

RV *INVESTIGATOR*HYDROCHEMISTRY DATA PROCESSING REPORT

Voyage:	in2023_e01					
Chief Scientist	N/A					
Principal Investigator	N/A					
Voyage title:	in2023_e01 - Sea Trials					
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Contents

Executive Summary	4
General Hydrochemistry Information	4
ltinerary	5
Key personnel list	5
Summary	6
Table 2: Sample Type and Number Assayed	6
CTD (Conductivity, Temperature, Density)	6
TSG (Thermosalinograph)	6
Data Processing Overview	7
Salinity Data Processing	8
Table 3: Salinity Parameter Summary	8
Salinity Method	8
CTD Salinity vs Bottle Salinity Plot	9
Dissolved Oxygen Data Processing	10
Dissolved Oxygen Measurement Parameters	10
Dissolved Oxygen Method	10
CTD Dissolved Oxygen vs Bottle Dissolved Oxygen Plot	11
Dissolved Oxygen Instrument titrant: thiosulphate normality and blank correction	12
Nutrient Data Processing	13
Nutrient Measurement Parameters	13
Nutrient Methods	13
HyPro Processing Summary for Nutrients	14
Accuracy - Reference Material for Nutrient in Seawater (RMNS)	15
Figure 6: Silicate RMNS Plot (μmol L ⁻¹)	17
Figure 7: Phosphate RMNS Plot (μmol L ⁻¹)	18
Figure 8: Nitrate + Nitrite (NOx) RMNS Plot (μmol L ⁻¹)	19
Figure 9: Nitrite RMNS Plot (μmol L ⁻¹)	20
Measurement Uncertainty	21
Sampling Precision	21
Redfield Ratio Plot (14.0) for CTD Deployments	21
Temperature & Humidity Change over Nutrient Analyses	23
Appendix	24
Salinity: Reference Material Used	24

	Nutrients: RMNS results for each Analysis Run & CTD Deployment	25
	RMNS Lot CP Results	25
	Missing or Suspect Salinity Data	25
	Missing or Suspect Oxygen Data	25
	Data Quality Flag Key	26
	GO-SHIP Specifications	27
	Salinity	27
	Dissolved Oxygen	27
	Si(OH) ₄	27
	PO ₄	27
	NO ₃	27
	Notes	27
R	eferences	28

Executive Summary

Please cite the following manuscript when reporting or publishing data for silicate, phosphate, nitrate+nitrite (NOx) and nitrite:

Rees, C., L. Pender, K. Sherrin, C. Schwanger, P. Hughes, S. Tibben, A. Marouchos, and M. Rayner. (2018) "Methods for reproducible shipboard SFA nutrient measurement using RMNS and automated data processing." Limnol. Oceanogr: Methods, 17(1): pp. 25-41. doi:10.1002/lom3.10294

If publishing ammonium data, please cite the following:

Rees, C., Janssens, J., Sherrin, K., Hughes, P., Tibben, S., McMahon, M., McDonald, J., Camac, A., Schwanger, C. and Marouchos, A., (2021) "Method for Reproducible Shipboard Segmented Flow Analysis Ammonium Measurement Using an In-House Reference Material for Quality Control." Frontiers in Marine Science, 8.

doi:10.3389/fmars.2021.581901

General Hydrochemistry Information

Water samples collected during the voyage were analysed in the ship's hydrochemistry laboratory for nutrients, dissolved oxygen, and salinity.

Five nutrients were determined: silicate, phosphate, nitrate + nitrite, nitrite and ammonium. Certified reference materials for nutrients in seawater (RMNS) were within 3% of their certified values, with the exception of silicate which exceeded 3% of the certified value. See table for the CTD deployment versus measured RMNS values.

Missing and suspect hydrology samples are listed in Appendix.

Final hydrology data, analytical methods, related log sheets and processing notes can be obtained from the CSIRO data centre.

For Data, contact: NCMI DataLibrarians@csiro.au

Itinerary

Henderson to Fremantle, January 7th – 12th, 2023.



Figure 1: Voyage Track

Key personnel list

Table 1: Key Personnel list

Name	Role	Organisation
N/A	Chief Scientist	N/A
Dave Flynn Julie Janssens	Voyage Manager Deputy Voyage Manager	CSIRO
Merinda McMahon Harris Anderson	Hydrochemist Hydrochemist	CSIRO
Maddy Lahm Narendra Pati	Hydrochemist Hydrochemist	CSIRO

Summary

Table 2: Sample Type and Number Assayed

Analysis (instrument)	Number of Samples
Salinity (Guildline Salinometer)	44 CTD
	9 TSG
Dissolved Oxygen (SIO automated titration)	44 CTD
Nutrients (Seal AA3HR segmented flow)	37 CTD

CTD (Conductivity, Temperature, Density)

- Sampling point, 36 bottle rosette with 12L Ocean Test Equipment bottles (Niskin) deployed at depth for water collection.
- 4 CTD deployments in total. Deployments 1 through 4 sampled by hydrochemistry.

