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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, Dmax, is compared with the individual residuals from the original concentrations.

If a replicate's residual is greater than Dmax this value can be rejected. Dmax 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 (Sp).

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 0.240 to 7.046 ml/l with a pooled standard deviation of 0.013 ml/l from 49 replicates after the removal of 2 outlier samples using Chauvenet's criteria.

The pooled standard deviation was 0.032 when using the complete set of 51 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
18	27	P4	1251.5	0.385	0.383		
18	35	P4	175.0	2.758	2.759		
18	43	P4	5.7	6.350	6.353		
32	109	P20	3500.2	2.888	2.867		
32	117	P20	600.4	0.488	0.485		
32	124	P20	124.2	5.128	5.127		
32	130	P20	6.1	6.826	6.836		
50	293	P26	2502.3	1.871	1.874		
50	302	P26	252.0	2.548	2.548		
50	308	P26	74.7	7.046	6.901	yes	Replicate outliers
50	312	P26	4.8	6.950	6.946		
68	356	P16	3501.2	2.699	2.689		
68	363	P16	801.4	0.336	0.325		
68	369	P16	175.5	3.204	3.197		
68	377	P16	5.2	6.800	6.792		
77	448	P12	2500.7	1.934	1.918		
77	454	P12	600.2	0.534	0.520		
77	461	P12	124.2	4.237	4.237		
77	467	P12	5.1	6.717	6.723		
90	537	P8	1001.7	0.241	0.240		
90	541	P8	301.0	1.922	1.908		
90	556	P8	5.6	6.612	6.608		
99	563	P4	1000.3	0.259	0.245		
99	569	P4	149.9	2.670	2.642		
105	591	P2	99.9	5.167	5.165		
105	597	P2	5.2	6.410	6.414		
106	600	P1	4.1	6.219	6.237		
109	605	102	151.1	4.512	4.512		
109	613	102	9.9	6.650	6.645		
111	619	JF2	100.8	5.111	5.108		
111	625	JF2	10.4	5.952	5.956		
112	631	59	150.5	5.605	5.609		
112	641	59	0.6	5.895	5.894		

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Duplicate samples from a single Niskin bottle, cont'd

Event Number	Sample Number	Station	Pressure dbar	Oxy:Dis 1 ml/l	Oxy:Dis 2 ml/l	Rejected yes / no	Comment
114	642	56	220.2	5.461	5.569		
114	651	56	30.0	5.788	5.795		
116	658	46	125.0	5.614	5.352	yes	Replicate outliers
116	662	46	39.6	4.890	4.896		
118	674	42	124.7	5.268	5.269		
118	681	42	10.0	6.631	6.632		
119	685	39	350.4	2.366	2.351		
119	694	39	50.3	4.953	4.962		
124	720	27	75.5	4.740	4.725		
124	726	27	5.3	6.568	6.573		
125	729	2	250.2	2.548	2.541		
125	732	2	150.4	4.259	4.258		
127	747	CPF2	100.4	3.845	3.845		
127	749	CPF2	50.4	4.583	4.581		
129	761	12	150.3	4.146	4.148		
129	767	12	30.5	5.190	5.193		
132	774	14	200.2	2.946	2.936		
132	781	14	39.8	5.225	5.226		

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 0.384 to 5.898 ml/l with a pooled standard deviation of 0.007 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
18	26 / 27	P4	1250	0.397	0.384		
32	108 / 109	P20	3500	2.888	2.877		
68	355 / 356	P16	3500	2.701	2.694		
77	446 / 447	P12	3000	2.231	2.245		
105	592 / 593	P2	75	5.896	5.898		