottle photometric end point titration method described by Carpenter (1965a,b). The system consists of a motor burette, stand and stirrer, dark blue alternating light photometer and electronics for the communication of photometer and burette via serial RS232 interface. The light source is a solid state device modulated to discriminate between the iodine signal and illumination effects.

Chemical pretreatment of the seawater sample releases iodine in proportion to the amount of dissolved oxygen in the sample. By computer control, the motor burette dispenses titrant into the treated sample continuously until a predetermined percentage transmission is reached, at which stage the addition of titrant is reduced to small doses until the endpoint is reached. An algorithm is used to exactly determine the endpoint of titration. The concentration of dissolved oxygen is calculated from values obtained from sample, standard and blank titration volumes together with reagent and sample volumes.

B.1.2 Equipment

B.1.2.1 Glassware and Dispensers

The motor burette described is a Metrohm Dosimat Model 665 (V.A. Howe). The reproducibility and absolute accuracy has been determined at JRC to be better than ± 0.0005 ml. The Dosimat is fitted with a 1 ml exchange unit and an antidiffusion tip on the delivery arm. The minimum recorded dosage of the 1 ml burette is 0.001 ml; however, the endpoint is determined algorithmically, allowing determinations better than this level of precision.

Standards are dispensed using a Dosimat fitted with a 5 ml exchange unit. The reproducibility and accuracy of the delivery are comparable with the values stated above.

The bottle dispensers (Anachem) used to add the manganese chloride, sodium hydroxide/sodium iodide and sulphuric acid reagents are adjusted to deliver 1 ml $\pm 0.2\%$. A 1 ml positive displacement pipette (Camlab) is used for blank determinations.

The sample bottles are 120 ml Erlenmeyer flasks individually weight calibrated at 20°C and fitted with ground glass stoppers. Bottle volumes used in the determination of dissolved oxygen concentration must be corrected to allow for the temperature of the seawater at the time of sampling (see calculations).

B.1.3 Reagent Preparation

1. Manganese Chloride (tetrahydrate) 3M:

600 g of MnCl_2 is dissolved in 600 ml distilled water. This solution is filtered and made up to 1 liter.

2. Sodium Hydroxide 8N/Sodium Iodide 4M:

320 g of sodium hydroxide is added to approximately 400 ml of distilled water. The solution is covered and allowed to cool. 600 g of sodium iodide is dissolved in the above solution. The reagent is filtered and made up to 1 liter. If the solution is cloudy or discoloured, it is discarded.

3. Sulphuric Acid 10N:

280 ml of concentrated sulphuric acid is added to 600 ml of dissolved water slowly. The reagent is allowed to cool and made up to 1 liter with distilled water.

4. Sodium Thiosulfate (0.2N)

50 g of sodium thiosulfate (tetrahydrate) is dissolved in and made up to 1 liter with distilled water.

5. Potassium Iodate (0.0100N):

0.3567 g of potassium iodate is carefully made up to 1 liter in a volumetric flask. All reagents are prepared from BDH (MERCK) analytical reagents. Scales are calibrated prior to all weighings and all standard solutions are prepared at 20°C. Reagents are prepared before the cruise and sealed in 1 liter brown glass bottles. Reagents 1 and 2 are filtered through glass fiber filters.

Batch numbers of reagents used during R/V *Vernadsky* Cruise 43.

Manganese Chloride	4274260J
Sodium Hydroxide	2104180L
Sodium Iodide	2101020L
Sulphuric Acid	3828370M
Sodium Thiosulfate	2822082M
Potassium Iodate	9830170K

B.1.4 Standardization

All analyses should be performed in a temperature-controlled environment of 20°C since the thermal expansion of the aqueous solutions will affect the results.

Standardization is performed before each set of sample analyses and whenever any of the reagents used for the procedure are changed.

1. 100 ml of distilled water is added to a clean Erlenmeyer flask.
2. 1 ml of 10N sulphuric acid is added to the water and the flask is mixed.
3. 1 ml of the sodium hydroxide/sodium iodide solution is added whilst mixing is continued. At this stage, the sample must be colorless.
4. 1 ml of the manganese chloride solution is added to the flask and mixed.
5. Exactly 10 ml of 0.01N potassium iodate standard is added to the flask using the Metrohm burette.
6. The titration is performed immediately in the standardization mode, and, when the endpoint is reached, the results are stored in a specific calibration file. The above procedure is repeated until the titration volume does not vary by more than 0.001 ml.

B.1.5 Blanking¹

1. 100 ml of distilled water is added to an Erlenmeyer flask. The reagent addition procedure is exactly the same as the standardization procedure except only 5 ml of potassium iodate standard is added. The titration is run in the blank mode of the program. When the endpoint is reached a further 5 ml of potassium iodate standard is added and the titration is performed again. The difference between the two titers is stored as the blank value. Blanking and standardization procedures are performed using distilled water not seawater.

