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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 0.00 to 46.09  $\mu\text{mol/l}$  was 0.03,  $k = 18$  (1 outlier removed) where  $k$  is the number of pairs of duplicates.

The pooled standard deviation was 0.04 when using the complete set of 19 replicates.

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 0.4 % of the 20  $\mu\text{mol/l}$  Nitrate Standard.

2 June 2015 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 $\mu\text{mol/l}$	Nitrate 2 $\mu\text{mol/l}$	Rejected yes / no	Comment
18	26	P2	100.6	33.79	33.88		
21	45	P2	25.1	19.67	19.68		
31	190	P4	9.8	1.64	1.68		
28	125	P4	125.3	21.88	21.89		
28	118	P4	600.2	44.14	44.16		
39	219	P8	149.9	20.41	20.42		
39	210	P8	1250.2	46.09	45.95	yes	
47	339	P12	99.7	14.39	14.38		
47	328	P12	1250.6	45.85	45.89		
53	384	P12	10.3	-0.06	-0.06		
70	567	P16	124.9	17.74	17.75		
70	551	P16	3500.0	39.71	39.65		
61	476	P16	10.7	-0.04	-0.04		
79	662	P20	51.4	7.04	7.05		
79	653	P20	399.9	41.42	41.33		
82	680	P20	9.7	2.44	2.43		
102	880	P26	75.2	14.09	14.12		
99	824	P26	177.1	34.00	34.03		
99	811	P26	3500.8	39.21	39.16		

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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 0.313 to 3.245  $\mu\text{mol/l}$  was 0.008,  
k = 18 (1 outlier removed) where k is the number of pairs of duplicates.

The pooled standard deviation was 0.063 when using the complete set of 19 replicates.

Accuracy of the stock standard batch for phosphate was determined by comparing an extra high standard (4  $\mu\text{mol/l}$ ) to the previously prepared batch.

2 June 2015 Phosphate stock standard solution (2 June 2015 secondary) was used for this cruise analyses.

The Phosphate values were within 0.22% of the previous (secondary) stock solution.

#### 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
18	26	P2	100.6	2.673	2.692		
21	45	P2	25.1	1.775	1.755		
31	190	P4	9.8	0.484	0.493		
28	125	P4	125.3	1.612	1.613		
28	118	P4	600.2	3.113	3.115		
39	219	P8	149.9	1.551	1.514		
39	210	P8	1250.2	3.245	3.245		
47	339	P12	99.7	1.238	1.239		
47	328	P12	1250.6	3.229	3.230		
53	384	P12	10.3	0.314	0.313		
70	567	P16	124.9	1.403	1.404		
70	551	P16	3500.0	2.727	2.733		
61	476	P16	10.7	0.317	0.317		
79	662	P20	51.4	0.886	0.881		
79	653	P20	399.9	2.893	2.897		
82	680	P20	9.7	0.923	0.540	yes	
102	880	P26	75.2	1.339	1.346		
99	824	P26	177.1	2.412	2.427		
99	811	P26	3500.8	2.685	2.684		

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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 0.40 to 178.24  $\mu\text{mol/l}$  was 0.04,  
k = 18 (1 outlier removed) where k is the number of pairs of duplicates.

The pooled standard deviation was 0.05 when using the complete set of 19 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 1.2 % of the 100  $\mu\text{mol/l}$  Silicate Standard.

3 June 2015 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 $\mu\text{mol/l}$	Silicate 2 $\mu\text{mol/l}$	Rejected yes / no	Comment
18	26	P2	100.6	63.55	63.54		
21	45	P2	25.1	27.13	27.10		
31	190	P4	9.8	4.09	4.08		
28	125	P4	125.3	25.93	25.93		
28	118	P4	600.2	97.01	97.20	yes	
39	219	P8	149.9	23.80	23.79		
39	210	P8	1250.2	150.71	150.56		
47	339	P12	99.7	15.77	15.76		
47	328	P12	1250.6	152.92	152.94		
53	384	P12	10.3	1.58	1.60		
70	567	P16	124.9	20.10	20.05		
70	551	P16	3500.0	178.24	178.19		
61	476	P16	10.7	0.42	0.40		
79	662	P20	51.4	8.97	8.95		
79	653	P20	399.9	89.00	89.00		
82	680	P20	9.7	7.37	7.34		
102	880	P26	75.2	21.32	21.33		
99	824	P26	177.1	60.48	60.52		
99	811	P26	3500.8	171.74	171.62		

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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 29.79 to 45.90  $\mu\text{mol/l}$  was 0.05,  $k = 5$  (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
21	42 / 43	P2	75	29.79	29.84		
28	114 / 115	P4	1250	45.81	45.90		
47	323 / 324	P12	3000	40.94	41.02		
70	551 / 552	P16	3500	39.68	39.73		
79	643 / 644	P20	3500	39.33	39.27		

### Phosphate: Bottle

The pooled standard deviation for Phosphate: Bottle for the range 2.309 to 3.249  $\mu\text{mol/l}$  was 0.004,  $k = 5$  (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
21	42 / 43	P2	75	2.309	2.313		
28	114 / 115	P4	1250	3.249	3.249		
47	323 / 324	P12	3000	2.819	2.820		
70	551 / 552	P16	3500	2.730	2.743		
79	643 / 644	P20	3500	2.705	2.708		

### Silicate: Bottle

The pooled standard deviation for Silicate: Bottle for the range 46.72 to 178.62  $\mu\text{mol/l}$  was 0.22,  $k = 5$  (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
21	42 / 43	P2	75	46.72	46.90		
28	114 / 115	P4	1250	149.36	148.71		
47	323 / 324	P12	3000	178.52	178.62		
70	551 / 552	P16	3500	178.22	178.20		
79	643 / 644	P20	3500	175.38	175.32		