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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.

Dissolved oxygen datasets with pooled standard deviations < 0.010 ml/l are considered of good quality.

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

Oxygen:Dissolved:Bottle:Volume ranged from 0.235 to 6.515 ml/l with a pooled standard deviation of 0.005 ml/l from 22 replicates after the removal of 1 outlier sample using Chauvenet's criteria.

The pooled standard deviation was 0.007 when using the complete set of 23 replicates.

Duplicate samples from a single Niskin bottle

Event Number	Sample Number	Station	Pressure dbar	Oxy:Dis 1 ml/l	Oxy:Dis 2 ml/l	Rejected yes / no	Comment
3	5	Haro59	126.3	4.776	4.784		
3	14	Haro59	6.2	5.075	5.077		
5	29	JF2	81.5	4.496	4.500		
10	49	P1	116.9	4.560	4.571		
16	96	P2	106.6	4.201	4.214		
30	286	P8	2001.8	1.264	1.257		
30	302	P8	26.4	6.419	6.425		
40	346	P12	2501.8	1.854	1.848		
40	350	P12	1002.1	0.246	0.235		
40	355	P12	250.7	3.782	3.781		
40	361	P12	76.5	6.354	6.359		
54	488	P16	2500.1	1.867	1.873		
54	499	P16	175.9	3.594	3.580		
54	503	P16	76.8	6.433	6.425		
67	575	P20	2503.5	1.869	1.854		
67	583	P20	302.1	2.224	2.219		
67	587	P20	152.0	4.131	4.128		
67	593	P20	11.1	6.515	6.514		
93	769	P26	4000.5	3.145	3.139		
93	775	P26	1251.0	0.468	0.439	yes	
93	781	P26	252.0	2.064	2.058		
93	785	P26	126.9	4.429	4.430		
121	245	P4	1251.0	0.385	0.393		
121	257	P4	76.5	5.164	5.162		

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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 duplicates 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.

Oxygen:Dissolved:Bottle:Volume ranged from 0.389 to 2.873 ml/l with a pooled standard deviation of 0.009 ml/l from 4 replicates after the removal of 0 outlier sample using Chauvenet's criteria.

Event Number	Sample Number	Station	Nominal Pressure dbar	Oxy:Dis 1 ml/l	Oxy:Dis 2 ml/l	Rejected yes / no	Comment
40	344 / 345	P12	3000	2.255	2.269		
54	485 / 486	P16	3500	2.669	2.675		
67	572 / 573	P20	3500	2.873	2.854		
121	244 / 245	P4	1250	0.392	0.389		