TSG (Thermosalinograph)

• Samples collected by hydrochemistry from underway lab for calibration of thermosalinograph.

For TSG sample information refer to the EverLog from the voyage.

Data Processing Overview

The sample meta-data, measured bottle salinity results, dissolved oxygen assay results and the nutrient assay raw data are processed by the CSIRO program HyPro. The final output is the hydrology data set. An overview of this process is illustrated in figure 1.



Figure 2: Hydrology Data Processing Flow Diagram.

Salinity Data Processing

Table 3: Salinity Parameter Summary

Details	
HyPro Version	5.7
Instrument	Guildline Autosal Laboratory Salinometer 8400(B) – SN 72008
Software	Ocean Scientific International Ltd (OSIL) Data Logger ver 1.2
CSIRO Hydrochem Method.	Sampling: WI_Sal_002 Measurement: SOP006
Accuracy	± 0.001 practical salinity units
Analysts	Merinda McMahon, Maddy Lahm, Narendra Pati, Harris Anderson
Lab Temperature (±0.5°C)	19.5 -20.5°C during analysis.
Bath Temperature	24.01°C
Reference Material	OSIL IAPSO ¹ - Batch P164, use by 23/03/2023, $K_{15} = 0.99985$
Sampling Container type	200 ml volume OSIL bottles made of type II glass (clear) with disposable plastic insert and plastic screw cap.
Sample Storage	Samples stored in the Salt lab for a minimum of 8 hrs before measurement.
Comments	Salinity bottle data from deployments 2-4 have been flagged as bad (133) by operators, due to incorrect settings on Guildline Salinometer.

Salinity Method

Salinity samples are measured on a high precision laboratory salinometer (Guildline Autosal 8400B) which is operated in accordance with its technical manual.

Practical salinity (S), is defined in terms of the ratio (K_{15}) of the electrical conductivity measured at 15°C 1atm of seawater to that of a potassium chloride (KCl) solution of mass fraction 32.4356 x 10⁻³.

Before each batch of sample measurements, the Autosal is calibrated with standard seawater (OSIL, IAPSO) of known K_{15} ratio. A new bottle of OSIL solution is used for each calibration. The frequency of calibration is one per set of samples per CTD deployment.

Method synopsis: Salinity samples are collected into 200ml OSIL bottles, filled from the bottom, via a polytetrafluoroethylene (PTFE) straw, till overflowing. The bottle is removed from the straw and the sample is decanted to allow a headspace of approximately 25cm³. A plastic insert is fitted, the bottle inverted and rinsed with water then capped and stored cap-down until measured. To measure, the Autosal cell is flushed three times with the sample and then measured after the fourth and fifth flush. The OSIL data logger software captures the conductivity ratio and calculates the practical salinity.

The output from the data logger software is imported into HyPro and collated with the CTD deployment meta-data.

¹ International Association for the Physical Sciences of the Oceans

CTD Salinity vs Bottle Salinity Plot

The difference between the unprocessed (uncorrected) CTD values and the measured bottle salinities is generally less than 0.01 PSU.

The unprocessed CTD values are adjusted (corrected) by DAP using the bottle results. Note that for deployments 2-4 bottle salinity data has been marked as bad by operator. The corrected values are not reported in the hydrology set. Please contact the DataLibrariansOAMNF@csiro.au for corrected CTD data.

Note: dots = bottle samples, circles = CTD instrument (unprocessed)

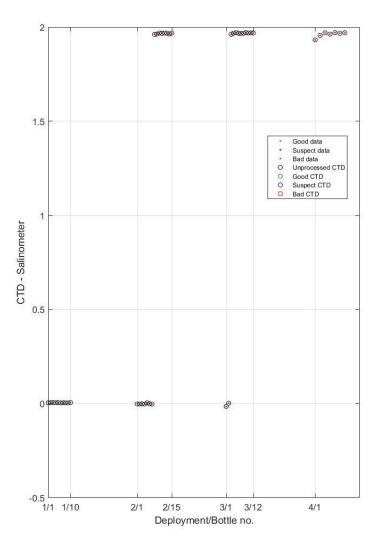


Figure 3: CTD Salinity vs Bottle Salinity Plot. Deployment/Bottle number (x-axis). Difference of Salinity bottle data from the corresponding CTD salinity value (y-axis). Note: dots = bottle samples, circles = CTD instrument (unprocessed). Units: μ mol L⁻¹. Refer to missing or suspect data table in appendix.

Dissolved Oxygen Data Processing

Dissolved Oxygen Measurement Parameters

Table 4: Dissolved oxygen measurement parameters.

