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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 2.88 to 46.99 $\mu\text{mol/l}$ was 0.07, $k = 20$ (1 outlier removed) where k is the number of pairs of duplicates.

The pooled standard deviation was 0.09 when using the complete set of 21 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 0.52 % of the 20 $\mu\text{mol/l}$ Nitrate Standard.

16 January 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 |
|--------------|---------------|---------|---------------|-----------------------------|-----------------------------|-------------------|---------|
| 3 | 7 | HARO59 | 81.4 | 26.60 | 26.53 | | |
| 5 | 31 | JF2 | 51.4 | 25.68 | 25.69 | | |
| 15 | 76 | P2 | 102.2 | 19.17 | 19.13 | | |
| 16 | 101 | P2 | 25.7 | 3.92 | 3.98 | | |
| 30 | 297 | P8 | 152.3 | 24.86 | 24.81 | | |
| 30 | 288 | P8 | 1252.9 | 46.62 | 46.78 | | |
| 40 | 360 | P12 | 102.5 | 17.04 | 17.39 | yes | |
| 40 | 347 | P12 | 2002.3 | 45.12 | 45.14 | | |
| 41 | 381 | P12 | 11.0 | 3.95 | 3.95 | | |
| 53 | 481 | P16 | 11.5 | 5.58 | 5.52 | | |
| 54 | 504 | P16 | 50.4 | 5.61 | 5.63 | | |
| 54 | 491 | P16 | 1252.2 | 46.99 | 46.81 | | |
| 67 | 591 | P20 | 51.8 | 5.77 | 5.78 | | |
| 67 | 578 | P20 | 1251.4 | 46.92 | 46.99 | | |
| 70 | 613 | P20 | 10.8 | 5.56 | 5.59 | | |
| 93 | 783 | P26 | 176.0 | 36.24 | 36.36 | | |
| 93 | 777 | P26 | 802.6 | 45.66 | 45.95 | | |
| 91 | 755 | P26 | 201.1 | 39.27 | 39.28 | | |
| 119 | 274 | P4 | 11.5 | 2.93 | 2.88 | | |
| 121 | 255 | P4 | 127.4 | 26.04 | 26.07 | | |
| 121 | 248 | P4 | 600.7 | 43.82 | 43.92 | | |

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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 0.572 to 3.250 $\mu\text{mol/l}$ was 0.004, $k = 20$ (1 outlier removed) where k is the number of pairs of duplicates.

The pooled standard deviation was 0.010 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 $\mu\text{mol/l}$) to the previously prepared batch.

16 January 2015 Phosphate stock standard solution (21 January 2015 secondary) was used for this cruise analyses. The Phosphate values were within 0.36% 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 |
|--------------|---------------|---------|---------------|-------------------------------|-------------------------------|-------------------|---------|
| 3 | 7 | HARO59 | 81.4 | 2.144 | 2.155 | | |
| 5 | 31 | JF2 | 51.4 | 2.061 | 2.060 | | |
| 15 | 76 | P2 | 102.2 | 1.588 | 1.589 | | |
| 16 | 101 | P2 | 25.7 | 0.633 | 0.636 | | |
| 30 | 297 | P8 | 152.3 | 1.814 | 1.829 | | |
| 30 | 288 | P8 | 1252.9 | 3.244 | 3.250 | | |
| 40 | 360 | P12 | 102.5 | 1.418 | 1.420 | | |
| 40 | 347 | P12 | 2002.3 | 3.036 | 3.035 | | |
| 41 | 381 | P12 | 11.0 | 0.657 | 0.655 | | |
| 53 | 481 | P16 | 11.5 | 0.739 | 0.740 | | |
| 54 | 504 | P16 | 50.4 | 0.743 | 0.739 | | |
| 54 | 491 | P16 | 1252.2 | 3.233 | 3.232 | | |
| 67 | 591 | P20 | 51.8 | 0.734 | 0.736 | | |
| 67 | 578 | P20 | 1251.4 | 3.225 | 3.227 | | |
| 70 | 613 | P20 | 10.8 | 0.718 | 0.720 | | |
| 93 | 783 | P26 | 176.0 | 2.470 | 2.530 | yes | |
| 93 | 777 | P26 | 802.6 | 3.144 | 3.143 | | |
| 91 | 755 | P26 | 201.1 | 2.724 | 2.725 | | |
| 119 | 274 | P4 | 11.5 | 0.572 | 0.577 | | |
| 121 | 255 | P4 | 127.4 | 1.987 | 1.981 | | |
| 121 | 248 | P4 | 600.7 | 3.081 | 3.067 | | |

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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 5.87 to 168.76 $\mu\text{mol/l}$ was 0.09,
k = 19 (2 outliers 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 1.00 % of the 100 $\mu\text{mol/l}$ Silicate Standard.