B.1.6 Calculations

Calculation of dissolved oxygen:

$$O_2 = \frac{\frac{(V_x - V_{\text{blk,dw}}) \cdot V_{\text{io3}} \cdot N_{\text{io3}} \cdot 5598}{(V_{\text{std}} - V_{\text{blk,dw}})} - 1000 \cdot \text{DO}_{\text{reg}}}{(V_{\text{bot}} - V_{\text{reg}})} \quad (1)$$

where:

¹Editor's note: Large blank values and greater than normal scatter of observations at oxygen concentrations less than 1 ml/l led to the realization that the titration program does not allow sufficient time for mixing at these low concentrations. Subsequent to this discovery, blanking was done with two additions of 5 ml standard solution and previously determined blank values were replaced with the later values.

V_x	=	thiosulfate titer of sample (ml)
$V_{\text{blk,dw}}$	=	thiosulfate titer of distilled water blank (ml)
V_{io3}	=	volume of iodate standard at temperature of standardization.
N_{io3}	=	normality of iodate standard at temperature of standardization.
DO_{reg}	=	absolute amount of oxygen added with the reagents, 0.0017 ml (Murray et al, 1968).
V_{std}	=	thiosulfate titer of standard (ml).
V_{bot}	=	volume of sample bottle at time of sampling (ml).
V_{reg}	=	volume of sample displaced by the reagents (2 ml).
O_2	=	sample oxygen concentration (ml/l).

Calculation of flask volume at sampling temperature

$$V_{\text{bot}} = \text{vol}(20) \cdot [1 + \text{TE}(\text{tsw} - 20)] \quad (2)$$

V_{bot}	=	volume of flask at temperature of the seawater.
$\text{vol}(20)$	=	volume of flask at 20°C.
TE	=	cubical coefficient of thermal expansion for borosilicate glass = 1×10^{-5}
tsw	=	temperature of the seawater.

B.2 The Marine Hydrophysical Institute of the Ukrainian Academy of Sciences

Determination of Dissolved Oxygen

The determination of dissolved oxygen in marine water is conducted by the Winkler method as described below.

B.2.1 Reagents

The reagents (v/o Soyuzreakhim) used in the analysis are: The manganese chloride reagent is prepared by dissolving 500 g of analytical grade $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in 600 ml of distilled water. This solution is filtered through a millipore glass filter and distilled water is added to make one liter. The solution is stored in a dark glass bottle with a ground glass stopper.

The alkaline iodate reagent is prepared by dissolving 700 g of analytical grade KOH in 700 ml of distilled water. Separately 300 g of KI is dissolved in 450 ml of distilled water and both solutions are mixed together and filtered through millipore glass filters.

The sulphuric acid (20% solution) is prepared by adding one volume of analytical grade, concentrated H_2SO_4 (density 1.84 g/cm^3) to four volumes of distilled water.

To prepare the sodium thiosulfate (0.02 N solution) dissolve 25 g of analytical grade $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in 5 l of distilled water. The distilled water is first boiled for 30 minutes to remove dissolved atmospheric carbon dioxide.

To prepare the potassium iodate (0.02 N) standard solution dissolve exactly 0.7134 g of analytical grade KIO_3 in distilled water and make to the mark in a 1 liter volumetric flask. The solution is stored in a dark glass bottle with a ground glass stopper.

The starch solution (0.5%) is prepared by mixing 0.5 g of soluble starch with a small amount of cold distilled water. Pour this paste into 100 ml of boiling distilled water and boil for 1-2 minutes.

B.2.2 Determination of the reagent blank

Two ml of sulphuric acid, 1 ml of alkaline KI and 1 ml of manganese chloride solutions are added to 96 ml of distilled water and thoroughly stirred after each addition. If, after the addition of 1 ml of the starch solution and subsequent mixing, a blue color does not appear, then the reagents do not contain oxidizing compounds. However, if a light blue color is present, then not more than 0.02 ml of thiosulfate solution should be used to titrate to the endpoint. If more than 0.02 ml of thiosulfate is required, the reagents should be changed.

B.2.3 Instruments

The capacity of the oxygen sample bottles is between 110-140 ml and each is carefully weight calibrated. The ground glass stoppers are elongated as described by Green and Carritt (1966).

A 12 ml calibrated automatic burette is used to dispense the thiosulfate to ± 0.02 ml. The 1 ml reagent dispensers are accurate to $\pm 0.4\%$.

A calibrated 10 ml pipette is used to dispense the potassium iodate solution during standardizations.

A magnetic stirrer is used to thoroughly mix the sample during each titration.

B.2.4 Procedure

The oxygen water samples are collected in plastic water samplers attached to the ISTOK CTD package. The oxygen samples are collected immediately after this package arrives on deck using a pipette immersed to the bottom of the sampling bottle. The sample bottle is filled slowly to avoid air bubbles and 1/3 of the bottle volume is allowed to overflow. Immediately after collection of the oxygen water sample 1 ml of the manganese chloride solution and 1 ml of the alkaline KI solution is dispensed beneath the water surface with the automatic reagent dispensers. The stopper is carefully placed in the bottle to avoid the introduction of air bubbles. The bottle is then vigorously shaken to mix the reagents and is stored in a dark place for about 30 minutes while the precipitate settles to the bottom.

