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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:

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

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 0.266 to 6.940 ml/l with a pooled standard deviation of 0.006 ml/l from 43 replicates after the removal of 0 outlier sample using Chauvenet's criteria.

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
2	25	Haro59	150.2	5.872	5.869		
2	33	Haro59	5.0	5.865	5.870		
12	44	P1	5.4	6.528	6.527		
15	59	P2	100.7	2.927	2.935		
15	64	P2	24.8	6.150	6.147		
18	88	P4	1316.0	0.555	0.546		
18	96	P4	249.9	2.545	2.545		
18	102	P4	74.9	6.527	6.543		
18	106	P4	4.7	6.605	6.608		
28	152	P8	800.0	0.292	0.274		
28	164	P8	40.4	6.590	6.596		
28	168	P8	15.0	6.623	6.622		
37	202	P12	2501.0	1.915	1.932		
37	207	P12	800.7	0.266	0.270		
37	211	P12	251.0	3.316	3.322		
37	217	P12	75.1	6.563	6.573		
46	285	P16	2502.3	1.816	1.811		
46	288	P16	1251.4	0.339	0.332		
46	294	P16	250.8	3.007	2.999		
46	302	P16	25.1	6.637	6.634		
57	337	P20	4024.8	2.946	2.936		
57	342	P20	1999.9	1.272	1.276		
57	346	P20	799.5	0.386	0.384		
57	359	P20	10.0	6.726	6.725		
65	446	Eddy	1249.2	0.353	0.336		
65	452	Eddy	249.4	1.696	1.700		
65	458	Eddy	74.2	6.721	6.723		
65	464	Eddy	4.3	6.740	6.756		
68	489	P25	299.8	2.012	2.000		
68	499	P25	25.2	6.785	6.787		
71	519	P26	3501.2	2.884	2.867		
71	522	P26	2000.7	1.182	1.171		
71	525	P26	999.7	0.376	0.381		
71	540	P26	4.9	6.818	6.809		

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Continued

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
80	580	PA013	15.2	6.940	6.932		
80	581	PA013	10.2	6.935	6.932		
80	582	PA013	4.9	6.934	6.932		
80	583	PA013	2.5	6.931	6.932		
96	715	CHAT3	30.0	6.812	6.813		
101	764	CH16	100.4	6.679	6.683		
104	809	HECS8	5.0	6.935	6.928		
106	820	HECS7	100.8	6.894	6.896		
112	891	CHAT1	75.2	6.577	6.571		

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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.

Oxygen:Dissolved:Bottle:Volume ranged from 0.461 to 2.834 ml/l with a pooled standard deviation of 0.011 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
18	89 / 90	P4	1250	0.485	0.461		
37	200 / 201	P12	3000	2.250	2.266		
46	282 / 283	P16	3500	2.663	2.656		
57	338 / 339	P20	3500	2.834	2.824		