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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  
 $\mu$  is the mean difference between duplicates  
and  $\sigma$  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 5.56 to 45.95 µmol/l was 0.27,  
k = 58 (1 outlier removed) where k is the number of pairs of duplicates.

The pooled standard deviation was 0.28 when using the complete set of 59 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
11	17	P2	25.1	13.67	13.82		
14	23	P2	40.5	20.33	20.47		
20	71	P4	50.5	5.56	5.79		
30	92	P8	1249.7	44.79	44.76		
30	104	P8	74.6	10.77	11.29		
39	137	P12	1249.8	45.95	45.10	yes	
39	145	P12	175.3	26.00	26.14		
41	164	P12	199.9	28.37	28.22		
52	227	P16	400.8	41.28	42.37		
52	232	P16	150.4	27.34	28.38		
54	260	P16	5.1	9.79	9.82		
60	306	P20	60.1	12.95	13.04		
64	327	P20	2502.0	41.28	41.46		
64	335	P20	300.3	39.14	39.43		
77	419	P26	4000.2	37.95	38.00		
79	464	P26	3.0	13.37	13.69		
94	483	DIX2	75.3	25.41	26.17		
95	496	DIX1	199.6	33.95	33.99		
96	514	CH03	250.3	30.16	30.32		
96	522	CH03	20.2	11.11	11.21		
97	531	CH02	250.1	30.07	29.99		
97	538	CH02	30.1	16.39	16.65		
98	549	Port3	50.1	23.77	24.17		
99	564	Port2	20.0	20.88	21.12		
100	570	Port1	30.1	23.72	24.10		
101	581	CH01	300.2	29.68	29.96		
101	587	CH01	50.1	19.25	19.25		
103	601	CH06	49.9	21.08	21.61		
104	610	CH05	75.5	25.44	25.96		
105	624	CH04	19.8	10.69	10.75		
106	628	CH07	84.7	27.89	28.45		
107	640	CHAT3	50.0	20.16	20.59		
108	653	CH08	75.6	26.95	27.71		

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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
110	678	CH11	30.5	17.11	17.26		
111	687	CH10	30.2	12.71	12.89		
112	700	CH13	5.2	11.08	11.18		
113	709	CH12	19.4	11.74	11.74		
114	719	CH17	20.0	13.11	13.16		
115	726	CH16	100.2	25.16	25.57		
116	743	CH15	20.3	13.42	13.53		
117	751	CH14	49.5	17.07	17.34		
118	766	HECS8	35.9	10.80	11.00		
120	777	HECS7	75.0	23.53	24.00		
121	789	CHAT2	150.1	23.74	24.48		
122	806	CH20	30.2	14.01	14.36		
123	817	CH21	30.2	10.49	10.85		
124	828	CH19	30.3	12.69	13.12		
128	836	CH18	30.1	10.68	11.01		
130	857	CH23	19.9	9.48	9.75		
131	867	CHAT1	50.2	13.78	14.36		
132	882	CH22	75.2	18.13	18.86		
133	889	CH24	87.0	19.00	18.63		
134	901	CH25	50.3	13.21	13.02		
136	920	CH27	30.6	9.50	9.40		
137	932	CH28	49.9	11.99	11.75		
138	944	CH29	19.9	8.99	8.97		
139	955	MP55	10.1	9.11	9.07		
140	966	OGCH50	10.1	13.38	13.20		
141	972	OGCH46	50.0	10.50	10.39		

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### Phosphate:Bottle

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

The pooled standard deviation for Phosphate:Bottle for the range 0.887 to 3.263  $\mu\text{mol/l}$  was 0.040,  
k = 56 (3 outliers removed) where k is the number of pairs of duplicates.