The precipitate dissolves when 2 ml of the sulphuric acid solution is added. A magnet is placed in the bottle and it is placed on a magnetic stirrer.

The iodine solution is titrated with the sodium thiosulfate solution until it becomes a light straw color. One ml of the starch solution is added as an indicator and the titration continues until the blue solution is completely colorless. The thiosulfate burette readings are recorded to ± 0.01 ml.

B.2.5 Standardization of the Thiosulfate Solution

Approximately 20-25 ml of distilled water is poured into an oxygen sample bottle and 2 ml of sulphuric acid and 1 ml of the alkaline KI reagents are added and thoroughly mixed. One ml of manganese chloride reagent is then added and mixed. Ten ml of the 0.02N iodate standard solution is dispensed with the calibrated pipette and distilled water is added to equal the calibrated volume of the sample bottle. A stirring magnet is placed in the sample bottle, and it is set upon the magnetic stirrer. The solution is titrated with thiosulfate until it is a pale straw color. At this point 1 ml of starch is added and the titration is continued until the solution is colorless. The burette reading is recorded to

± 0.01 ml. This titration is repeated 2–3 times and, if the difference between titrations is less than 0.02 ml, the arithmetic mean is used in the following calculation.

The calculation of the correction factor is as follows. One ml of the 0.02N sodium thiosulfate solution corresponds to 0.0112 ml of dissolved oxygen. The correction factor (K) for the thiosulfate solution is calculated from the formula:

$$K = (A_1 + D_1) / (B_1 + D_2) \quad (1)$$

where:

A_1 = the volume of the standard solution;

D_1 = a pipette correction;

B_1 = the mean value of the thiosulfate used to titrate the standard solution;

D_2 = the instrumental correction for the burette reading.

B.2.6 Calculation and reporting of results

The calculation of the dissolved oxygen concentration (ml/l) is carried out using the formula:

$$O_2(\text{ml/l}) = 8nNK \cdot 1000 / ((V - 2) \cdot 1.429) \quad (2)$$

where:

8 = an equivalent mass of the oxygen;

n = the volume of thiosulfate (ml) used to titrate the sample;

N = the normality of the thiosulfate solution;

K = a correction factor for the thiosulfate normality;

$(V-2)$ = the volume of the oxygen sample bottle minus the volume of the reagents;

1.429 = the weight of 1 ml of oxygen at $T=0^\circ\text{C}$ and pressure = 760 mm Hg.

Simplifying the above expression:

$$8nNK \cdot 1000 / ((V - 2) \cdot 1.429)$$

we get: $O_2(\text{ml/l}) = (111.97nK) / (V - 2)$.

To express the oxygen concentration in millimoles per liter multiply the value in ml/l by 0.089.

The concentration of the oxygen saturation is calculated from the following formula:

$$O_2(\%) = (O_2 \cdot 100) / O'_2 \quad (3)$$

where:

O_2 = the amount of oxygen measured from a sample by the Winkler method;

O'_2 = the amount of oxygen saturating sea water at the same temperature and salinity as the sample as presented in the Unesco (1974) tables.

B.3 Instituto Español de Oceanografía, Centro Oceanográfico de Canarias

Determination of Dissolved Oxygen in Sea Water as Carried out in the Oceanographic Laboratory at the Canary Islands

The method followed by this laboratory is basically the method of Strickland and Parsons (1972).

B.3.1 Reagents

1. All of the reagents used in these measurements are analytical grade "Merck Pro-Analysi".
2. Alkaline iodide solution: Dissolve 500 g NaOH in 500 ml double-distilled water (DDW). Dissolve 300 g KI in 450 ml DDW and mix the two solutions.
3. Manganese sulfate reagent: Dissolve 365 g $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ in DDW and make to 1 liter.
4. Sulphuric acid: Concentrated H_2SO_4 .
5. Sodium thiosulfate (0.01N): Dissolve 2.9 g of sodium thiosulfate pentahydrate in one liter of DDW.
6. Potassium biiodate standard solution (0.0100N): Exactly 0.32495 g of $\text{KH}(\text{IO}_3)_2$ is dissolved in DDW and the volume is made to 1 liter.
7. Starch solution as indicator: Make a 0.1 to 0.2% starch solution in DDW.

B.3.2 Calibration of the thiosulfate solution

Fill a BOD bottle with sea water and add 1 ml H_2SO_4 and 1 ml of alkaline iodide solution and mix thoroughly. Add 1 ml of the MnSO_4 solution and mix again. Finally add 10 ml of the 0.0100N biiodate solution and let iodine liberation occur for three minutes. Titrate with 0.01N thiosulfate solution. Three replicate determinations are made and the average is taken to calculate the factor F.

$$\text{Thiosulfate Factor} = K = 10/V \text{ (Volume of thiosulfate)}$$

B.3.3 Calculation

One ml of 0.01N thiosulfate is equivalent to 0.0056 ml O₂. If 2 ml of reagents are added to the sample the oxygen content is calculated as:

$$\text{O}_2\text{ml/l} = (A \cdot K \cdot 0.056 \cdot 10^3)/(B - 2) \quad (1)$$

where:

A = ml of thiosulfate solution (0.01N) added during the titration.