Details	
HyPro Version	5.7
Instrument	Automated Photometric Oxygen System
Software	Scripps Institution of Oceanography (SIO)
CSIRO Hydrochem. Method	Sampling: WI_DO_001 Assay: SOP005
Accuracy	± 0.5 μmol L ⁻¹
Analyst(s)	Merinda McMahon, Narendra Pati, Maddy Lahm, Harris Anderson
Lab Temperature (±1°C)	Variable, 18.5 - 20.5°C
Sample Container type	Pre-numbered 140 mL glass iodine determination flasks with glass stopper. 18 flasks per light-proof container.
Sample Storage	Samples stored in the hydrochemistry lab until analysis. All samples were analysed within ~48 hrs
Comments	None.

Dissolved Oxygen Method

SIO method used. The method is based on the whole bottle modified Winkler titration of Carpenter (1965) plus modifications by Culberson *et al* (1991).

Method: The sample is collected in an iodine determination flask of known volume. 1mL of manganese (II) chloride solution followed by 1 mL of alkaline iodide solution is added to the sample, the flask stoppered and inverted a minimum of 15 times. The dissolved oxygen oxidizes an equivalent amount of Mn (II) to Mn (IV) which precipitates. Just before titration, the sample is acidified, Mn (IV) is reduced to the divalent state liberating iodine. The iodine is titrated with a standardised thiosulphate solution using a Metrohm 665 Dosimat fitted with a 1 mL burette. The endpoint is determined by measuring the decrease in the UV absorption 365 nm.

The thiosulphate solution is standardised by with a 10ml aliquot of potassium iodate primary standard. A blank correction is also determined from the difference between two titres of consecutive additions of 1 mL aliquots of potassium iodate to the same blank sample. The standardisation is done at least once per 24 hours when samples are being assayed.

The output from the SIO instrument software is imported into HyPro and collated with the CTD deployment meta-data.

CTD Dissolved Oxygen vs Bottle Dissolved Oxygen Plot

The CTD values in this plot are unprocessed raw data.

The unprocessed CTD values are adjusted (corrected) by DAP using the bottle results. The corrected values are not reported in the hydrology set. Please contact the DataLibrariansOAMNF@csiro.au for corrected CTD data.

Note: dots = bottle samples, circles = CTD instrument (unprocessed)

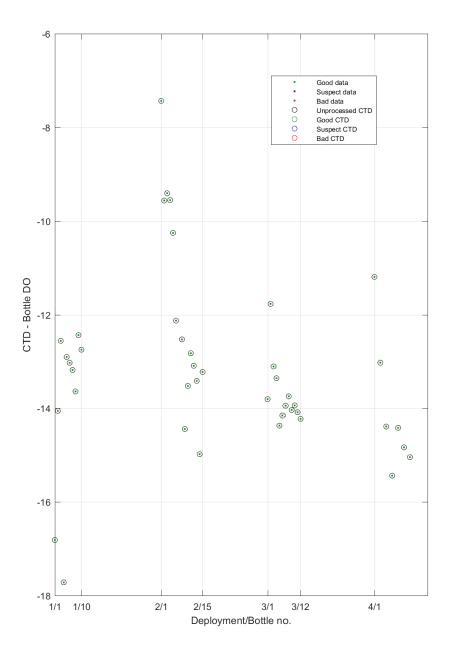
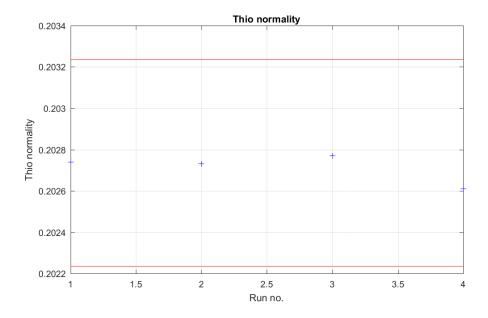


Figure 4. CTD Dissolved Oxygen vs Bottle Dissolved Oxygen Plot. Deployment/Bottle number (x-axis). Difference in dissolved oxygen results from the bottle sample to its corresponding CTD measurement (y-axis). Note: dots = bottle samples, circles = CTD instrument (unprocessed). Units: μ mol L⁻¹

Dissolved Oxygen Instrument titrant: thiosulphate normality and blank correction.

The normality of the thiosulphate titrant (0.22N) varied less than 0.0002 N for all dissolved oxygen sample titrations. The blank corrections are less than 0.0007 mL with a voyage mean of 0.0003 mL and standard deviation of 0.0002 mL (n=4). For reference, titre volumes for dissolved oxygen bottle samples lay in the range 0.55 to 0.68 mL.



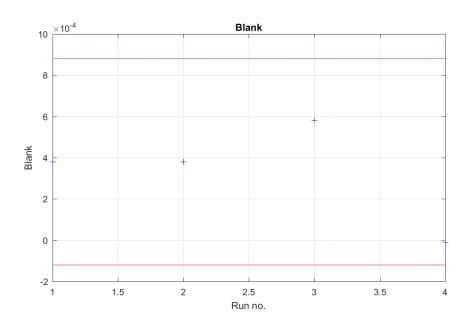


Figure 5. Auto-titrator calibration plots. In Figure 5a the red lines indicate ± 0.0005 N either side of the mean titrant (thiosulfate) concentration. In Figure 5b red lines indicate acceptable variation either side of the mean blank concentration. The titrant should not vary more than 0.0005 N between analyses.

