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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 σ 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 34.3580 to 34.6790 with a pooled standard deviation of 0.0010 from 13 replicates - after the removal of 2 outlier samples using the Chauvenet criteria.

The pooled standard deviation was 0.0025 when using the complete set of 15 replicates.

Duplicate samples from a single Niskin bottle

Event Number	Sample Number	Station	Pressure dbar	Salinity 1	Salinity 2	Rejected yes / no	Comment
121	245	P4	1251.0	34.4612	34.4613		
121	246	P4	1001.1	34.3741	34.3757		
30	286	P8	2001.8	34.5786	34.5689	yes	
30	289	P8	1004.2	34.3845	34.3765	yes	
40	344	P12	3003.4	34.6468	34.6440		
40	346	P12	2501.8	34.6249	34.6221		
40	350	P12	1002.1	34.3605	34.3610		
54	487	P16	3001.4	34.6495	34.6505		
54	489	P16	2001.6	34.5821	34.5832		
54	491	P16	1252.2	34.4295	34.4305		
67	574	P20	3002.3	34.6530	34.6536		
67	576	P20	2000.4	34.5796	34.5799		
67	579	P20	1001.3	34.3580	34.3588		
93	769	P26	4000.5	34.6790	34.6775		
93	773	P26	2002.2	34.5794	34.5794		