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Precision analysis and the determination of outliers

Precision was determined by analyzing replicate samples drawn from one Niskin.

Outliers are discarded on the basis of Chauvenet's criteria. The statistic is calculated by finding the Chauvenet critical value (Z-critical) for the total degrees of freedom (v) of the dataset:

$$Z\text{-critical} = \text{ABS}(\text{NORM.S.INV}(1/(4*v)))$$

The maximum deviation, D_{max} , is compared with the individual residuals from the original concentrations.

If a replicate's residual is greater than D_{max} this value can be rejected. D_{max} is determined by the following formula:

$$D_{max} = Z\text{-critical} * \sigma$$

where σ is the standard deviation of residuals

Precision is assessed by calculating the pooled standard deviation (S_p).

Pooled standard deviation is calculated for a combination of duplicates and triplicates using the following formula:

$$s_p = \sqrt{\frac{SS_1 + SS_2 + \dots + SS_k}{v_1 + v_2 + \dots + v_k}}$$

where: v = total degrees of freedom (1 for duplicates, 2 for triplicates).

SS = sum of squares of the residuals.

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Precision statement for replicate samples drawn from a single Niskin bottle:

Salinity: Bottle ranged from 34.3526 to 34.6706 with a pooled standard deviation of 0.0014 from 18 replicates - after the removal of 1 outlier sample using the Chauvenet criteria. The pooled standard deviation was 0.0017 when using the complete set of 19 replicates.

Duplicate samples from a single Niskin bottle

Event Number	Sample Number	Station	Pressure dbar	Salinity 1	Salinity 2	Rejected yes / no	Comment
18	90	P4	1249.7	34.4730	34.4702		
18	91	P4	1000.3	34.3797	34.3798		
28	148	P8	2002.6	34.5952	34.5949		
28	151	P8	1000.0	34.3806	34.3810		
37	200	P12	2998.7	34.6455	34.6472		
37	204	P12	1499.8	34.5180	34.5185		
37	206	P12	1000.2	34.3793	34.3768		
42	242	P14	1999.8	34.5832	34.5852		
42	246	P14	1000.2	34.3581	34.3600		
46	282	P16	3498.2	34.6619	34.6646		
46	285	P16	2502.3	34.6186	34.6188		
46	289	P16	999.9	34.3677	34.3611	yes	
57	341	P20	2500.5	34.6283	34.6282		
57	345	P20	1000.4	34.3614	34.3611		
61	386	P22	3000.0	34.6519	34.6530		
63	416	P24	3000.0	34.6517	34.6501		
65	443	Eddy	1999.8	34.5736	34.5725		
71	519	P26	3501.2	34.6706	34.6664		
71	525	P26	999.7	34.3526	34.3564		

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Duplicate Niskins at the same pressure

Note: Although the precision statement for samples drawn from duplicate Niskin bottles is calculated using the same formula as the precision statement for duplicate samples drawn from one single Niskin, this process is mainly used to identify problem samples and is not being used as a measure of analytical precision.

Salinity: Bottle ranged from 34.4711 to 34.6764 with a pooled standard deviation of 0.0011 from 3 replicates after the removal of 1 outlier sample using the Chauvenet criteria.

The pooled standard deviation was 0.0041 when using the complete set of 4 replicates.

Event Number	Sample Number	Station	Nominal Pressure dbar	Salinity 1	Salinity 2	Rejected yes / no	Comment
18	89 / 90	P4	1250	34.4711	34.4716		
37	200 / 201	P12	3000	34.6464	34.6458		
46	282 / 283	P16	3500	34.6633	34.6657		
57	338 / 339	P20	3500	34.6651	34.6764	yes	