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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 0.236 to 6.905 ml/l with a pooled standard deviation of 0.011 ml/l from 29 replicates after the removal of 1 outlier sample using Chauvenet's criteria.

The pooled standard deviation was 0.020 when using the complete set of 30 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
16	19	P1	102.8	1.983	1.987		
21	43	P2	75.7	2.519	2.516		
28	115	P4	1250.4	0.392	0.395		
28	127	P4	75.0	5.611	5.597		
39	208	P8	2000.8	1.266	1.261		
39	216	P8	250.4	3.867	3.866		
39	224	P8	25.4	5.576	5.583		
47	323	P12	3001.7	2.277	2.266		
47	330	P12	800.7	0.355	0.350		
47	336	P12	175.8	4.760	4.762		
70	552	P16	3499.1	2.651	2.654		
70	559	P16	798.3	0.331	0.324		
70	565	P16	173.9	4.299	4.296		
70	571	P16	24.9	5.944	5.932		
79	646	P20	2501.2	1.856	1.834		
79	650	P20	1000.9	0.524	0.397	yes	Replicate outliers
79	657	P20	176.4	3.855	3.853		
79	665	P20	5.1	5.891	5.888		
99	813	P26	2501.4	1.935	1.930		
99	822	P26	249.3	2.407	2.414		
99	828	P26	74.9	6.900	6.905		
99	832	P26	5.8	5.999	5.999		
115	970	P4	1325.2	0.480	0.525	no	Very poor replication
115	971	P4	1000.4	0.245	0.236		
115	972	P4	802.0	0.265	0.27		
115	973	P4	400.1	1.321	1.325		
115	974	P4	101.9	5.175	5.227	no	Very poor replication
115	975	P4	51.1	6.377	6.378		
115	976	P4	10.4	5.791	5.813		
115	977	P4	4.9	5.793	5.804		

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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 0.394 to 2.844 ml/l with a pooled standard deviation of 0.020 ml/l from 5 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
21	42 / 43	P2	75	2.540	2.518		
28	114 / 115	P4	1250	0.396	0.394		
47	323 / 324	P12	3000	2.272	2.262		
70	551 / 552	P16	3500	2.656	2.653		
79	643 / 644	P20	3500	2.821	2.844		