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Precision analysis and the determination of outliers

Precision was determined by analyzing replicate samples drawn from one Niskin and calculating the pooled standard deviation with outliers removed based on the Chauvenet criterion.

The criterion was applied by generating a population of differences between duplicates.

A z-score was generated for each pair and compared to the z-critical value.

The z-critical value was calculated using the excel function =ABS(NORM.S.INV(1/(4*n))), where n is the number of pairs.

Samples with z-scores greater than the z-critical value were rejected and the pooled standard deviation of pairs then calculated:

$$Z - score = \frac{|x - \mu|}{\sigma}$$

where: x is the difference between duplicates
 μ is the mean difference between duplicates
and σ is the standard deviation

For an outlier to be discarded:

$$Z - score \geq Z_{critical}$$

For precision, calculate pooled standard deviation (s_p) with the above outliers removed with the simplified formula for the case of duplicates:

$$s_p = \sqrt{\frac{\sum (x_{i1} - x_{i2})^2}{2k}}$$

where: x_1 and x_2 are the individual measurements of the duplicates
and k = no. of pairs

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Nitrate_plus_Nitrite: Bottle

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

The pooled standard deviation for Nitrate_plus_Nitrite: Bottle for the range 6.14 to 45.45 µmol/l was 0.21, k = 51 (2 outliers removed) where k is the number of pairs of duplicates.

The pooled standard deviation was 0.29 when using the complete set of 53 replicates.

Data has been corrected to a certified reference material provided by KANSO Co, LTD.

Duplicate samples from a single Niskin bottle

Event Number	Sample Number	Station	Pressure dbar	Nitrate 1 µmol/l	Nitrate 2 µmol/l	Rejected yes / no	Comment
2	27	Haro59	75.3	26.61	26.71		
13	53	P2	14.9	11.87	12.01		
15	62	P2	50.3	8.48	8.93		
17	77	P4	59.8	6.14	6.50		
18	91	P4	1000.3	44.48	44.00		
28	152	P8	800.0	44.46	43.93		
28	161	P8	60.5	6.24	6.43		
35	176	P12	199.7	29.03	28.66		
37	202	P12	2501.0	41.52	40.56		
37	213	P12	175.5	25.72	25.31		
46	284	P16	3001.6	39.87	39.78		
46	299	P16	100.6	11.78	11.96		
57	337	P20	4024.8	38.35	38.07		
57	357	P20	50.0	7.86	7.86		
59	369	P20	75.5	8.05	7.95		
65	444	Eddy	1749.3	44.44	43.84		
65	454	Eddy	174.6	33.94	33.73		
69	490	P35	250.2	35.34	35.47		
70	507	P26	75.4	9.75	9.76		
71	524	P26	1249.8	45.45	44.79		
71	532	P26	174.8	26.58	25.44	yes	
86	588	DIX3	200.3	29.69	29.86		
88	610	CH3	501.2	28.27	28.21		
89	631	CH2	176.0	25.45	25.39		
90	647	CH1	500.0	30.44	30.61		
90	657	CH1	19.9	18.37	18.64		
92	665	CH6	150.1	24.49	24.71		
93	681	CH5	30.1	15.88	16.56		
94	693	CH4	5.4	16.60	16.69		
95	705	CH8	5.0	15.74	15.89		
96	711	CHAT3	99.9	18.56	18.89		

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Nitrate_plus_Nitrite: Bottle (continued)