Nutrient Data Processing

Nutrient Measurement Parameters

Table 5: Nutrient measurement parameters. All instrument parameters, reagent batches and instrument events are logged for each analysis run. This information is available on request.

Details						
CSIRO Software	HyPro 5.7	HyPro 5.7				
Instrument	Seal AA3HR					
Instrument Software	Seal AACE 7.0	ס				
CSIRO Hydrochem. Method, sampling	WI_Nut_001					
CSIRO Hydrochem. Method, nutrient	SOP001	SOP002	SOP003	SOP003	SOP004	
Nutrient	Silicate Phosphate Nitrate + Nitrite Ammonium					
Concentration range (μmol L ⁻¹)	112 3.0 36.4 1.4 2.0					
Method Detection Limit (MDL)(μmol L ⁻¹)	0.2	0.02	0.02	0.02	0.02	
Matrix Corrections	none	none	none	none	none	
Analysts	Merinda Mcl	Mahon, Harris	Anderson, Nar	endra Pati, M	addy Lahm	
Lab Temperature (±1°C)	Variable, 18.	5– 20.5°C				
Reference Material	KANSO, RMN	IS lot CP				
Sampling Container type	CTD: 50ml HDPE with screw cap lids. MTR: 12ml PP tubes with screw cap lids.					
Sample Storage	< 2 hrs at roc	< 2 hrs at room temperature or ≤ 12 hrs @ 4°C				
Pre-processing of Samples	CTD: None.					
Comments						

Nutrient Methods

When using silicate, phosphate, nitrate+nitrite (NOx) and nitrite data set for publication, please cite the paper:

Rees, C., L. Pender, K. Sherrin, C. Schwanger, P. Hughes, S. Tibben, A. Marouchos, and M. Rayner. (2018) "Methods for reproducible shipboard SFA nutrient measurement using RMNS and automated data processing." Limnol. Oceanogr: Methods, 17(1): pp. 25-41. doi:10.1002/lom3.10294

Nutrient samples are assayed on a Seal AA3HR segmented flow auto-analyser fitted with 1cm flow-cells for colorimetric measurements and a JASCO FP2020 fluorescence instrument as the ammonium detector.

Silicate (SOP001): colourimetric, molybdenum blue method. Based on Armstrong et al. (1967). Silicate in seawater is reacted with acidified ammonium molybdate to produce silicomolybdic acid. Tartaric acid is added to remove the phosphate molybdic acid interference. Tin (II) chloride is then added to reduce the silicomolybdic acid to silicomolybdous acid and its absorbance is measured at 660nm.

Phosphate (SOP002): colourimetric, molybdenum blue method. Based on Murphy and Riley (1962) with modifications from the NIOZ-SGNOS¹ Practical Workshop 2012 optimizing the antimony catalyst/phosphate ratio and the reduction of silicate interferences by pH. Phosphate in seawater forms a phosphomolybdenum complex with acidified ammonium molybdate. It is then reduced by ascorbic acid and its absorbance is measured at 880nm.

Nitrate (SOP003): colourimetric, Cu-Cd reduction – naphthylenediamine method. Based on Wood et.al (1967). Nitrate is reduced to nitrite by first adding an ammonium chloride buffer then sending it through a copper - cadmium column. Sulphanilamide is added under acidic conditions to form a diazo compound. This compound is coupled with 1-N-naphthly-ethylenediamine di-hydrochloride to produce a reddish purple azo complex and its absorbance is measured at 520 nm.

Nitrite (SOP003): colourimetric, naphthylenediamine method. As per nitrate method without the copper cadmium reduction column and buffer.

Ammonium (SOP004): fluorescence, ortho-phtaldiadehyde method. Based on Kérouel and Aminot (1997). Ammonium reacted with ortho-phtaldialdehyde and sulphite at a pH of 9.0-9.5 to produce an intensely fluorescent product. Its emission is measured at 460nm after excitation at 370nm.

SOP methods can be obtained from the CSIRO Oceans and Atmosphere Hydrochemistry Group.

¹ Royal Netherlands Institute for Sea Research – Study Group on Nutrient Standards.

HyPro Processing Summary for Nutrients

After a run, the raw absorbance/ fluorescence data is exported from the instrument and processed by HyPro. For each analyte, HyPro re-creates the peak traces, defines the region on the peak's plateau (peak window) used to determine the peak heights, constructs the calibration curve, applies corrections for carry-over, baseline and sensitive drifts then, derives the nutrient concentrations for each sample. The corrections are quantified using dedicated solutions included in every run.

HyPro uses criteria to identify suspect calibration points, noisy peaks, method detection limits that are above the nominal limit and, duplicate sample results that do not match.

