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### Precision analysis and the determination of outliers

Precision was determined by analyzing replicate samples drawn from one Niskin.

Outliers are discarded on the basis of Chauvenet's criteria. The statistic is calculated by finding the Chauvenet critical value (Z-critical) for the total degrees of freedom ( $v$ ) of the dataset:

$$Z\text{-critical} = \text{ABS}(\text{NORM.S.INV}(1/(4*v)))$$

The maximum deviation,  $D_{max}$ , is compared with the individual residuals from the original concentrations.

If a replicate's residual is greater than  $D_{max}$  this value can be rejected.  $D_{max}$  is determined by the following formula:

$$D_{max} = Z\text{-critical} * \sigma$$

where  $\sigma$  is the standard deviation of residuals

Precision is assessed by calculating the pooled standard deviation ( $S_p$ ).

Pooled standard deviation is calculated for a combination of duplicates and triplicates using the following formula:

$$s_p = \sqrt{\frac{SS_1 + SS_2 + \dots + SS_k}{v_1 + v_2 + \dots + v_k}}$$

where:  $v$  = total degrees of freedom (1 for duplicates, 2 for triplicates).

$SS$  = sum of squares of the residuals.

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

Salinity: Bottle ranged from 34.3520 to 34.6773 with a pooled standard deviation of 0.0017 from 20 replicates - after the removal of 1 outlier sample using the Chauvenet criteria.

The pooled standard deviation was 0.0021 when using the complete set of 21 replicates.

### Duplicate samples from a single Niskin bottle

Event Number	Sample Number	Station	Pressure dbar	Salinity 1	Salinity 2	Rejected yes / no	Comment
18	27	P4	1251.5	34.4551	34.4558		
18	28	P4	1000.4	34.3900	34.3872		
32	110	P20	2999.6	34.6625	34.6599		
32	112	P20	1999.2	34.5908	34.5899		
32	114	P20	1251.1	34.4494	34.4497		
50	291	P26	3501.2	34.6689	34.6773	yes	Replicate outliers
50	293	P26	2502.3	34.6277	34.6293		
50	295	P26	1501.2	34.4947	34.4939		
50	297	P26	1003.2	34.3675	34.3709		
68	355	P16	3501.9	34.6679	34.6690		
68	357	P16	3001.3	34.6563	34.6585		
68	359	P16	1998.9	34.5931	34.5919		
68	361	P16	1250.6	34.4448	34.4511		
68	362	P16	1002.1	34.3806	34.3782		
77	446	P12	2998.1	34.6488	34.6481		
77	448	P12	2500.7	34.6361	34.6349		
77	450	P12	1500.1	34.5171	34.5191		
77	452	P12	1000.8	34.3555	34.3520		
90	534	P8	2001.1	34.6057	34.6022		
90	537	P8	1001.7	34.3807	34.3816		
99	562	P4	1249.7	34.4679	34.4687		

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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 duplicate 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.

Salinity: Bottle ranged from 34.4555 to 34.6762 with a pooled standard deviation of 0.0010 from 3 replicates after the removal of 1 outlier sample using the Chauvenet criteria. The pooled standard deviation was 0.0019 when using the complete set of 4 replicates.

Event Number	Sample Number	Station	Nominal Pressure dbar	Salinity 1	Salinity 2	Rejected yes / no	Comment
18	26 / 27	P4	1250	34.4579	34.4555		
32	108 / 109	P20	3500	34.6762	34.6713	yes	Replicate outliers
68	355 / 356	P16	3500	34.6684	34.6686		
77	446 / 447	P12	3000	34.6484	34.6478		