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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:

$$Z-score \geq Zcritical$$

For precision, calculate pooled standard deviation (Sp) 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 measurments 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 1.1 to 47.7 µmol/l was 0.1,
k = 21 (0 outlier removed) where k is the number of pairs of duplicates.

Accuracy of the stock standard batch for nitrate_plus_nitrite was determined by comparing to commercially available standards from WAKO Chemicals (Sagami Chemical Company of Japan) during analysis of the samples.
The values were within 0.63 % of the 20 µmol/l Nitrate Standard.

04 April 2014 Nitrate stock standard solution was used for this cruise analyses.

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
1	7	Haro 59	80.1	28.0	27.9		
5	44	JF2	50.6	30.1	30.2		
10	76	P2	108.9	36.8	36.8		
12	95	P2	25.3	1.5	1.5		
18	164	P4	124.6	29.8	29.8		
18	157	P4	600.1	45.0	44.9		
20	192	P4	10.2	1.3	1.1		
26	264	P8	150.1	31.4	31.3		
26	255	P8	1250.4	47.0	47.0		
31	305	P12	100.1	19.3	19.3		
31	291	P12	2500	43.7	43.4		
38	377	P12	50.7	6.7	6.7		
43	410	P16	300	39.2	39.5		
45	448	P16	50.4	7.3	7.3		
45	435	P16	1250.4	47.7	47.4		
53	496	P20	150	27.5	27.6		
53	490	P20	600	45.4	45.6		
56	508	P20	75.4	7.2	7.3		
74	634	P26	75	11.9	11.9		
72	615	P26	175.5	33.8	33.7		
72	609	P26	800.6	45.8	46.1		

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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 0.506 to 3.274 µmol/l was 0.010,
k = 20 (1 outlier removed) where k is the number of pairs of duplicates.

The pooled standard deviation was 0.014 when using the complete set of 21 replicates.

Accuracy of the stock standard batch for phosphate was determined by comparing an extra high standard (4 µmol/l) to the previously prepared batch.
14 May 2014 Phosphate stock standard solution (16 May 2014 secondary) was used for this cruise analyses.
The Phosphate values were within 1.47% of the previous (secondary) stock solution.

Duplicate samples from a single Niskin bottle

Event Number	Sample Number	Station	Pressure dbar	Phosphate 1 µmol/l	Phosphate 2 µmol/l	Rejected yes / no	Comment
1	7	Haro 59	80.1	2.131	2.128		
5	44	JF2	50.6	2.211	2.216		
10	76	P2	108.9	2.666	2.598	yes	
12	95	P2	25.3	0.511	0.529		
18	164	P4	124.6	2.141	2.144		
18	157	P4	600.1	3.163	3.152		
20	192	P4	10.2	0.506	0.507		
26	264	P8	150.1	2.265	2.258		
26	255	P8	1250.4	3.274	3.254		
31	305	P12	100.1	1.538	1.538		
31	291	P12	2500	2.946	2.898		
38	377	P12	50.7	0.896	0.894		
43	410	P16	300	2.681	2.689		
45	448	P16	50.4	0.867	0.869		
45	435	P16	1250.4	3.234	3.252		
53	496	P20	150	1.931	1.925		
53	490	P20	600	3.103	3.103		
56	508	P20	75.4	0.871	0.872		
74	634	P26	75	1.172	1.165		
72	615	P26	175.5	2.364	2.369		
72	609	P26	800.6	3.194	3.196		

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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 3.31 to 177.25 µmol/l was 0.08,
k = 20 (1 outlier removed) where k is the number of pairs of duplicates.

The pooled standard deviation was 0.10 when using the complete set of 21 replicates.

Accuracy of the stock standard batch for silicate was determined by comparing to commercially available standards from WAKO Chemicals (Sagami Chemical Company of Japan) during analysis of the samples.
The values were within 1.20 % of the 100 µmol/l Silicate Standard.
10 April 2014 Silicate stock standard solution was used for this cruise analyses.

Duplicate samples from a single Niskin bottle

Event Number	Sample Number	Station	Pressure dbar	Silicate 1 µmol/l	Silicate 2 µmol/l	Rejected yes / no	Comment
1	7	Haro 59	80.1	43.20	43.15		
5	44	JF2	50.6	42.76	42.74		
10	76	P2	108.9	59.06	59.01		
12	95	P2	25.3	3.31	3.33		
18	164	P4	124.6	36.66	36.63		
18	157	P4	600.1	93.78	93.66		
20	192	P4	10.2	6.97	6.84		
26	264	P8	150.1	40.17	40.13		
26	255	P8	1250.4	148.49	148.22		
31	305	P12	100.1	23.59	23.67		
31	291	P12	2500	176.88	177.25	yes	
38	377	P12	50.7	10.95	10.94		
43	410	P16	300	73.55	73.42		
45	448	P16	50.4	9.62	9.62		
45	435	P16	1250.4	154.69	154.73		
53	496	P20	150	41.59	41.57		
53	490	P20	600	110.16	109.99		
56	508	P20	75.4	8.36	8.37		
74	634	P26	75	15.52	15.52		
72	615	P26	175.5	58.28	58.27		
72	609	P26	800.6	133.21	132.89		

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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 29.25 to 46.72 µmol/l was 0.04,
k = 5 (0 outlier removed) where k is the number of pairs of duplicates.

Event Number	Sample Number	Station	Nominal Pressure dbar	Nitrate 1 µmol/l	Nitrate 2 µmol/l	Rejected yes / no	Comment
12	92 / 93	P2	75	29.30	29.25		
18	153 / 154	P4	1250	46.72	46.67		
31	289 / 290	P12	3000	42.48	42.45		
45	429 / 430	P16	3500	41.05	41.08		
53	481 / 482	P20	3500	40.69	40.60		

Phosphate:Bottle

The pooled standard deviation for Phosphate:Bottle for the range 2.106 to 3.283 µmol/l was 0.016,
k = 5 (0 outlier removed) where k is the number of pairs of duplicates.

Event Number	Sample Number	Station	Nominal Pressure dbar	Phosphate 1 µmol/l	Phosphate 2 µmol/l	Rejected yes / no	Comment
12	92 / 93	P2	75	2.106	2.110		
18	153 / 154	P4	1250	3.283	3.283		
31	289 / 290	P12	3000	2.855	2.827		
45	429 / 430	P16	3500	2.762	2.737		
53	481 / 482	P20	3500	2.730	2.697		

Silicate:Bottle

The pooled standard deviation for Silicate:Bottle for the range 39.11 to 176.93 µmol/l was 0.23,
k = 5 (0 outlier removed) where k is the number of pairs of duplicates.

Event Number	Sample Number	Station	Nominal Pressure dbar	Silicate 1 µmol/l	Silicate 2 µmol/l	Rejected yes / no	Comment
12	92 / 93	P2	75	39.11	39.32		
18	153 / 154	P4	1250	143.78	143.15		
31	289 / 290	P12	3000	176.81	176.93		
45	429 / 430	P16	3500	176.29	176.26		
53	481 / 482	P20	3500	171.95	172.19		