With suspect calibration points, their contribution to the curve is given less weighting dependent on their distance from the final curve. The cut-off limits for good calibration data are:

- ±0.5% of the concentration of the top standard for silicate and nitrate+nitrite (as per WOCE¹).
- Within 0.02uM for phosphate, nitrite and ammonium.

HyPro classifies the quality of data as good, suspect or bad and flags accordingly. The flagged nutrient calibration data is in appendix.

Missing or suspect nutrient data is tabulated in appendix, the flags are also in the final hydrology data set. The Flag key is in Appendix.

Table 6: All instrument parameters and reagent batches and operation events are logged for each analysis run. This information is available on request.

Result Details	Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite	Ammonia		
Data Reported as	μmol L ⁻¹	μmol L ⁻¹	μmol L ⁻¹	μmol L ⁻¹	μmol L ⁻¹		
Calibration Curve degree	Linear	Linear	Linear	Linear	Quadratic		
# of points in Calibration	6	6	6	6	6		
Forced through zero?	N	N	N	N	N		
Matrix correction	N	N	N	N	N		
Blank correction	N	N	N	N	N		
Peak window defined by	HyPro	HyPro	HyPro	HyPro	HyPro		
Carryover correction (HyPro)	Y	Υ	Y	Y	Y		
Baseline drift correction (HyPro)	Y	Y	Y	Y	Y		
Sensitivity drift correction (HyPro)	Y	Y	Y	Υ	Y		
Data Adj for RMNS variance.	N	N N N N					
Medium of Standards	Low nutrient seawater (LNSW, bulk on deck of Investigator). Allowed to stand for at least one year in the sun, sub-lot passed through a 10 micron filter and stored in 20 L carboys in the clean dry laboratory at 22°C.						
Medium of Baseline	18.2 Ω water	. Dispensed f	rom Milli Q				
Proportion of samples in duplicate.	<10%. CTD: Niskin fired at the greatest depth sampled in duplicate. Single samples collected1 for remaining depths.						
Comments	The reported data is not corrected to the RMNS. Per deployment RMNS data tabulated in appendix.						

Accuracy - Reference Material for Nutrient in Seawater (RMNS)

Descriptive statistics are used to ascertain the accuracy and precision of the analysis from the repetitive measurement of the RMNS for silicate, phosphate, NOx, and nitrite in seawater.

Japanese KANSO certified RMNS lot CP was assayed in triplicate in each run to monitor accuracy. The certified values are in Table 10.

¹ World Ocean Circulation Experiment

The GO-SHIP criteria (Hyde *et al.*, 2010), appendix, specifies using 1-3 % of full scale (depending on the nutrient) as acceptable limits of accuracy.

The assayed RMNS values per CTD deployments are listed in the Appendix.

Table 7: RMNS certified concentrations ± expanded uncertainty (U) at 21°C. Units: μmol L-1

RMNS	Nitrate	Nitrite	NO ₃ + NO ₂	Phosphate	Silicate
	(NO₃)	(NO ₂)	(NO _X)	(PO ₄)	(Si(OH) ₄)
Lot CP	25.396 ± 0.386	0.318 ± 0.072	25.714 ± 0.379	1.795 ± 0.018	62.569 ± 0.307

KANSO publishes the RMNS nutrient values in μ mol kg⁻¹. These are converted to μ mol L⁻¹ at 21°C. The RMNS is not certified for ammonium. NO_x is derived by summing the NO₃ and NO₂ values.

Nutrient plots of RMNS

The green pink and red lines are the 1%, 2% and 3% contours from the RMNS certified mean value. Exception: nitrite, the contours are at 0.02 μ mol L-1 increments from the certified value. The blue line is the certified value's expanded uncertainty.

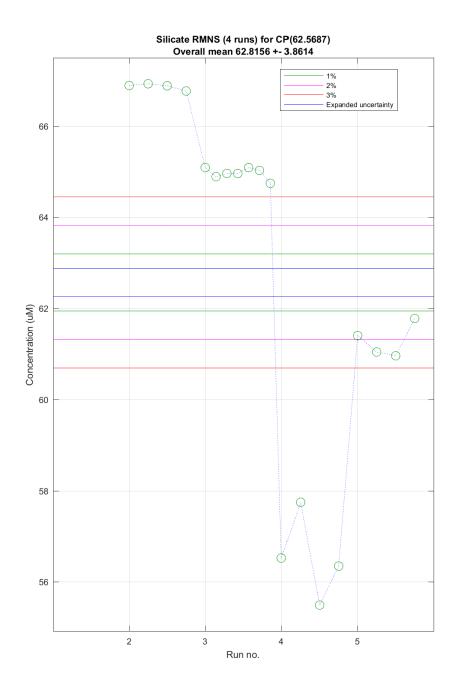


Figure 6: Silicate RMNS Plot (μmol L⁻¹)

