Manual for Marine Monitoring in the

COMBINE

Programme of HELCOM

Part B

General guidelines on quality assurance for monitoring in the Baltic Sea

Annex B-2

Validation of established analytical methods

ANNEX B-2. VALIDATION OF ESTABLISHED ANALYTICAL METHODS

By means of the experimental design described in this Annex, data are obtained for calculation of the following:

- Range.
- Linearity of calibration on the day when N2 and N6 are analysed.
- Sensitivity.
- Verification of the precision at the limit of detection.
- Accuracy of synthetic samples at two concentration levels (N2 and N5) and of a spiked sample (N4 minus N3).
- Repeatability at four levels for synthetic and natural samples.
- Standard deviation between series for synthetic and natural samples at four concentration levels.

Start by performing six replicate measurements of a blank sample (or a sample with a concentration close to the expected detection limit), and calculate the detection limit (see Section 4.2.3, in body of report). Wherever possible, use natural samples with a known concentration. As these are rarely available, the experimental design could be as follows:

Concentration level	N1	N2	N3	N4	N5	N6
Measurements in each analytical series	2	2	2	2	2	2
Number of analytical series	6	1	6	6	6	1

Level N1: A synthetic sample, or if possible a natural sample with a concentration near the detection limit.
Level N2: A synthetic sample with concentration between N1 and N3.
Level N3: A natural sample with a concentration in the middle of the concentration range.
Level N4: The natural sample N3 with addition of property/variable (a spiked sample).
Level N5: A synthetic sample with a concentration at the upper level of the range.
Level N6: A synthetic sample with a concentration approximately 20 % higher than N5.

In at least one of the analytical series, a calibration is performed with replicate measurements at all six concentration levels.

If the natural samples are not reference materials and for this reason the true concentrations are unknown, synthetic samples with approximately the same concentrations are also analysed. These samples are only measured in the same series as N2 and N6.

The analyses are performed in randomized order to obtain a realistic value for the standard deviation within a series.

All data are thus obtained by performing six determinations in one series, twelve determinations in another series and eight determinations in each of five further series, which is in total 58 determinations. This design gives sufficient data for determination of the range, the linearity, the selectivity, the detection limit and the accuracy. If a reference material has been applied as a natural sample, the data documentation is of an even higher quality.

If the type and concentration of the samples that have been chosen for the method validation have been chosen appropriately, they can be applied as the first data in the internal quality control charts. This is, of course, presuming that the method validation was satisfactory.