Duplicate samples from a single Niskin bottle

Event Number	Sample Number	Station	Pressure dbar	Nitrate 1 $\mu\text{mol/l}$	Nitrate 2 $\mu\text{mol/l}$	Rejected yes / no	Comment
97	728	CH10	1.7	15.65	15.92		
98	735	CH13	20.1	15.93	15.93		
99	749	CH12	4.7	17.46	17.68		
100	754	CH17	75.2	16.21	16.43		
101	766	CH16	50.1	16.12	16.12		
102	778	CH15	124.8	15.50	15.81		
103	796	CH14	5.5	15.25	15.54		
104	800	HECS8	117.2	30.02	30.29		
106	827	HECS7	5.4	14.60	14.65		
107	836	CHAT2	100.1	15.98	14.28	yes	
108	855	CH20	10.0	15.95	16.15		
109	865	CH19	5.2	16.03	16.21		
110	869	PRHR74	31.2	16.99	17.18		
111	884	CH23	10.1	17.01	17.01		
112	891	CHAT1	75.2	16.54	16.51		
113	909	CH25	75.1	16.02	16.16		
114	924	CH26	5.0	17.44	17.43		
116	930	CH27	20.2	17.99	18.22		
117	941	CH29	132.1	15.94	16.12		
118	955	MP55	20.3	17.56	17.54		
119	961	CH31	83.1	16.09	16.08		
120	971	OGCH50	100.4	16.77	16.76		

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Silicate: Bottle

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

The pooled standard deviation for Silicate: Bottle for the range 4.75 to 184.22 $\mu\text{mol/l}$ was 0.52, $k = 51$ (2 outliers removed) where k is the number of pairs of duplicates.

The pooled standard deviation was 0.72 when using the complete set of 53 replicates.

Data has been corrected to a certified reference material provided by KANSO Co, LTD.

Duplicate samples from a single Niskin bottle

Event Number	Sample Number	Station	Pressure dbar	Silicate 1 $\mu\text{mol/l}$	Silicate 2 $\mu\text{mol/l}$	Rejected yes / no	Comment
2	27	Haro59	75.3	52.91	50.97		
13	53	P2	14.9	26.84	25.67		
15	62	P2	50.3	13.09	12.95		
17	77	P4	59.8	5.97	5.75		
18	91	P4	1000.3	134.27	133.14		
28	152	P8	800.0	126.11	125.44		
28	161	P8	60.5	5.08	4.75		
35	176	P12	199.7	45.69	44.43		
37	202	P12	2501.0	181.25	181.88		
37	213	P12	175.5	36.10	34.83		
46	284	P16	3001.6	177.59	180.02	yes	
46	299	P16	100.6	12.35	12.04		
57	337	P20	4024.8	184.22	183.53		
57	357	P20	50.0	8.01	7.76		
59	369	P20	75.5	8.06	7.69		
65	444	Eddy	1749.3	172.54	172.25		
65	454	Eddy	174.6	50.44	49.22		
69	490	P35	250.2	62.86	61.98		
70	507	P26	75.4	9.64	9.66		
71	524	P26	1249.8	158.71	157.76		
71	532	P26	174.8	41.59	38.91		
86	588	DIX3	200.3	51.52	50.18		
88	610	CH3	501.2	56.30	56.13		
89	631	CH2	176.0	48.12	47.26		
90	647	CH1	500.0	62.76	62.65		
90	657	CH1	19.9	34.26	33.81		
92	665	CH6	150.1	47.48	46.52		
93	681	CH5	30.1	26.09	25.80		
94	693	CH4	5.4	28.30	27.94		
95	705	CH8	5.0	25.87	25.50		
96	711	CHAT3	99.9	32.69	32.38		

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Silicate: Bottle (continued)