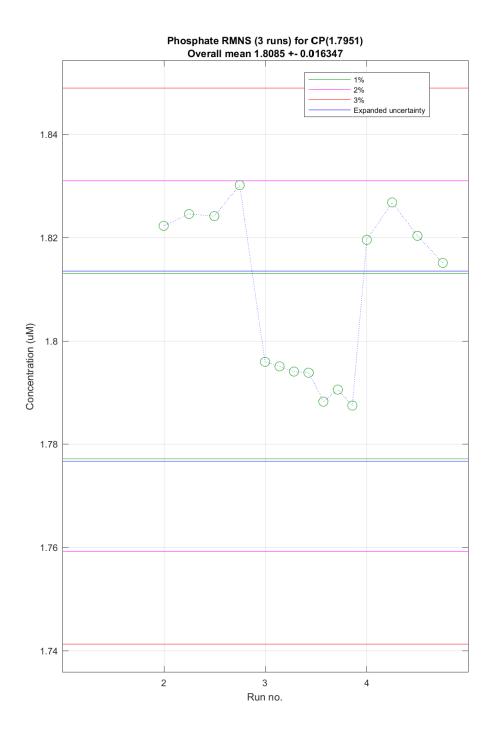


Figure 7: Phosphate RMNS Plot (μmol L⁻¹)

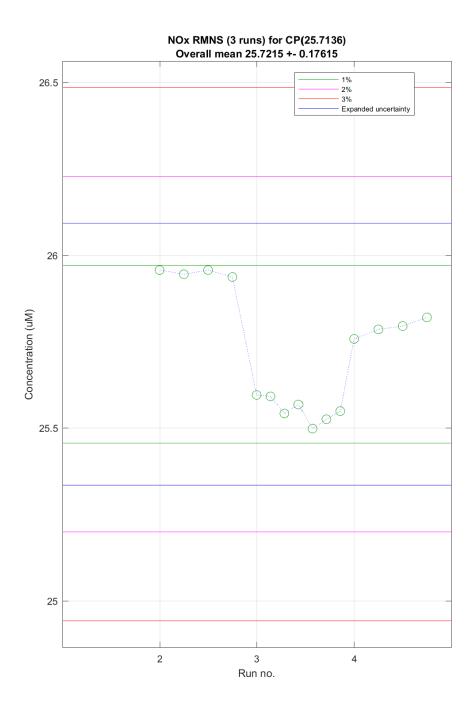


Figure 8: Nitrate + Nitrite (NOx) RMNS Plot (μmol L⁻¹)

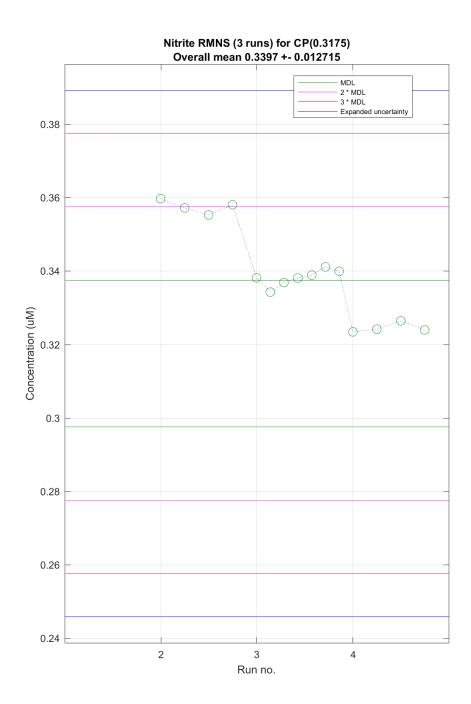


Figure 9: Nitrite RMNS Plot (μmol L⁻¹)

Measurement Uncertainty

The CSIRO hydrochemistry method measurement uncertainty (MU) has been calculated for each nutrient based on the variation in the calibration curve, calibration standards, pipette and glassware calibration, and precision of the RMNS over time (Armishaw 2003).

Table 8: CSIRO Hydrochemistry nutrient analysis uncertainty values. Units: μmol L-1

Calculated Measurement Uncertainty @ 1 μmol L ⁻¹						
Silicate	Phosphate	Nitrate + Nitrite (NOx)	Nitrite	Ammonia		
±0.017	±0.024	±0.019	±0.14	±0.30 [¥]		

^{*}The reported uncertainty is an expanded uncertainty using a coverage factor of 2 giving a 95% level of confidence.

Sampling Precision

The sampling precision for this voyage is GOOD. Initial sampling precision is determined with the CTD test deployment (CTD 1) where multiple bottles are fired the same depth, each of which is then sampled for hydrochemistry (Table 12). Duplicate nutrient samples are also collected from the greatest depth of subsequent CTD deployments (Table 11).

For nutrients, the sampling precision is good if the difference from the mean of duplicate measurements is less than the nominal method detection limit (table 6). The exception: NOx (nitrate+nitrite) which uses the limit 0.06µmol L-1. Duplicate samples that exceed this limit are flagged 69 (suspect). These are tabulated in appendix 8.6.