19 January 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 |
|--------------|---------------|---------|---------------|------------------------------|------------------------------|-------------------|---------|
| 3 | 7 | HARO59 | 81.4 | 47.13 | 47.00 | | |
| 5 | 31 | JF2 | 51.4 | 42.14 | 42.23 | | |
| 15 | 76 | P2 | 102.2 | 24.55 | 24.55 | | |
| 16 | 101 | P2 | 25.7 | 5.99 | 6.01 | | |
| 30 | 297 | P8 | 152.3 | 32.17 | 32.24 | | |
| 30 | 288 | P8 | 1252.9 | 150.02 | 149.01 | yes | |
| 40 | 360 | P12 | 102.5 | 18.93 | 18.95 | | |
| 40 | 347 | P12 | 2002.3 | 167.12 | 168.76 | yes | |
| 41 | 381 | P12 | 11.0 | 5.88 | 5.87 | | |
| 53 | 481 | P16 | 11.5 | 6.97 | 6.94 | | |
| 54 | 504 | P16 | 50.4 | 6.89 | 6.90 | | |
| 54 | 491 | P16 | 1252.2 | 151.72 | 151.70 | | |
| 67 | 591 | P20 | 51.8 | 6.14 | 6.15 | | |
| 67 | 578 | P20 | 1251.4 | 154.06 | 154.07 | | |
| 70 | 613 | P20 | 10.8 | 6.11 | 6.09 | | |
| 93 | 783 | P26 | 176.0 | 65.96 | 66.23 | | |
| 93 | 777 | P26 | 802.6 | 135.54 | 135.17 | | |
| 91 | 755 | P26 | 201.1 | 74.66 | 74.72 | | |
| 119 | 274 | P4 | 11.5 | 5.94 | 5.90 | | |
| 121 | 255 | P4 | 127.4 | 32.26 | 32.22 | | |
| 121 | 248 | P4 | 600.7 | 95.42 | 95.63 | | |

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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 8.60 to 46.30 $\mu\text{mol/l}$ was 0.15, $k = 5$ (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 |
|--------------|---------------|---------|-----------------------|-----------------------------|-----------------------------|-------------------|---------|
| 16 | 98 / 99 | P2 | 75 | 8.62 | 8.60 | | |
| 40 | 344 / 345 | P12 | 3000 | 41.74 | 42.07 | | |
| 54 | 485 / 486 | P16 | 3500 | 40.02 | 40.09 | | |
| 67 | 572 / 573 | P20 | 3500 | 39.80 | 40.09 | | |
| 121 | 244 / 245 | P4 | 1250 | 46.17 | 46.30 | | |

Phosphate: Bottle

The pooled standard deviation for Phosphate: Bottle for the range 0.970 to 3.262 $\mu\text{mol/l}$ was 0.008, $k = 5$ (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 |
|--------------|---------------|---------|-----------------------|-------------------------------|-------------------------------|-------------------|---------|
| 16 | 98 / 99 | P2 | 75 | 0.972 | 0.970 | | |
| 40 | 344 / 345 | P12 | 3000 | 2.839 | 2.823 | | |
| 54 | 485 / 486 | P16 | 3500 | 2.723 | 2.722 | | |
| 67 | 572 / 573 | P20 | 3500 | 2.696 | 2.676 | | |
| 121 | 244 / 245 | P4 | 1250 | 3.260 | 3.262 | | |

Silicate: Bottle

The pooled standard deviation for Silicate: Bottle for the range 10.85 to 175.14 $\mu\text{mol/l}$ was 0.39, $k = 5$ (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 |
|--------------|---------------|---------|-----------------------|------------------------------|------------------------------|-------------------|---------|
| 16 | 98 / 99 | P2 | 75 | 10.89 | 10.85 | | |
| 40 | 344 / 345 | P12 | 3000 | 172.36 | 172.66 | | |
| 54 | 485 / 486 | P16 | 3500 | 174.88 | 175.14 | | |
| 67 | 572 / 573 | P20 | 3500 | 170.58 | 171.74 | | |
| 121 | 244 / 245 | P4 | 1250 | 146.85 | 146.64 | | |