The pooled standard deviation was 0.057 when using the complete set of 59 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	Phosphate 1 $\mu\text{mol/l}$	Phosphate 2 $\mu\text{mol/l}$	Rejected yes / no	Comment
11	17	P2	25.1	1.348	1.396		
14	23	P2	40.5	1.721	1.730		
20	71	P4	50.5	0.900	0.887		
30	92	P8	1249.7	3.252	3.263		
30	104	P8	74.6	1.102	1.072		
39	137	P12	1249.8	3.156	3.095		
39	145	P12	175.3	2.061	1.795	yes	
41	164	P12	199.9	2.159	1.895	yes	
52	227	P16	400.8	2.882	2.887		
52	232	P16	150.4	2.134	2.039		
54	260	P16	5.1	1.305	1.041	yes	
60	306	P20	60.1	1.474	1.253		
64	327	P20	2502.0	2.805	2.725		
64	335	P20	300.3	2.765	2.726		
77	419	P26	4000.2	2.610	2.624		
79	464	P26	3.0	1.270	1.240		
94	483	DIX2	75.3	2.004	1.984		
95	496	DIX1	199.6	2.512	2.371		
96	514	CH03	250.3	2.254	2.211		
96	522	CH03	20.2	1.195	1.255		
97	531	CH02	250.1	2.276	2.185		
97	538	CH02	30.1	1.474	1.507		
98	549	Port3	50.1	1.965	1.961		
99	564	Port2	20.0	1.698	1.734		
100	570	Port1	30.1	1.973	1.959		
101	581	CH01	300.2	2.320	2.202		
101	587	CH01	50.1	1.710	1.719		
103	601	CH06	49.9	1.830	1.833		
104	610	CH05	75.5	2.050	2.104		
105	624	CH04	19.8	1.222	1.207		
106	628	CH07	84.7	2.205	2.165		
107	640	CHAT3	50.0	1.736	1.759		
108	653	CH08	75.6	2.148	2.129		

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### Phosphate:Bottle (continued)

#### Duplicate samples from a single Niskin bottle

Event Number	Sample Number	Station	Pressure dbar	Phosphate 1 $\mu\text{mol/l}$	Phosphate 2 $\mu\text{mol/l}$	Rejected yes / no	Comment
110	678	CH11	30.5	1.545	1.583		
111	687	CH10	30.2	1.295	1.360		
112	700	CH13	5.2	1.070	1.059		
113	709	CH12	19.4	1.218	1.255		
114	719	CH17	20.0	1.308	1.299		
115	726	CH16	100.2	1.965	2.075		
116	743	CH15	20.3	1.363	1.336		
117	751	CH14	49.5	1.598	1.610		
118	766	HECS8	35.9	1.257	1.262		
120	777	HECS7	75.0	2.034	2.009		
121	789	CHAT2	150.1	2.004	2.010		
122	806	CH20	30.2	1.474	1.414		
123	817	CH21	30.2	1.256	1.238		
124	828	CH19	30.3	1.390	1.363		
128	836	CH18	30.1	1.260	1.253		
130	857	CH23	19.9	1.192	1.150		
131	867	CHAT1	50.2	1.483	1.481		
132	882	CH22	75.2	1.745	1.722		
133	889	CH24	87.0	1.788	1.731		
134	901	CH25	50.3	1.382	1.348		
136	920	CH27	30.6	1.159	1.132		
137	932	CH28	49.9	1.292	1.271		
138	944	CH29	19.9	1.117	1.226		
139	955	MP55	10.1	1.133	1.113		
140	966	OGCH50	10.1	1.298	1.271		
141	972	OGCH46	50.0	1.154	1.188		

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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 8.26 to 177.05  $\mu\text{mol/l}$  was 0.18,  
k = 58 (1 outlier removed) where k is the number of pairs of duplicates.

The pooled standard deviation was 0.27 when using the complete set of 59 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
11	17	P2	25.1	17.19	17.25		
14	23	P2	40.5	26.10	26.08		
20	71	P4	50.5	8.26	8.34		
30	92	P8	1249.7	154.23	153.39		
30	104	P8	74.6	11.02	11.21		
39	137	P12	1249.8	152.25	152.36		
39	145	P12	175.3	37.13	37.27		
41	164	P12	199.9	43.24	43.58		
52	227	P16	400.8	91.58	89.37	yes	
52	232	P16	150.4	39.21	39.21		
54	260	P16	5.1	9.56	10.05		
60	306	P20	60.1	15.52	15.48		
64	327	P20	2502.0	177.05	177.03		
64	335	P20	300.3	69.88	69.73		
77	419	P26	4000.2	172.25	172.02		
79	464	P26	3.0	21.12	20.87		
94	483	DIX2	75.3	42.06	42.86		
95	496	DIX1	199.6	61.53	61.90		
96	514	CH03	250.3	53.96	54.22		
96	522	CH03	20.2	16.44	16.67		
97	531	CH02	250.1	53.95	53.88		
97	538	CH02	30.1	26.15	26.20		
98	549	Port3	50.1	41.25	41.64		
99	564	Port2	20.0	36.61	36.60		
100	570	Port1	30.1	41.58	41.70		
101	581	CH01	300.2	54.11	53.67		
101	587	CH01	50.1	31.93	31.97		
103	601	CH06	49.9	35.59	35.89		
104	610	CH05	75.5	44.74	44.59		
105	624	CH04	19.8	15.42	15.42		
106	628	CH07	84.7	50.12	50.25		
107	640	CHAT3	50.0	33.10	33.11		
108	653	CH08	75.6	49.20	48.77		