	Silicate (Si(OH) ₄)	Phosphate (PO ₄)	Nitrite (NO ₂)	NO ₃ + NO ₂ (NO _X)	Ammonia (NH₄)
Minimum	0.100	0.000	0.000	0.010	0.000
Maximum	0.200	0.010	0.001	0.020	0.290
Mean	0.167	0.74e-17	0.000	0.010	0.090
Variance	0.089	0.004	0.0005	0.009	0.114

Redfield Ratio Plot (14.0) for CTD Deployments

Calculating and plotting the Redfield Ratio is a check for the accuracy of phosphate and nitrate+nitrite (NOx) analysis. The ratio is the required amount of P to N for marine phytoplankton growth. The ratio is very consistent in the deep ocean with phosphate to nitrate equalling 14. The ratio for this voyage was 14.3. Note, only two CTD deployments went deeper than 1000m, the remaining deployments were less than 500m

^{*}The ammonia MU precision does not include data for the RMNS.

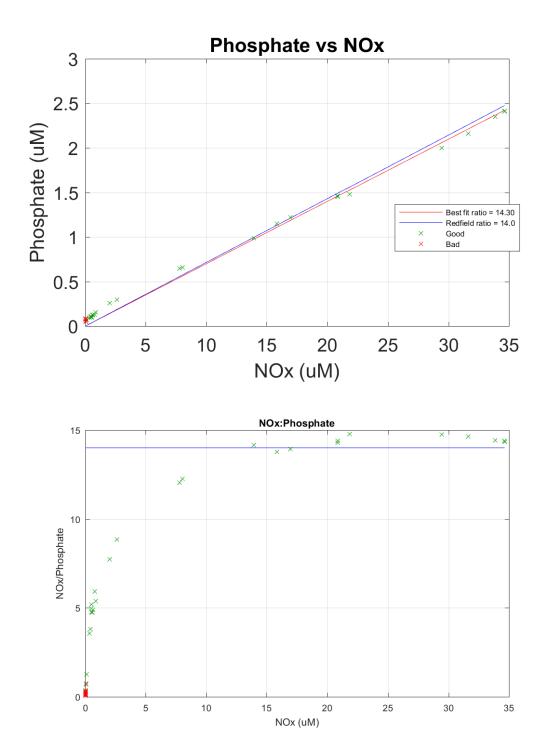


Figure 10. Redfield ratio plots.

Temperature & Humidity Change over Nutrient Analyses

The ambient conditions in the hydrochemistry laboratory and within the AA3HR instrument were measured and logged as follows:

- (1) Above the AA3HR instrument, temperature only.
- (2) On the deck of the nitrate & nitrite AA3HR chemistry module, temperature and humidity. Data on request.
- (3) On the outboard bulkhead, Temperature, humidity and pressure. Data on request.

Appendix

Salinity: Reference Material Used

OSIL IAPSO Standard Seawater		
Batch	P164	
Use by date	23/03/2023	
K ₁₅	0.99985	
PSU	34.994	

Nutrients: RMNS results for each Analysis Run & CTD Deployment. RMNS Lot CP Results

Analysis Run	CTD#	Silicate (Si(OH) ₄) (μmol L ⁻¹)	Phosphate (PO ₄) (μmol L ⁻¹)	Nitrite (NO ₂) (μmol L ⁻¹)	NOx (NO ₂ + NO ₃) (μmol L ⁻¹)
CP reported	-	62.569 ± 0.31	1.795 ± 0.02	0.318 ± 0.07	25.714 ± 0.38
1		62.735	-	0.305	25.647
2	1	66.865	1.825	0.358	25.949
3	2	64.963	1.792	0.338	25.553
4	3	56.528	1.820	0.324	25.789

Note: analysis run 4 (CTD deployment 3) has a low silicate RMNS value doe to leak in connection.

The submitted nutrient results do **NOT** have RMNS corrections applied.

How to use the RMNS for Correction

Ratio = Certified RMNS Concentration/Measured RMNS Concentration in each run Corrected Concentration = Ratio x Measured Nutrient Concentration

Or for smoothing data

Ratio = Average RMNS Concentration across voyage/Measured RMNS Conc. in each run Corrected Concentration = Ratio x Measured Nutrient Concentration

Missing or Suspect Salinity Data

CTD	RP	Run	Flag	Reason for Flag or Action
2	All	sal001	133	All samples were offset from the CTD salinity. Due to instability of instrument.
3	All	sal002	133	All samples were offset from the CTD salinity. Due to instability of instrument. Bottom 7 samples bad due to changed suppression
4	All	sal003	133	All samples were offset from the CTD salinity. Due to instability of instrument. Bottom 7 samples bad due to changed suppression

Missing or Suspect Oxygen Data

CTD	RP	Run	Flag	Reason for Flag or Action
2	7	Oxy002	192	No result. Operator error. Sample collected and
				assayed. No end point found

