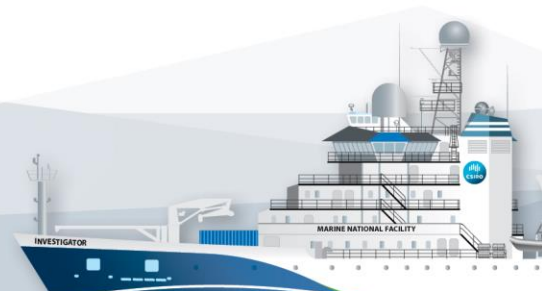


RV INVESTIGATOR

HYDROCHEMISTRY DATA PROCESSING REPORT

Voyage:	in2022_t01
Chief Scientist	N/A
Principal Investigator	N/A
Voyage title:	Transit: Cairns to Darwin 2022
Report compiled by:	Alicia Camac



Contents

1	Executive Summary	4
2	Itinerary	5
3	Key personnel list	5
4	Summary.....	6
4.1	Sample Type and Number Assayed.....	6
4.1.1	CTD (Conductivity, Temperature, Density)	6
4.1.2	TMR (Trace Metal Rosette)	6
4.1.3	EXP (Experimental samples).....	6
4.1.4	TSG (Thermosalinograph)	6
4.2	Data Processing Overview	7
5	Salinity Data Processing.....	8
5.1	Salinity Parameter Summary	8
5.2	Salinity Method.....	8
5.3	CTD Salinity vs Bottle Salinity Plot	9
5.4	OSIL Salinity Standard PSU across the Voyage.....	10
5.5	Missing or Suspect Salinity Data	10
6	Dissolved Oxygen Data Processing.....	11
6.1	Dissolved Oxygen Parameter Summary.....	11
6.2	Dissolved Oxygen Method	11
6.3	CTD Dissolved Oxygen vs Bottle Dissolved Oxygen Plot	12
6.4	Dissolved Oxygen Instrument titrant: thiosulphate normality and blank correction.....	13
6.5	Missing or Suspect Dissolved Oxygen Data.	13
7	Nutrient Data Processing.....	14
7.1	Nutrient Assay Parameter Summary	14
7.2	Nutrient Methods	14
7.3	HyPro Processing Parameters.....	15
7.4	HyPro Data Processing Summary.....	16
7.5	Accuracy - Reference Material for Nutrient in Seawater (RMNS)	16
7.5.1	Figure 4: Silicate RMNS Plot (μM).....	18
7.5.2	Figure 5: Phosphate RMNS Plot (μM)	19
7.5.3	Figure 6: Nitrate + Nitrite (NO_x) RMNS Plot (μM).....	20
7.5.4	Figure 7: Nitrite RMNS Plot (μM)	21
7.6	Analytical Precision	21
7.6.1	Nutrient Measurement Uncertainty.....	21

7.7	Sampling Precision	22
7.7.1	Silicate Duplicates Plot.....	22
7.7.2	Phosphate Duplicates Plot	22
7.7.3	Nitrate + Nitrite (NO _x) Duplicates Plot	22
7.7.4	Nitrite Duplicates Plot.....	22
7.7.5	Ammonia Duplicates Plot.....	22
7.8	Redfield Ratio Plot (14.0) for CTD Deployments.....	23
7.9	Missing or Suspect Nutrient Data.	24
7.10	Temperature & Humidity Change over Nutrient Analyses	24
8	Appendix.....	25
8.1	Salinity: Reference Material Used.....	25
8.2	Nutrients: Flagged Calibration and Quality Control Data	25
8.3	Nutrients: RMNS results for each Analysis Run & CTD Deployment.	26
8.3.1	RMNS Lot CP Results.....	26
8.4	Nutrients: Measured Detection Limit for each Analysis Run & CTD Deployment.....	27
8.5	Flag Key for Hydrology Data Set.....	28
8.6	GO-SHIP Specifications.....	29
8.6.1	Salinity.....	29
8.6.2	Dissolved Oxygen	29
8.6.3	SiO ₂	29
8.6.4	PO ₄	29
8.6.5	NO ₃	29
8.6.6	Notes.....	29
9	References	30

1 Executive Summary

The main objective of the voyage was to transit from Cairns to Darwin in preparation for IN2022_V08. Underway training, repairs, maintenance and science operations occurred whilst en route without impacting the voyage departure and arrival times. Piggy back projects included 3D-GBR & underway scientific mapping, sea surface temperature radiometer comparisons/calibrations and the deployment of an ARGO BiGeoChemical (BGC) float. This involved a CTD on station where the Hydrochemist sampled for all normal Hydrochemistry parameters and in addition the DIC/Alkalinity samples.

TSG samples were taken in triplicate as per usual procedure and some screen shots and additional photos were taken to improve and update the working instructions for this. Water samples collected during the voyage were assayed in the ship's hydrochemistry laboratory for nutrients, dissolved oxygen, and their salinity measured. The samples came from deployments of the CTD rosette.