Duplicate samples from a single Niskin bottle

Event Number	Sample Number	Station	Pressure dbar	Silicate 1 $\mu\text{mol/l}$	Silicate 2 $\mu\text{mol/l}$	Rejected yes / no	Comment
97	728	CH10	1.7	25.86	25.62		
98	735	CH13	20.1	26.62	26.57		
99	749	CH12	4.7	32.82	32.44		
100	754	CH17	75.2	27.30	27.05		
101	766	CH16	50.1	26.76	26.75		
102	778	CH15	124.8	25.20	25.72		
103	796	CH14	5.5	24.88	24.76		
104	800	HECS8	117.2	54.77	54.08		
106	827	HECS7	5.4	22.57	22.57		
107	836	CHAT2	100.1	26.28	21.70	yes	
108	855	CH20	10.0	26.45	26.27		
109	865	CH19	5.2	26.77	26.36		
110	869	PRHR74	31.2	30.22	29.85		
111	884	CH23	10.1	29.85	29.89		
112	891	CHAT1	75.2	28.08	27.97		
113	909	CH25	75.1	26.99	26.64		
114	924	CH26	5.0	30.01	30.03		
116	930	CH27	20.2	32.65	32.28		
117	941	CH29	132.1	28.23	28.48		
118	955	MP55	20.3	31.27	31.21		
119	961	CH31	83.1	27.58	27.60		
120	971	OGCH50	100.4	28.00	28.15		

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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.

Nitrate_plus_Nitrite: Bottle

The pooled standard deviation for Nitrate_plus_Nitrite: Bottle for the range 6.23 to 44.29 $\mu\text{mol/l}$ was 0.11, $k = 10$ (0 outlier removed) where k is the number of pairs of duplicates.

Event Number	Sample Number	Station	Nominal Pressure dbar	Nitrate 1 $\mu\text{mol/l}$	Nitrate 2 $\mu\text{mol/l}$	Rejected yes / no	Comment
2	34 / 35	Haro59	0	26.67	26.58		
12	44 / 45	P1	5	9.64	9.65		
15	60 / 61	P2	75	8.73	8.81		
17	85 / 86	P4	5	7.40	7.24		
18	89 / 90	P4	1250	44.29	43.90		
28	170 / 171	P8	5	6.23	6.24		
35	189 / 190	P12	5	7.09	7.08		
57	338 / 339	P20	3500	38.64	38.58		
65	464 / 465	Eddy	5	10.42	10.40		
89	627 / 628	CH2	303	29.91	29.73		

Phosphate: Bottle

The pooled standard deviation for Phosphate: Bottle for the range 0.830 to 3.229 $\mu\text{mol/l}$ was 0.015, $k = 10$ (0 outlier removed) where k is the number of pairs of duplicates.

Event Number	Sample Number	Station	Nominal Pressure dbar	Phosphate 1 $\mu\text{mol/l}$	Phosphate 2 $\mu\text{mol/l}$	Rejected yes / no	Comment
2	34 / 35	Haro59	0	2.231	2.221		
12	44 / 45	P1	5	1.005	1.000		
15	60 / 61	P2	75	0.945	0.952		
17	85 / 86	P4	5	0.863	0.830		
18	89 / 90	P4	1250	3.229	3.190		
28	170 / 171	P8	5	0.834	0.837		
35	189 / 190	P12	5	0.903	0.891		
57	338 / 339	P20	3500	2.691	2.702		
65	464 / 465	Eddy	5	1.091	1.085		
89	627 / 628	CH2	303	2.448	2.409		

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Silicate: Bottle

The pooled standard deviation for Silicate: Bottle for the range 5.06 to 181.33 $\mu\text{mol/l}$ was 0.15,
 $k = 12$ (0 outlier removed) where k is the number of pairs of duplicates.

Event Number	Sample Number	Station	Nominal Pressure dbar	Silicate 1 $\mu\text{mol/l}$	Silicate 2 $\mu\text{mol/l}$	Rejected yes / no	Comment
2	34 / 35	Haro59	0	53.84	53.82		
12	44 / 45	P1	5	16.20	16.24		
15	60 / 61	P2	75	13.31	13.42		
17	85 / 86	P4	5	10.78	10.59		
18	89 / 90	P4	1250	152.67	152.99		
28	170 / 171	P8	5	5.06	5.10		
35	189 / 190	P12	5	6.71	6.66		
37	200 / 201	P12	3000	181.15	181.33		
46	282 / 283	P16	3500	179.60	179.02		
57	338 / 339	P20	3500	177.83	177.97		
65	464 / 465	Eddy	5	11.76	11.68		
89	627 / 628	CH2	303	59.27	59.25		