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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
110	678	CH11	30.5	27.71	27.46		
111	687	CH10	30.2	18.71	18.60		
112	700	CH13	5.2	20.50	20.33		
113	709	CH12	19.4	17.05	16.95		
114	719	CH17	20.0	19.18	19.25		
115	726	CH16	100.2	45.04	45.17		
116	743	CH15	20.3	20.66	20.61		
117	751	CH14	49.5	28.43	28.38		
118	766	HECS8	35.9	17.33	17.36		
120	777	HECS7	75.0	41.99	41.90		
121	789	CHAT2	150.1	43.14	43.48		
122	806	CH20	30.2	22.55	22.63		
123	817	CH21	30.2	15.66	15.93		
124	828	CH19	30.3	19.18	19.53		
128	836	CH18	30.1	16.39	16.40		
130	857	CH23	19.9	14.05	14.06		
131	867	CHAT1	50.2	22.76	22.94		
132	882	CH22	75.2	32.13	32.52		
133	889	CH24	87.0	33.92	34.02		
134	901	CH25	50.3	20.12	20.15		
136	920	CH27	30.6	12.73	12.90		
137	932	CH28	49.9	17.54	17.80		
138	944	CH29	19.9	12.40	12.60		
139	955	MP55	10.1	13.78	13.55		
140	966	OGCH50	10.1	22.74	22.57		
141	972	OGCH46	50.0	15.04	14.80		

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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 0.00 to 44.44  $\mu\text{mol/l}$  was 0.09,  $k = 11$  (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
11	14 / 15	P2	75	28.09	28.05		
14	29 / 30	P2	5	0.36	0.35		
19	53 / 54	P4	5	0.00	0.00		
20	57 / 58	P4	1250	44.12	44.44		
39	132 / 133	P12	3000	41.00	41.17		
41	176 / 177	P12	5	5.35	5.44		
52	218 / 219	P16	3000	39.76	39.69		
54	259 / 260	P16	5	9.70	9.80		
60	314 / 315	P20	5	11.10	11.08		
64	325 / 326	P20	3000	39.78	39.75		
79	462 / 463	P26	5	13.49	13.67		

### Phosphate: Bottle

The pooled standard deviation for Phosphate: Bottle for the range 0.320 to 3.332  $\mu\text{mol/l}$  was 0.039,  $k = 11$  (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
11	14 / 15	P2	75	2.061	2.052		
14	29 / 30	P2	5	0.320	0.390		
19	53 / 54	P4	5	0.410	0.438		
20	57 / 58	P4	1250	3.329	3.332		
39	132 / 133	P12	3000	2.882	2.867		
41	176 / 177	P12	5	1.170	1.214		
52	218 / 219	P16	3000	2.782	2.782		
54	259 / 260	P16	5	1.308	1.173		
60	314 / 315	P20	5	1.397	1.381		
64	325 / 326	P20	3000	2.667	2.750		
79	462 / 463	P26	5	1.274	1.283		



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### Silicate: Bottle

The pooled standard deviation for Silicate: Bottle for the range 2.65 to 179.95  $\mu\text{mol/l}$  was 0.06,  
k = 11 (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
11	14 / 15	P2	75	37.86	38.02		
14	29 / 30	P2	5	2.67	2.65		
19	53 / 54	P4	5	6.06	6.03		
20	57 / 58	P4	1250	146.64	146.64		
39	132 / 133	P12	3000	179.95	179.80		
41	176 / 177	P12	5	4.35	4.41		
52	218 / 219	P16	3000	178.76	178.73		
54	259 / 260	P16	5	9.70	9.80		
60	314 / 315	P20	5	12.86	12.85		
64	325 / 326	P20	3000	175.97	176.03		
79	462 / 463	P26	5	20.85	20.93		