High quality data was produced for the three measured parameters. Five nutrients were analysed; silicate, phosphate, nitrate + nitrite, nitrite and ammonium. Certified reference materials for nutrients in seawater were within the specified limits of the certified value. When using silicate, phosphate, nitrate+nitrite (NO_x) 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

There were no issues during the transit with analysis or instruments.

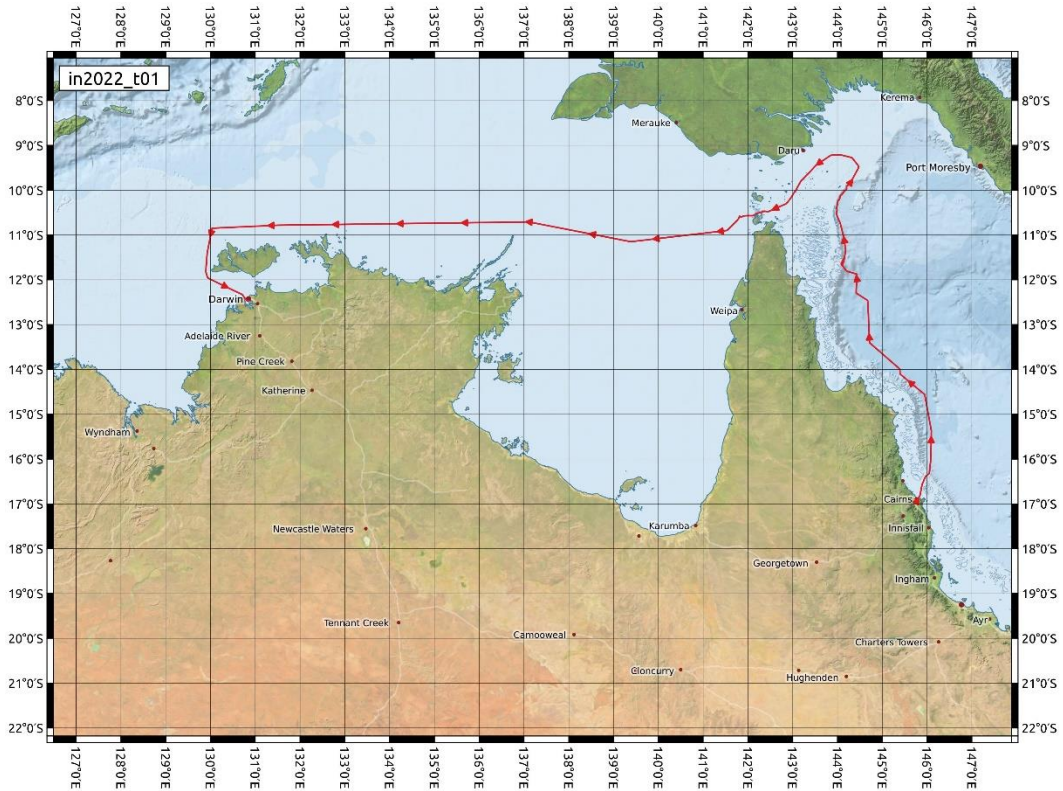
Final hydrology data, analytical methods, and related log sheets and processing notes can be obtained from the CSIRO data centre.

Contact: DataLibrariansOAMNF@csiro.au

2 Itinerary

Cairns to Darwin, 11th to 17th of September, 2022.

Voyage Track:



3 Key personnel list

Name	Role	Organisation
David Flynn	VDL	CSIRO
Hugh Barker	Voyage Manager	CSIRO
Alicia Camac	Hydrochemist	CSIRO

4 Summary

4.1 Sample Type and Number Assayed

Analysis (instrument)	Number of Samples
Salinity (Guildline Salinometer)	26 CTD
	0 TMR
	0 UWY
	9 TSG
Dissolved Oxygen (SIO automated titration)	26 CTD
	0 UWY
Nutrients (Seal AA3HR segmented flow)	27 CTD
	0 TMR
	0 EXP
	0 UWY

4.1.1 CTD (Conductivity, Temperature, Density)

- Sampling point, 36 bottle rosette with 12L Ocean Test Equipment bottles (Niskin) deployed at depth for water collection.
- 1 CTD deployment in total. Deployment 1 was sampled by Alicia with helpers Carol Rawnsley, Ian Hawkes and Stephanie Petillo.

4.1.2 TMR (Trace Metal Rosette)

- NA

4.1.3 EXP (Experimental samples)

- NA

4.1.4 TSG (Thermosalinograph)

- Samples collected by DAP or hydrochemistry from underway lab for calibration of thermosalinograph.

TSG sample information refer to the everLog from the voyage.

4.2 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.