Data Quality Flag Key

Flag	Description
0	Data is GOOD – nothing detected.
192	Data not processed.
63	Below nominal detection limit.
69	Data flagged suspect by operator. Set suspect by software if Calibration or Duplicate data is outside of set limits but not so far out as to be flagged bad.
65	Peak shape is suspect.
133	Error flagged by operator. Data is bad – operator identified by # in slk file or by clicking on point.
129	Peak exceeds maximum A/D value. Data is bad.
134	Error flagged by software. Peak shape is bad - Median Absolute Deviation (MAD) analysis used. Standards, MDL's and Duplicates deviate from the median, Calibration data falls outside set limits.
141	Missing data, no result for sample ID. Used in netcdf file as an array compiles results. Not used in csv file.
79	Method Detection Limit (MDL) during run was equal to or greater than nominal MDL. Data flagged as suspect.

GO-SHIP Specifications

Salinity

Accuracy of 0.001 is possible with AutosalTM salinometers and concomitant attention to methodology. Accuracy with respect to one particular batch of Standard Sea Water can be achieved at better than 0.001 PSS-78. Autosal precision is better than 0.001 PSS-78. A precision of approximately 0.0002 PSS-78 is possible following the methods of Kawano with great care and experience. Air temperature stability of \pm 1°C is very important and should be recorded².

Dissolved Oxygen

Target accuracy is that 2 sigma should be less than 0.5% of the highest concentration found in the ocean. Precision or reproducibility (2 sigma) is 0.08% of the highest concentration found in the ocean.

Si(OH)₄

Approximately 1-3% accuracy¹, 0.2% precision³, full scale.

PO₄

Approximately 1-2% accuracy¹, 0.4% precision³, full scale.

NO₃

Approximately 1% accuracy¹, 0.2% precision³, full scale.

Notes

- ¹ If no absolute standards are available then accuracy should be taken to mean the reproducibility presently obtainable in the better laboratories.
- ² Keeping constant temperature in the room where salinities are determined greatly increases their quality. Also, room temperature during the salinity measurement should be noted for later interpretation, if queries occur. Additionally, monitoring and recording the bath temperature is also recommended. The frequent use of IAPSO Standard Seawater is endorsed. To avoid the changes that occur in Standard Seawater, the use of the most recent batch is recommended. The bottles should also be used in an interleaving fashion as a consistency check within a batch and between batches.
- ³ Developments of reference materials for nutrients are underway that will enable improvements in the relative accuracy of measurements and clearer definition of the performance of laboratories when used appropriately and the results are reported with the appropriate meta-data.

References

- Armishaw, P. (2003) "Estimating measurement uncertainty in an afternoon. A case study in the practical application of measurement uncertainty." Accred Qual Assur, 8: pp. 218-224
- Armstrong, F.A.J., Stearns, C.A., and Strickland, J.D.H. (1967) "The measurement of upwelling and subsequent biological processes by means of the Technicon Autoanalyzer and associated equipment," Deep-Sea Res., 14: pp.381-389. doi: 10.1016/0011-7471(67)90082-4
- Hood, E.M. (2010). "Introduction to the collection of expert reports and guidelines." The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines. IOCCP Report No 14, ICPO Publication Series No. 134, Version 1, 2010.
- Hydes, D., Aoyama, M., Aminot, A., Bakker, K., Becker, S., Coverly, S., Daniel, A.G., Dickson, O., Grosso, R., Kerouel, R., van Ooijen, J., Sato, K., Tanhua, T., Woodward, E.M.S., and Zhang, J.Z. (2010). "Determination of dissolved nutrients (N, P, Si) in seawater with high precision and intercomparability using gas-segmented continuous flow analysers." The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines. IOCCP Report No 14, ICPO Publication Series No. 134, Version 1, 2010. (UNESCO/IOC)
- Kérouel, R., and Aminot, A. (1997) "Fluorometric determination of ammonia in sea and estuarine waters by direct segmented flow analysis". Mar. Chem., 57: pp. 265-275. doi: 10.1016/S0304-4203(97)00040-6
- Murphy, J. And Riley, J.P. (1962)" A Modified Single Solution Method for the Determination of Phosphate in Natural Waters", Anal. Chim. Acta, 27: p.30. doi: 10.1016/S0003-2670(00)88444-5
- Rees, C., L. Pender, K. Sherrin, C. Schwanger, P. Hughes, S. Tibben, A. Marouchos, and M. Rayner. (2018) "Methods for reproducible shipboard SFA nutrient measurement using RMNS and automated data processing." Limnol. Oceanogr: Methods, 17(1): pp. 25-41. doi:10.1002/lom3.10294
- Wood, E.D., Armstrong, F.A.J., and Richards, F.A. (1967) "Determination of nitrate in seawater by cadmium-copper reduction to nitrite." Journal of the Marine Biological Association of U.K. 47: pp. 23-31.