K = Thiosulfate factor as described above.

B = Volume of BOD bottle.

B.4 The State Oceanographic Institute of Odessa

Determination of Dissolved Oxygen

B.4.1 Reagents

The producers of the oxygen reagents and their batch numbers are listed below.

1. The manganese chloride (46) - The Leningrad plant 'Krasnykhimik'.
2. The potassium hydroxide (7) - Lisichansky khimbobinat.
3. The sodium iodide (124) and the potassium iodate (15) - Ural plant of chemical reagents.
4. The sulphuric acid (36) - The Odessa superphosphate plant.
5. The sodium thiosulfate - The Charkassky plant of chemical reagents.
6. The starch - The Pazdelnyansky plant of biocompounds (54).

B.4.2 Reagent preparation

1. The manganese chloride solution is prepared by dissolving 250 g in distilled water and making to the mark in a 0.5 liter volumetric flask.
2. The alkaline sodium iodide solution is prepared as follows:
 - a) Dissolve 392 g NaI in 300 ml distilled water.
 - b) Dissolve 490 g KOH in 560 ml distilled water.
 - c) Mix both solutions and add distilled water to make to the mark in a 1 liter volumetric flask.
3. The potassium iodate (0.0200N) is dried to a constant weight of 40°C in a vacuum dessicator for three days. Exactly 0.7134 g of potassium iodate is dissolved in distilled water and made to the mark in a 1 liter volumetric flask at a room temperature of 20°C.
4. The sulphuric acid solution is prepared by adding 1 volume of concentrated sulphuric acid with a density of 1.84 to four volumes of distilled water.
5. The sodium thiosulfate solution (0.02N) is prepared by dissolving 50 g in 5 liters of distilled water which has been boiled to remove CO₂. Three ml of chloroform is added as a preservative and the solution is stored in dark glass bottles with ground glass stoppers.
6. The starch solution (0.5%) is prepared by adding 0.5 g of soluble starch to 15-20 ml of distilled water. This solution is gradually poured into 80-85 ml of boiling water and boiled for 1-3 minutes. The starch is preserved by the addition of 1-2 drops of chloroform.

B.4.3 Procedure for the determination of the titer of the sodium thiosulfate

Because the 0.02N thiosulfate is not stable, it is necessary to determine its normality daily. The thiosulfate correction factor is determined by titration of the sodium iodate standard in an acid solution.

One mole of iodate is equivalent to six moles of thiosulfate. Two ml of sulphuric acid is added to 40–50 ml of distilled water in a conical titration flask. Then 1 g of dry potassium iodate is added to the flask. The flask is stoppered and carefully mixed. After about one minute the iodine solution is titrated with thiosulfate until the solution becomes a pale yellow color. At this point 1 ml of starch and 50 ml of distilled water is added and the titration is continued until the solution is colorless. This procedure is repeated 2–3 times or until the differences in burette readings does not exceed 0.01 ml. The arithmetic mean is taken as the final value.

The correction factor for the sodium thiosulfate solution normality is calculated from the following formula:

$$K = a/b$$

where:

a = The volume of the calibrated pipette.

b = True calibrated pipette reference.

B.4.4 Volume of the glassware and the burette gradation spacing

1. The 1.0 liter calibrated measuring flask.
2. The calibrated automatic pipette with volumes of 15.07, 15.02, and 15.11 ml.
3. The calibrated 25 ml burette with scale lines every 0.05 ml.
4. The calibrated sample bottles with tight stoppers. The volumes are listed separately.

B.4.5 Description of the finite point of the detection method

Two ml of sulphuric acid solution after the precipitate has settled to half the height of the sampling bottle. The contents are then poured into the 250 ml titration flask and the

bottle is rinsed with distilled water that is also added to the titration flask. The sample is then titrated with the sodium thiosulfate in the same way as the titration of the standard solution. The titration is finished if a slight blue color does not reappear 3-5 seconds after the addition of the last drop of thiosulfate.

B.4.6 Equations used for the calculations of the dissolved oxygen

1. The absolute concentration (ml/l) of dissolved oxygen is calculated from the formula:

$$O_2 = (111.96 \cdot n \cdot k) / (V - 2) \quad (1)$$

where:

n = The burette reading

k = A correction factor for the normality of the thiosulfate solution.

$V - 2$ = The volume of the sample bottle minus the 2 ml of added reagents.

The calculated oxygen volume is respect to 0°C and 760 mm Hg. If using only one sample bottle the multiplier $M = 111.96/(V-2)$ should be calculated. The formula is thus simplified

$$O_2 = M \cdot n \cdot k \quad (2)$$

2. The percent of oxygen saturation (which is the ratio of measured oxygen concentration at the *in situ* temperature and salinity to the saturated concentration at the same temperature, salinity and pressure, 760 mm Hg) is calculated from the following formula:

$$O_2(\%) = (O_2 \cdot 100)/O'_2 \quad (3)$$

where:

O_2 = the measured concentration in ml/l.