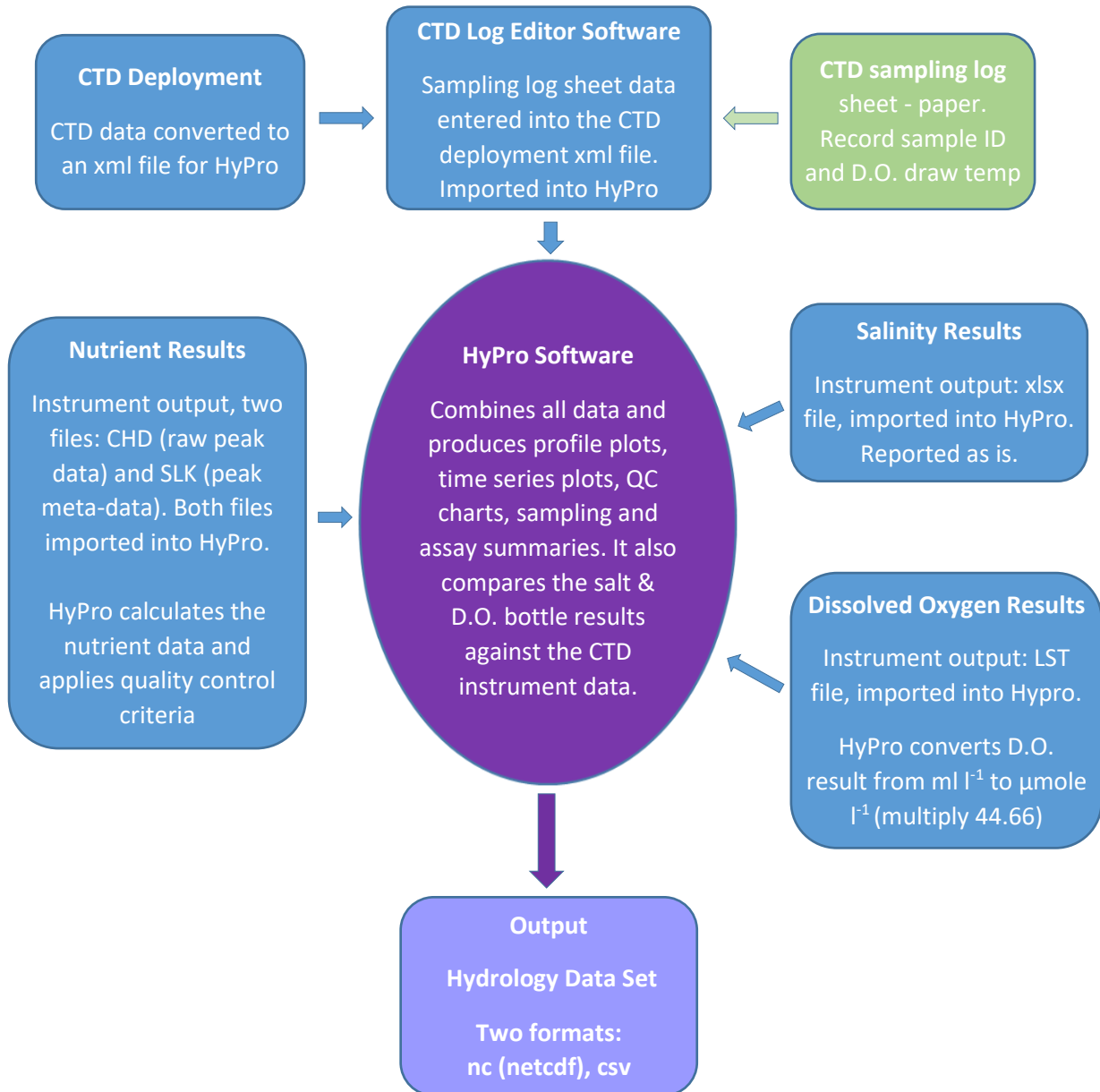


Figure 1: Hydrology Data Processing Flow Diagram.

5 Salinity Data Processing

5.1 Salinity Parameter Summary

Details	
HyPro Version	5.7
Instrument	Guildline Autosal Laboratory Salinometer 8400(B) – SN 71611
Software	OSIL Data Logger ver 1.2
CSIRO Hydrochem Method.	Sampling: WI_Sal_002 Measurement: SOP006
Accuracy	± 0.001 practical salinity units
Analysts	Alicia Camac
Lab Temperature (±0.5°C)	21.9 -22.5°C during analysis.
Bath Temperature	24.01°C
Reference Material	OSIL I IAPSO - Batch P164, use BY 23/3/2023, $K_{15} = 0.99985$
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	None.

5.2 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 32.4356×10^{-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 25cm^3 . 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.

5.3 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. The corrected values are not reported in the hydrology set. Please contact the DataLibrarians@csiro.au for corrected CTD data.

