

2021-006 Salinity duplicates - page 1

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.

2021-006 Salinity duplicates - page 2

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

Salinity: Bottle ranged from 34.2714 to 34.6856 with a pooled standard deviation of 0.0021 from 14 replicates - after the removal of 0 outlier sample using the Chauvenet criteria.

Duplicate samples from a single Niskin bottle

Event Number	Sample Number	Station	Pressure dbar	Salinity 1	Salinity 2	Rejected yes / no	Comment
20	59	P4	999.8	34.3844	34.3857		
30	90	P8	2000.8	34.5901	34.5872		
30	94	P8	799.8	34.2749	34.2714		
39	135	P12	1999.4	34.5879	34.5906		
45	181	P14	2001.2	34.5849	34.5875		
52	220	P16	2501.9	34.6270	34.6278		
52	223	P16	1250.1	34.4450	34.4478		
56	265	P18	2000.5	34.5841	34.5903		
64	324	P20	3500.3	34.6700	34.6703		
64	327	P20	2502.0	34.6291	34.6284		
67	350	P22	2000.2	34.5924	34.5872		
71	376	P24	1999.8	34.5844	34.5847		
77	419	P26	4000.2	34.6820	34.6856		
77	422	P26	2500.2	34.6221	34.6207		

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 34.4580 to 34.6570 with a pooled standard deviation of 0.0010 from 4 replicates after the removal of 0 outlier sample using the Chauvenet criteria.

Event Number	Sample Number	Station	Nominal Pressure dbar	Salinity 1	Salinity 2	Rejected yes / no	Comment
20	57 / 58	P4	1250	34.4582	34.4580		
39	132 / 133	P12	3000	34.6449	34.6458		
52	218 / 219	P16	3000	34.6559	34.6533		
64	325 / 326	P20	3000	34.6570	34.6570		