O'_2 = the saturated value at the *in situ* temperature and salinity given in the tables by Yidrometizdat, (1976).

3. The oxygen content is mg O_2 /l is calculated from the formula:

$$O_2(\text{mg/l}) = R \cdot 1.429 \quad (4)$$

where:

R = The content of dissolved oxygen in the seawater sample in ml/l.

B.5 Woods Hole Oceanographic Institution, Woods Hole, MA USA

Automated Oxygen Titration and Salinity Determination presented by G.P. Knapp, M.C. Stalcup and R.J. Stanley

The recent acquisition of IBM PC-AT compatible computer systems by the Hydrographic Group at the Woods Hole Oceanographic Institution (WHOI) has resulted in the development of an automated technique for the measurement of dissolved oxygen in seawater and the acquisition of conductivity ratio measurements made with an Autosol Salinometer. The method for determining the endpoint in the modified Winkler titration is similar to that described by Culberson and Huang (1987) and has proven to be more precise and reliable than the titroprocessor-based "dead stop" method employed previously at WHOI (Knapp *et al.*, 1989).

B.5.1 Oxygen Equipment Description and Calibration

B.5.1.1 Dispensers, Burettes and Sample Bottles

The Metrohm Dosimat Model 665 (Brinkmann Instruments, Inc.) is generally recognized as one of the best and most reliable titrant dispensers currently available. The manufacturer claims a resolution of 0.001 ml, a reproducibility of ± 0.0005 ml and an absolute accuracy of ± 0.002 ml. Several of the Dosimats at WHOI have been weight calibrated at six points throughout their range and show a reproducibility of ± 0.0003 ml and an absolute accuracy of ± 0.0005 ml, somewhat better than the manufacturer's specifications. It is recommended that the Dosimat be ordered as the Metrohm Titration Stand 665 which comes equipped with a magnetic stirrer and electrode holder. The DC motor in the stirrer maintains a constant, easily controlled speed not available in most AC stirrers. A 10 ml Buret Unit is used to dispense the titrant and a 20 ml Buret unit is used to dispense the 0.0100 N potassium biiodate standard solution. The minimum dosage of the former is 0.001 ml. However, since the amount of thiosulfate needed to reach the endpoint is calculated, the precision of the endpoint determination is better than 0.001 ml. Using the Metrohm keypad (Brinkmann Instruments Inc.) the 20 ml Buret unit is adjusted to dispense a calibrated 15.000 ml of standard solution for standardization of the thiosulfate. This unit is also used to dispense exactly 1.000 ml of standard during reagent blank determinations.

B.5.1.2 Volume Calibrations

Both the 50 ml and the 150 ml volumetric pipets (Lurex Scientific Co.) used to collect the aliquot samples and to dispense distilled water during standardizations are individually weight calibrated to ± 0.01 ml. The dispensers (Brinkmann Instruments) used to add the MnCl_2 , NaI-NaOH and H_2SO_4 reagents are adjusted to dispense 1 ml ± 0.01 ml. The calibration of these dispensers is checked periodically to ensure that all of the precipitate dissolves and that the final pH of the iodine solution is near 2.0. The 150 ml Tincture

sample bottles (Curtin Matheson Scientific, Inc.) are weight calibrated and then grouped together by volume in tote cases so that the standard deviation of the bottle volumes within each case is less than 0.25 ml. The average volume for each case is used in the calculation for dissolved oxygen. Each bottle is equipped with a ground glass stopper secured to the bottle with a rubber leash (Thomas Scientific Co.).

B.5.1.3 Sample mixing

Iodine volatility losses during titration are proportional to both the concentration of iodine in the sample solution and time. At the start of the titration, when the iodine concentrations are highest, the titrant must be added quickly and stirred to mix and react with the iodine. However, mixing too rapidly produces a deep vortex which may introduce bubbles into the sample and result in excessive iodine loss. Stirring too slowly reduces the mixing rate and greatly increases the time needed to reach the endpoint and thus the was iodine lost during the titration.

A one-inch magnetic Spinplus stir bar (VWR Scientific Co.) works well with the present equipment when the stirring speed is adjusted to produce a vortex about one-half inch in depth. The titrant is dispensed into the vortex and the electrode is positioned near the side of the beaker in the high speed flow.

B.5.1.4 Anti-diffusive tip

The anti-diffusive tip on the Dosimat eliminates contamination errors resulting from diffusion between the sample and the thiosulfate reagent. Experience with this tip has shown that increments as small as 0.001 ml can be reliably dispensed.

B.5.1.5 Aliquot collection

A small vacuum pump (Neptune Products, Inc.) is used with the automatic volumetric transfer pipets to collect both the aliquot sample and the distilled water used in the preparation of the standardization samples. A vacuum switch (Imo Delaval, Inc.) maintains a constant vacuum sufficient to collect the aliquot in about 10 seconds. A low voltage, solid state relay (Sager Electrical Supply Co.) eliminates electrical noise caused by 120 volt arcing when the switch is opened or closed.