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

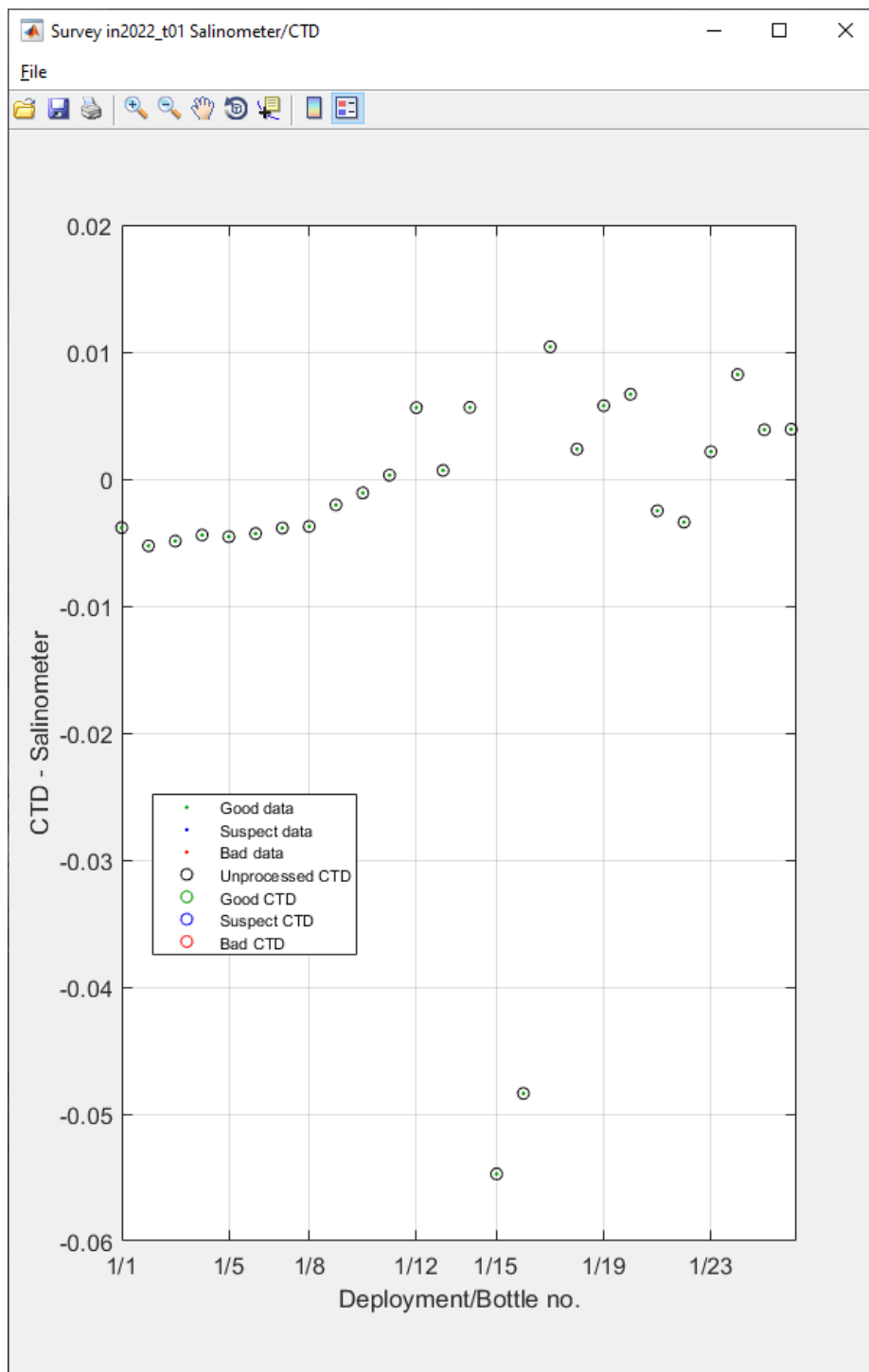


Figure 2: CTD Salinity - Bottle Salinity vs CTD deployment plot. The data quality is coded by colour, green indicating good bottle data. Please ignore the black ring, indicating unprocessed CTD data, this plot is generated using the pre-processed CTD output. Units: PSU.

5.4 OSIL Salinity Standard PSU across the Voyage

The instrument is calibrated with OSIL standard seawater lot P164 (PSU = 34.994). Only one salinity run done so no need for plot. Maybe add the OSIL measurements so the value is displayed somewhere

5.5 Missing or Suspect Salinity Data

NA

6 Dissolved Oxygen Data Processing

6.1 Dissolved Oxygen Parameter Summary

Details	
HyPro Version	5.7
Instrument	Automated Photometric Oxygen system (SIO)
Software	SCRIPPS
CSIRO Hydrochem. Method	Sampling: WI_DO_001 Assay: SOP005
Accuracy	± 0.5 µM
Analyst(s)	Alicia Camac
Lab Temperature (±1°C)	Variable, 18.7 – 20.3°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.

6.2 Dissolved Oxygen Method

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

Method synopsis: 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 39 times. The dissolved oxygen oxidizes an equivalent amount of Mn (II) to Mn (IV) which precipitates. Just before titration, the sample is acidified, oxidizing the Mn (IV) back to the divalent state liberating iodine twice the original dissolved oxygen content of the sample. The tri-iodine is auto-titrated with a standardised thiosulphate solution using a Metrohm 665 Dosimat fitted with a 1ml burette. The endpoint is determined by measuring changes in the UV absorption of the tri-iodide ion at 365 nm. The point at which there is no change in absorbance is the endpoint.

Before each batch of sample assays, the thiosulphate solution is standardised by using it to titrate a 10ml aliquot of potassium iodate primary standard. A blank correction is also determined from the difference between two consecutive titres for 1ml aliquots of the same potassium iodate solution.

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

6.3 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 DataLibrarians@csiro.au for corrected CTD data.

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

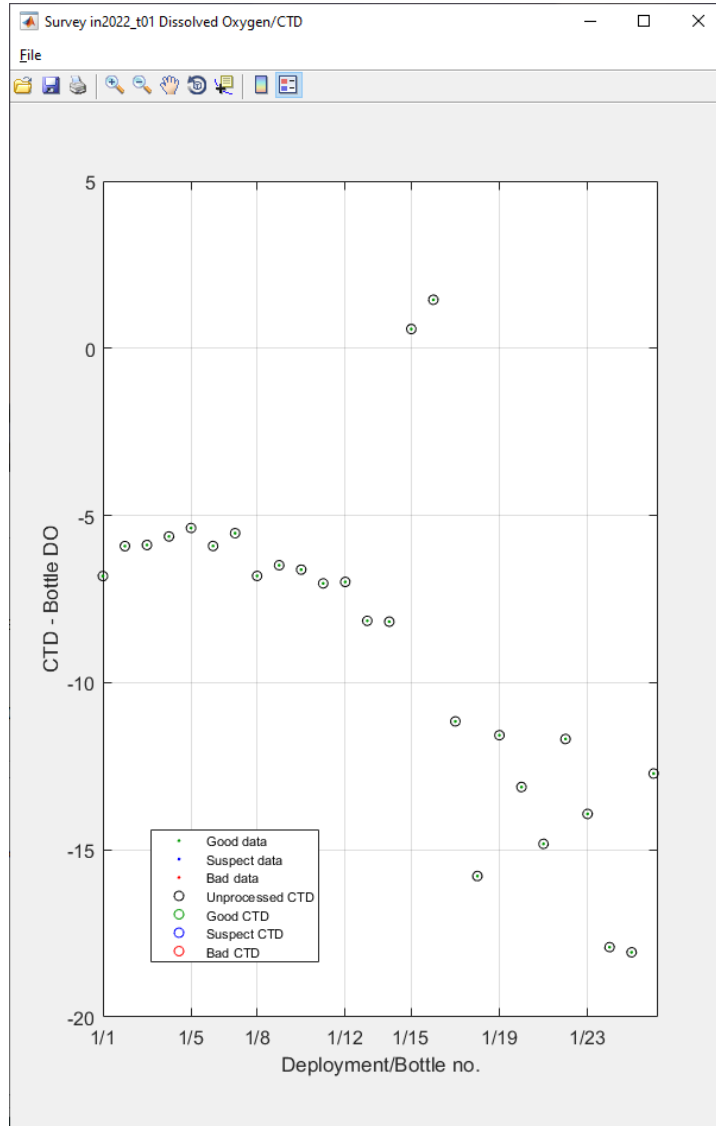


Figure 3. CTD Dissolved Oxygen - Bottle Dissolved Oxygen vs Deployment Plot. The data quality is coded by colour, green indicating good bottle data. Please ignore the black ring, indicating unprocessed CTD data, this plot is generated using the pre-processed CTD output. Units: $\mu\text{mol L}^{-1}$.

6.4 Dissolved Oxygen Instrument titrant: thiosulphate normality and blank correction.

The normality of the thiosulphate titrant (0.2N) varied less than 0.00003 N between this voyage and the previous. One batch of thiosulphate reagent was used during the voyage. There was only one analysis run so comparisons between runs is not relevant.

6.5 Missing or Suspect Dissolved Oxygen Data.

NA

7 Nutrient Data Processing

7.1 Nutrient Assay Parameter Summary

Details					
CSIRO Software	HyPro 5.7				
Instrument	Seal AA3HR				
Instrument Software	Seal AACE 7.0				
CSIRO Hydrochem. Method, sampling	WI_Nut_001				
CSIRO Hydrochem. Method, nutrient	SOP001	SOP002	SOP003	SOP003	SOP004
Nutrient	Silicate	Phosphate	Nitrate + Nitrite	Nitrite	Ammonium
Concentration range	112 µM	3.0 µM	42 µM	1.4 µM	2.0 µM
Method Detection Limit (MDL)	0.2 µM ¹	0.02 µM	0.02 µM	0.02 µM	0.02 µM
Matrix Corrections	none	none	none	none	none
Analysts	Alicia Camac				
Lab Temperature (±1°C)	Variable, 18.7– 20.3°C				
Reference Material	KANSO, RMNS lot CP				
Sampling Container type	CTD: 50ml HDPE with screw cap lids.				
Sample Storage	< 2 hrs at room temperature or ≤ 12 hrs @ 4°C				
Pre-processing of Samples	CTDY: None.				
Comments					

7.2 Nutrient Methods

When using silicate, phosphate, nitrate+nitrite (NO_x) 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-SGNOS 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-phtaldialdehyde method. Based on Roger K erouel and Alain Aminot, IFREMER (1997 Mar.Chem.57). 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.