B.5.1.6 Electrode

The dual-plate Platinum Sheet Electrode (Brinkmann Instruments, Inc.) used in the present system exhibits a markedly non-linear response to changes in iodine concentration. At the beginning of the titration, when the iodine concentration is high and the thiosulfate must be dispensed as rapidly as possible, its sensitivity is low. At this stage of the titration

the addition of 1 ml of 0.01N sodium thiosulfate results in a change of about 1 mV in the dual-plate voltage. Near the endpoint, however, when the iodine concentration is low and maximum sensitivity is needed to precisely determine the endpoint, the electrode voltage changes approximately 20 mV per ml of added thiosulfate. Electrode drift, which is a common problem with dual-wire electrodes, is minimal with the dual-plate platinum electrodes. During the past 12 months the endpoint voltage measured with the present system has varied between 0.018 mV and 0.030 mV which is equal to a change in equivalent dissolved oxygen concentrations of about 0.002 ml/l. The observed drift between standardizations is less than a third this value. The electrode is kept in distilled water between analytical sessions and care is exercised to keep the platinum plates as clean as possible.

B.5.1.7 Starch

Starch may be used to check the validity of the automated endpoint determinations until the analyst gains confidence in the system. It is not routinely used, however, since it appears to reduce the response of the electrode and change the slope of the titration curve.

B.5.2 Sample Collection

The oxygen samples are collected as soon as possible after each station cast is completed. The deepest sample is collected first since it is generally the water farthest from equilibrium with surface temperature and pressure and might possibly become supersaturated and out-gas as the sample warms up. Before each water sample is collected the spigot on the sampling bottle is opened while keeping the breather valve closed. If water flows out of the spigot then air must be entering the sampling bottle through a leak and the seawater within the bottle has probably been contaminated with water from shallower depths. This information should be noted on the station log to identify this sample as suspect. If water does not flow out the spigot it is unlikely that the bottle has leaked and the breather valve is opened to start the flow of water through the spigot. The brown Tincture oxygen sample bottle is rinsed twice with the sample water and then filled slowly using a hose inserted to the bottom of the bottle. Special care is taken to minimize turbulence and aeration of the sample. Approximately 150 ml of water is allowed to overflow the bottle. One ml of 3M MnCl_2 and one ml of 8N NaI-NaOH are added to the sample using the reagent dispensers previously described. As discussed in Strickland and Parsons (1972), the tip of each dispenser is inserted about 1 cm beneath the surface of the sample to avoid the introduction of bubbles and the unwanted addition of atmospheric oxygen. The dense reagents immediately sink and only sample water is displaced over the rim of the bottle. After these reagents have been added the stopper is carefully replaced so as to avoid trapping a bubble beneath it. When the stopper is seated, it is pressed firmly in place and the bottle is shaken vigorously 10 to 15 times with a downward snapping movement of the wrist. Violent agitation is necessary to reduce the size of the flocculent and increase its surface area thus ensuring that all the dissolved oxygen in the sample rapidly oxidizes an equivalent amount of manganous hydroxide. When all the samples have been collected, they are stored in subdued light in the controlled temperature laboratory to thermally equilibrate and await titration. An hour or so after the last sample has been collected, the precipitate has generally settled to about

half the volume of the bottle and the samples are shaken a second time. Care is taken during this shaking so that the stopper is not inadvertently opened and air introduced into the bottle. Strickland and Parsons (1972) state that the sample can be allowed to stand indefinitely at this point, though care must be exercised to avoid photodissociation of the iodine. In practice one should wait no longer than 8-10 hours and generally only 2-4 hours before titrating. Shortly before the samples are to be titrated, one ml of 10N H_2SO_4 is added to each sample which is vigorously shaken to completely dissolve the precipitate and liberate iodine equivalent to the dissolved oxygen originally contained in the sample. If the precipitate does not dissolve completely it may be necessary to add an additional drop of acid and shake the sample again. However, it is important that the final pH of the sample at the time of titration is near 2.0 to minimize atmospheric oxidation of iodide to iodine (Carpenter, 1965a). If the precipitate does not readily dissolve or if the pH is much less than 2.0, then the NaI-NaOH and H_2SO_4 reagent dispensers should be checked to make certain they are dispensing 1.0 ml $\pm 5\%$. A small adjustment may be necessary to ensure that the final pH is correct and that the precipitate readily dissolves.

An aliquot of the iodine solution is drawn up with the calibrated 50 ml volumetric pipet. The top 10-15 ml of the sample is allowed to overflow into the vacuum sump, since this volume will be slightly deficient in iodine (Strickland and Parsons, 1972). The 50 ml sample is then dispensed into a 100 ml beaker containing a stirring magnet. Touch the tip of the pipet to the surface of the sample 3 seconds after the pipet has drained to collect the calibrated volume. This pipet has been carefully calibrated to dispense the measured volume after the 3 second wait. The beaker is then placed on the titration stand, the electrode and antidiffusion dispenser tip are lowered into the sample and the computer is instructed to begin the titration. From this point onwards the titration is completely automated and the operator may begin to prepare the next sample.