7.3 HyPro Processing Parameters

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	Quadratic	Quadratic	Quadratic
# of points in Calibration	7	6	7	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	Y	Y	Y	Y
Baseline drift correction (HyPro)	Y	Y	Y	Y	Y
Sensitivity drift correction (HyPro)	Y	Y	Y	Y	Y

Result Details	Silicate	Phosphate	Nitrate + Nitrite (NO _x)	Nitrite	Ammonia
Data Adj for RMNS variance.	N	N	N	N	N
Medium of Standards	LNSW (bulk on deck of Investigator) collected on 11/9/2022. 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 from Milli Q				
Proportion of samples in duplicate.	<10%. CTD: Niskin fired at the greatest depth sampled in duplicate. Single samples collected for remaining depths.				
Comments	The reported data is not corrected to the RMNS. Per deployment RMNS data tabulated in appendix 8.3.				

7.4 HyPro Data Processing Summary

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:

- $\pm 0.5\%$ of the concentration of the top standard for silicate and nitrate+nitrite (as per WOCE).
- Within 0.02μM 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 8.2.

Missing or suspect nutrient data is tabulated in section 7.9, the flags are also in the final hydrology data set. The Flag key is in Appendix 8.5.

7.5 Accuracy - Reference Material for Nutrient in Seawater (RMNS)

Japanese KANSO certified RMNS lot CP was assayed in triplicate or quadruplicate in each run to monitor accuracy. The certified values are in table 1.

For in2022_T01, the majority of RMNS results are within 1% of their certified mean and within 0.02μM for nitrite. Plots of RMNS values for all runs are below.

The assayed RMNS values per Analysis run and CTD deployments are listed in appendix 8.3

The GO-SHIP criteria (Hyde *et al.*, 2010), appendix 8.6, specifies using 1-3 % of full scale (depending on the nutrient) as acceptable limits of accuracy.

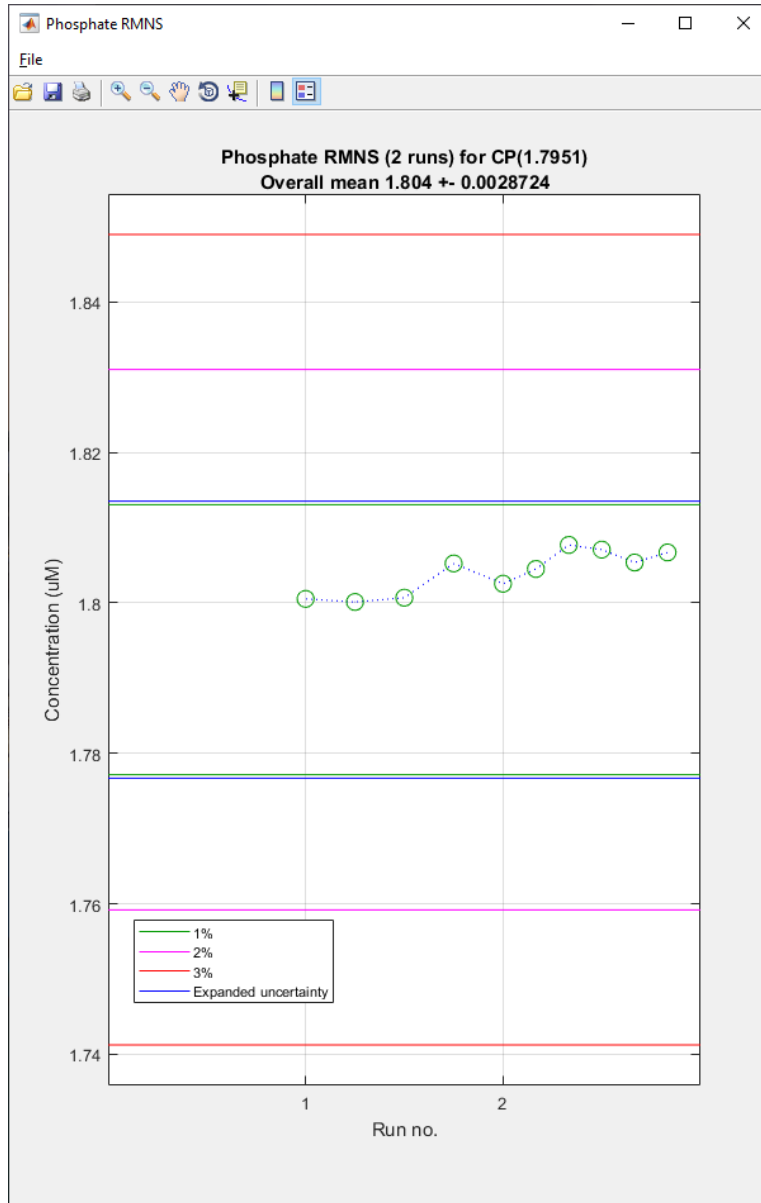
Table 1: RMNS concentrations with expanded uncertainty at 21°C

RMNS	NO ₂ (μmol L ⁻¹)	NO ₃ + NO ₂ (NO _x , μmol L ⁻¹)	PO ₄ (μmol L ⁻¹)	SiO ₄ (μmol L ⁻¹)
Lot CP	0.3175 ± 0.0717	25.7136 ± 0.379	1.7951 ± 0.0184	62.5687 ± 0.307

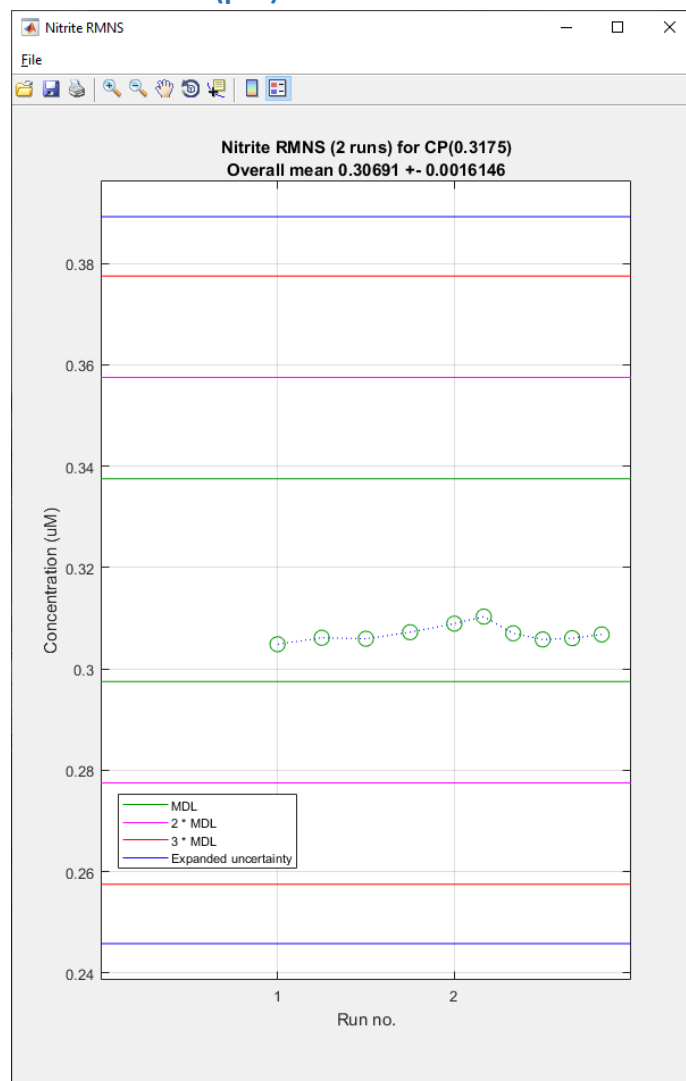
KANSO publishes the RMNS nutrient values in μmol kg⁻¹. These are converted to μmol L⁻¹ at 21°C. The RMNS is not certified for ammonium. NO_x is derived by adding the NO₃ and NO₂ values.

Plot key. 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 μM increments from the certified value. The blue line is the expanded uncertainty of the certified value.

7.5.2 Figure 5: Phosphate RMNS Plot (μM)



7.5.4 Figure 7: Nitrite RMNS Plot (μM)



7.7 Sampling Precision

Sampling precision is monitored by assaying duplicate samples collected from the greatest depth for each CTD deployment. The sampling precision is good if the difference between the duplicate concentrations is less than the MDL value. The exception is nitrate+nitrite, which uses 0.06 μM as the MDL boundary.

Plots of the difference between the duplicate and their mean for the CTD deployments are below. The red line is the boundary below which sampling precision is deemed good.

For in2022_T01, there was only one duplicate for the 101 sample (deepest sample from the one CTD001). All 5 nutrients showed great sampling precision for this one sample but not necessary to show the plots.

7.7.1 Silicate Duplicates Plot

NA

7.7.2 Phosphate Duplicates Plot

NA

7.7.3 Nitrate + Nitrite (NO_x) Duplicates Plot

NA

7.7.4 Nitrite Duplicates Plot

NA

7.7.5 Ammonia Duplicates Plot

NA

7.8 Redfield Ratio Plot (14.0) for CTD Deployments.

Plots consist of phosphate versus NOx for all CTD deployments. Best fit ratio = 14.13 for in2022_t01