B.5.3 Standardization and blank determination

The sodium thiosulfate titrant is prepared at sea as needed from dry, pre-weighed reagent stored in small plastic vials kept in a container with dessicant. The thiosulfate in each vial is dissolved in 2 l of distilled water and yields a solution with a normality near 0.01. Its exact normality is determined by standardizing with potassium biiodate which has a normality of exactly 0.0100. A calibrated 150 ml of distilled water is collected with the 150 ml pipet and placed in a clean, dry, manganese free flask. Seawater should not be substituted for distilled water in either the standardization or blank measurements since it has its own "blank". One ml of the 10 N sulphuric acid is added to the distilled water and thoroughly stirred. Next 1 ml of the sodium iodide-sodium hydroxide reagent is added and stirred. If the solution is not colorless at this point the sample has been contaminated with manganese which has liberated iodine and discolored the solution. If this occurs the sample should be discarded and the flask carefully washed and dried before trying again. If the sample is colorless add 1 ml of the manganese chloride reagent and stir. Finally add exactly 15.000 ml of the 0.0100 N Standard solution with the 20 ml Dosimat and stir thoroughly. The iodine concentration in this solution is similar to that of the average water sample and requires ≈ 4.5 ml of thiosulfate to titrate to the endpoint. Collect a 50 ml aliquot of this solution exactly as described in the collection of the seawater sample and titrate this sample

using the 'standardization' option in the Winkler titration program. When the endpoint is reached the results of the titration are automatically stored in the calibration file with the date and time. Three standardizations should be performed with agreement to at least 0.003 ml of thiosulfate. Standardizations are generally performed whenever the thiosulfate is renewed or replaced or every two days during a cruise.

Carritt and Carpenter (1966) note that, "The complexity of the behavior of thiosulfate suggests that the solutions must be standardized with the particular oxidant under precisely the same conditions that exist during sample analysis." The standardization technique described above has been designed to follow this suggestion and closely parallels the method used to analyze the seawater samples. Any iodine lost through volatilization or gained by the oxidation of iodide while handling the seawater samples will be similar to similar errors occurring during this standardization procedure. This method of standardization has been shown to compensate for iodine lost during the collection and titration of aliquot samples, (Knapp *et al.*, 1991).

To measure the reagent blank, add about 50 ml of distilled water to a clean beaker. Add 1 ml of the sulphuric acid and stir, add 1 ml of the sodium iodide-sodium hydroxide reagent and stir. If the solution is not colorless at this point, the sample has been contaminated and should be discarded and the beaker carefully washed before trying again. Add 1 ml of the manganese chloride reagent and stir. Next add exactly 1.000 ml of the standard with the Dosimat, stir and titrate to the endpoint using the "blank" option in the Winkler titration program. When the endpoint is reached add another 1 ml of the standard and titrate again. The difference between the two titers is equal to the blank and may be positive or negative. The 0.005 ml of excess thiosulfate added during the first titration and present during the second titration is accounted for within the program.

B.5.4 Oxygen calculation and units

The following equations of Carpenter's (1965b) have been modified for the titration of an aliquot sample by Culberson (personal communication) and provide results in units of ml/l. (To convert ml/l to $\mu\text{mol/kg}$ multiply by 43.57, or by 44.66 to yield $\mu\text{mol/l}$).

Reagent blank

$$R_{\text{blk}} = R_1 - R_2 - .005$$

where:

R_1 = first thiosulfate titer

R_2 = second thiosulfate titer

.005 = excess thiosulfate remaining after first titer

Normality of thiosulfate:

$$N_{thio} = \frac{V_{IO3} \times N_{IO3}}{R_{std} \times \frac{V_{150} + V_{IO3} + V_3}{V_x} - R_{blk}} \quad (1)$$

where:

V_{IO3} = volume of iodate standard

N_{IO3} = normality of iodate standard

R_{std} = thiosulfate titer of standard

V_{150} = volume of distilled water dispenser used to prepare standards (≈ 150 ml)

V_3 = volume of reagents (3 ml) used to prepare standards

R_{blk} = measured reagent blank

V_x = volume of aliquot (≈ 50 ml)

Oxygen concentration (ml/l) in seawater:

$$O_2 = \frac{\left(R_x \times \frac{V_{bot}}{V_x} - R_{blk} \right) \times N_{thio} \times 5598 - (DO_{reg} \times 1000)}{(V_{bot} - V_2)} \quad (2)$$

where:

R_x = thiosulfate titer of sample

V_{bot} = volume of sample bottle

V_x = volume of aliquot (≈ 50 ml)

R_{blk} = measured reagent blank

N_{thio} = normality of thiosulfate

DO_{reg} = absolute amount of oxygen added with reagents, 0.0017 ml (Murray, Riley and Wilson, 1968)

V_2 = volume of reagents (2 ml) used to prepare samples

B.5.5 Reagent preparation

The potassium biiodate and potassium iodate reagents are stored in a drying chamber with dessicant. Two different lots of reagents are used each time standards are prepared. If the normalities of the resulting solutions differ by more than 0.0001 then additional batches are mixed and compared. The scales used to weigh the reagents are calibrated before each batch is mixed and the distilled water and volumetric flask used in the preparation of the standard solution are at a temperature near 20°C. Each reagent is prepared in dedicated glassware to avoid manganese contamination. All of the following reagents, except for the sodium thiosulfate, are mixed in the shore laboratory, carefully sealed and taken to sea in brown, one-liter PVC bottles. To minimize reagent blanks the $MnCl_2$ and $NaI-NaOH$ reagents are filtered twice before dilution to the proper concentration. Because of the large quantity of sodium thiosulfate used during an average cruise it is pre-weighed and stored in plastic vials to be mixed with two liters of distilled water as needed. These vials are stored with dessicant in an air-tight container.

B.5.5.1 Manganese Chloride (3M)

Dissolve 600 g of Fisher: Certified A.C.S. Crystal $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ or equivalent in 600 ml of distilled water. This solution is filtered twice through a glass fiber filter and then distilled water is added to make one liter.

B.5.5.2 Sodium Iodide (4M) - Sodium Hydroxide (8N)

Dissolve 600 g of Fisher: Certified A.C.S. Crystal NaI or equivalent in 600 ml of distilled water and note the color of the solution. If the solution is not clear (*i.e.* yellow-brown), it must be discarded and a new reagent used. Slowly add 320 g of Baker: USP, FCC NaOH Pellets or equivalent and 2 g of sodium azide, NaN_3 , while continuously stirring. Cool this mixture to room temperature and filter it twice before adding distilled water to make one liter.

B.5.5.3 Sulphuric Acid (10N)

Slowly add 280 ml of concentrated Fisher: Reagent A.C.S. H_2SO_4 or equivalent to 600 ml of distilled water. Cool this mixture to room temperature and add distilled water to make one liter.

B.5.5.4 Sodium Thiosulfate (0.01N)

Weigh 5.0 g of Fisher: Certified A.C.S. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ crystals or equivalent, add 0.25 g of sodium borate for a preservative and place in a small plastic vial. When dissolved in two liters of distilled water, each vial will make a solution approximately 0.01N. This solution is stable for many months if kept in a dark well-stoppered bottle.

B.5.5.5 Potassium Biiodate Standard (0.0100N)

Carefully weigh 0.3250 g of Fisher Purified $\text{KH}(\text{IO}_3)_2$ or equivalent. Transfer to 1000 ml volumetric flask and make to the mark with distilled water. This solution is stable indefinitely.

B.5.5.6 Potassium Iodate Standard (0.0100N)

Carefully weigh 0.3567 g of Fisher: Certified A.C.S. KIO_3 or equivalent. Transfer to 1000 ml volumetric flask and make to the mark with distilled water. This solution is stable indefinitely.

B.5.5.7 Starch Indicator (not used during automatic titrations)

Weigh 5 grams of Certified A.C.S. starch, add 5 mg of mercuric iodide for preservative, and store in a small plastic vial. When needed, add distilled water to the starch to make a paste. While stirring, slowly add the paste to 500 ml of boiling, distilled water. Continue stirring until cool. The solution is stable for several months.

Appendix C: Standardization History of Guildline 9 Salinometer

Table C1 gives the standardization history of the Guildline 9 salinometer during the cruise. Figure C1 shows the series of standard conductivity ratios from this table converted to salinity deviations from the overall mean standard salinity (derived with reference to the overall mean conductivity ratio as "standard"), with suitable allowance for change in batch salinity between P113 and P114. The standard deviation of these values is 0.001 in salinity.

Table C1: Guildline 9 Standardization History

Time:Date	Batch	Standard	Comments
<u>All values at 24 °C.</u>			
1715:29/6/91	P114	1.99991	Start of RRW first run.
1815:29/6/91	P114	1.99991	End of RRW first run.
1325:30/6/91	P114	1.99977	Start, casts 2/1 and 2/2. Ship steaming - some instability.
1725:30/6/91	P1147	1.99972	Start of RRW second run.
1845:30/6/91	P114	1.99979	End of RRW second run.
1855:30/6/91	P114	1.99981	Check on previous standard.
1825: 1/7/91	P113	1.99973	Start, cast 3/1.
2030: 1/7/91	P114	1.99983	Start, cast 3/2.
1815: 2/7/91	P113	1.99968	Start, casts 4/1 and 4/2.
1800: 3/7/91	P114	1.99983	Start, linearity check and low and high salinity RRW.
1930: 3/7/91	P114	1.99983	End, linearity check and low and high salinity RRW.
1800: 5/7/91	P113	1.99985	Start, casts 5/1, 6/1 and 6/2.
1800: 6/7/91	P114	1.99983	Start, casts 7/1, 7/2, 8/1 and 8/2.

Figure C1: Salinity deviation of Guildline 9 standards from mean standard salinity

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