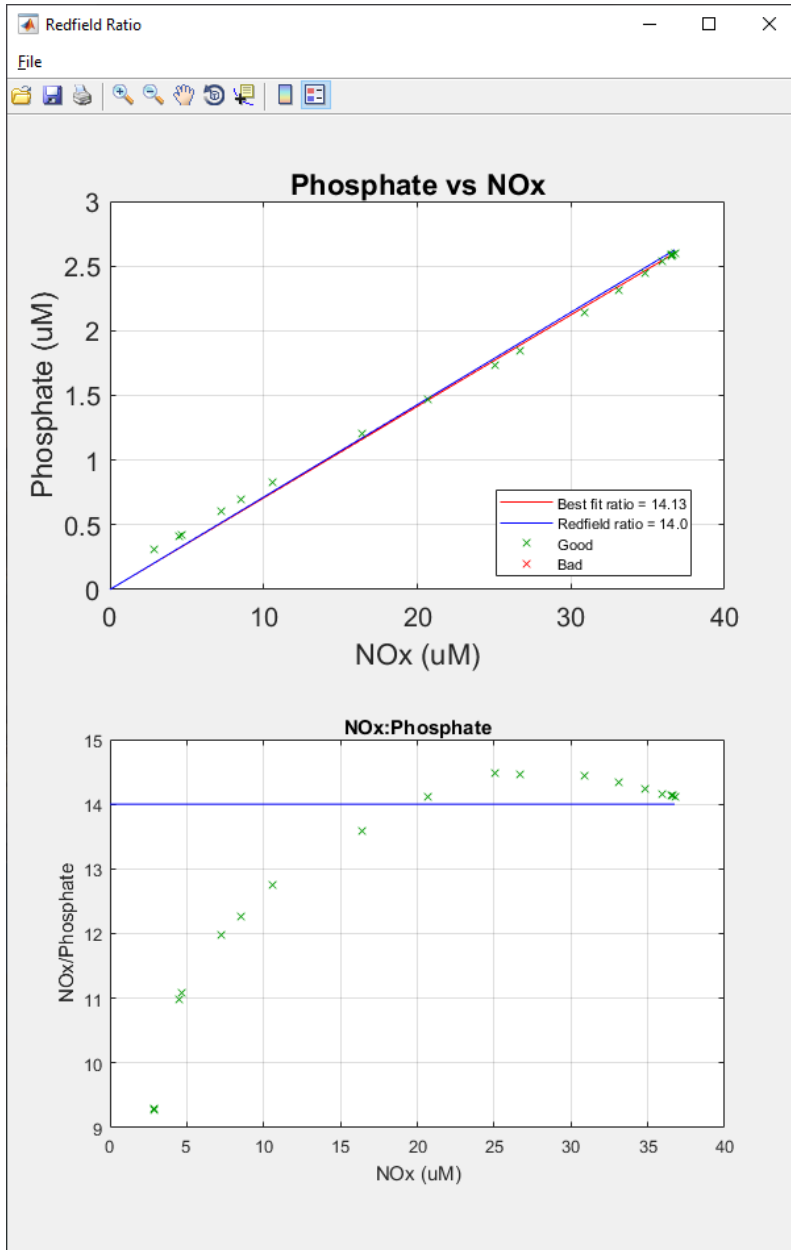


Figure 8: Redfield ratio plots.

7.9 Missing or Suspect Nutrient Data.

NA

7.10 Temperature & Humidity Change over Nutrient Analyses

The ambient conditions in the hydrochemistry lab were measured for the short period of time. There was acceptable change in temperature and there was only one analysis run so no comparisons over the voyage necessary.

8 Appendix

8.1 Salinity: Reference Material Used

Osil IAPSO Standard Seawater	
Batch	P164
Use by date	23/3/2023
K ₁₅	0.99985
PSU	34.994

8.2 Nutrients: Flagged Calibration and Quality Control Data

HyPro classifies the quality of data as good, suspect or bad and flags accordingly. All data was good.

8.3 Nutrients: RMNS results for each Analysis Run & CTD Deployment.

8.3.1 RMNS Lot CP Results

Analysis Run	CTD #	Silicate (Si, $\mu\text{mol L}^{-1}$)	Phosphate (PO_4 , $\mu\text{mol L}^{-1}$)	Nitrite (NO_2 , $\mu\text{mol L}^{-1}$)	NOx ($\text{NO}_2 + \text{NO}_3$, $\mu\text{mol L}^{-1}$)
<i>CP reported</i>	-	62.57	1.7951	0.3175	25.71
1	-	62.75	1.8025	0.306	25.73
2	1	62.75	1.8067	0.308	25.62

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

8.4 Nutrients: Measured Detection Limit for each Analysis Run & CTD Deployment.

Measured Detection Limit

Analysis Run	CTD #	Silicate (Si, $\mu\text{mol L}^{-1}$)	Phosphate (PO_4 , $\mu\text{mol L}^{-1}$)	Nitrite (NO_2 , $\mu\text{mol L}^{-1}$)	NOx ($\text{NO}_2 + \text{NO}_3$, $\mu\text{mol L}^{-1}$)	Ammonia (NH_4^+ , $\mu\text{mol L}^{-1}$)
1	-	0.0549	0.0089	0.0026	0.0057	0.0039
2	1	0.0216	0.0079	0.0009	0.0002	0.0040

8.5 Flag Key for Hydrology Data Set

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.

8.6 GO-SHIP Specifications

8.6.1 Salinity

Accuracy of 0.001 is possible with Autosol™ 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. Autosol 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 $\pm 1^\circ\text{C}$ is very important and should be recorded².

8.6.2 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.

8.6.3 SiO₂

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

8.6.4 PO₄

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

8.6.5 NO₃

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

8.6.6 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.

9 References

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