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Suggested QC Practices for On-line Analyzers

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Introduction

The USEPA regulates by establishing a contaminant, an MCL, and a method, or methods, that are required to use for compliance purposes. These methods are almost all laboratory methods and include sampling, sample preservation, holding times, and batch QC criteria. Even if an on-line analyzer uses the same measurement technique as a laboratory method, you cannot assume equivalence of an on-line test to a laboratory method because the on-line lacks some of the required QC. This poster suggests QC practices that could be applied to new on-line analyzer methods.

Discussion

On-line monitoring is needed because laboratory analysis only provides a “snapshot” of the concentration of a pollutant in the stream monitored. Often, this “snapshot” sample is collected only on a good day and usually is an effluent at the end of a pipe. However, it is not these NPDES point sources that have been linked to much of the nutrient pollution occurring in anoxic zones (1).

Recently, EPA has passed regulation expanding the Clean Water Act to include tributaries (2). These new pollutant sources will need to be monitored. Since most nutrient pollution is released during periods of stream flooding (3), the most economical means of measuring these pollutants is using on-line analyzers.

On-line analyzers can be classified into two groups; in-situ monitors/sensors and ex-situ analyzers. For the purposes of this poster, In-situ sensors are “probes” that are immersed in the sample and ex-situ analyzers sit out of the sample and the sample is transferred to it for processing and analysis. An in-situ probe is capable of duplicating any lab test that does not require preliminary processing of a sample. For example, a pH or conductivity probe whether laboratory or in-situ is calibrated with standard solution and the tip is immersed in sample solution. There is no sample preservation, preliminary processing, or buffer reagent addition. Ex-situ analyzers, on the other hand, usually run analytes whose laboratory methods require sample preservation, addition of reagents, and possibly sample digestion.

On-line analyzers are located at the sampling site. In-situ sensors provide an instantaneous reading and require very little maintenance. Sensors do have a potential for fouling and calibration drift. Because the sensor is immersed directly in the sample stream, it cannot be automatically re-calibrated or run periodic Quality Control (QC) checks. Ex-situ analyzers are essentially a laboratory analyzer in a box located near the sampling point. Ex-situ analyzers are more expensive than probes and are also more susceptible to malfunction. They can, however, be manufactured to perform almost all of the QC required by currently approved U.S. EPA laboratory methods.

The malfunction of ex-situ analyzers is almost always associated with the sampling system (4), or the process of extracting the sample from the sample stream, transporting it to the analyzer, filtering if necessary, digestion and/or addition of reagents, and analyzing.

Suggested QC Practices for On-line Analyzers

Commercially available on-line analyzers, such as the Shimadzu TOC-4200 Total Organic Carbon and Total Nitrogen on-line analyzer (Figure 1) include sample preparation modules designed specifically for samples containing high concentrations of suspended solids. These sample pretreatment options, such as shown in Figure 2, pre-filter large particles, and homogenize the sample. Combined with automated back flushing immediately after sampling to prevent slime and algae buildup this pre-treatment minimizes carryover from previous samples and reduces maintenance.

Figure 1 Shimadzu TOC-4200

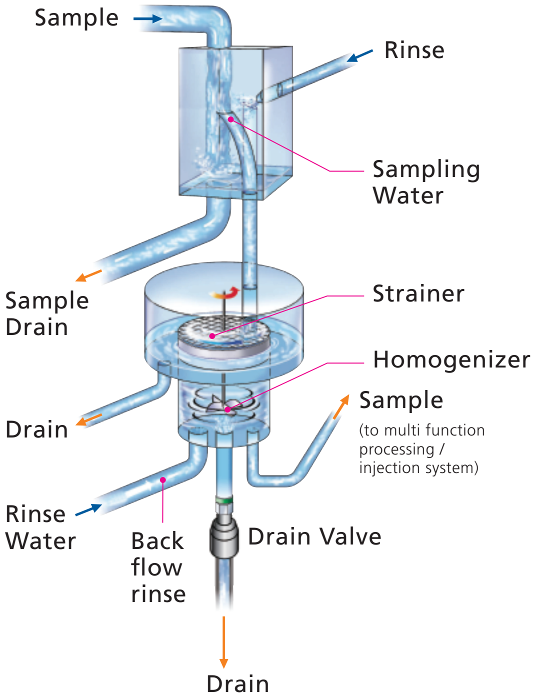

Figure 2 Shimadzu Multi-stream suspended solids sampling unit

EPA has an increased interest in on-line monitoring and how it can be applied to rule-based environmental monitoring. A major concern is calibration and how to ensure that QC is met. Although there is one EPA approved method for on-line analysis of chlorine in drinking water (5), there are no 40 CFR Part 136 approved on-line methods for the analysis of nutrients. Since EPA desires to use on-line methods for Clean Water Act (CWA) compliance reporting there is a need to define the required QC practices for these new methods (6).

Suggested QC for on-line analyzers

Using on-line analyzers for compliance purposes is a goal for many in the regulated community. The technology must, however, gain acceptance and approval as an alternative to laboratory testing. There are many on-line analyzers that measure pollutants using the same technique as an approved method. These cannot be automatically considered equivalent because the on-line analyzer method must meet the QC acceptance criteria of the approved method. The approved methods are almost exclusively laboratory methods with batch QC criteria that must be met. This QC criteria includes:

1. Multiple point calibration and calibration verification
2. Blanks
3. Determination of a method detection limit (MDL)
4. Demonstration of capability (DOC)
5. Analysis of Laboratory Control Samples
6. Analysis of Matrix Spikes
7. Analysis of Matrix Spike Duplicates

Methods intended for CWA compliance monitoring must be approved at 40 CFR part 136. As discussed earlier, current methods are laboratory methods capable of bracketing samples with QC. However, the following practices can readily be implemented on on-line analyzers:

1. Completely automated multiple point calibration, or routine re-calibration and/or verification by trained technicians.
2. Completely automated continuing calibration verification (CCV). If a CCV fails the automated analyzer either re-calibrates or automatically notifies a technician that service is needed.
3. Automated analysis of blanks if needed. Process control may not need blanks, however, ambient measurements should run blanks at defined intervals.
4. Evaluation of precision in the matrix at commissioning. The method should require analyzers to be capable of collecting repeatability data.
5. Evaluation of matrix spike recovery at commissioning. The method should require analyzers to be capable of collecting matrix spike data.
6. Periodic comparison of the on-line method results to laboratory results obtained by an approved method at an accredited laboratory.
   a) Required closeness of results needs to be established in the method.
   b) Sampling procedures to ensure representativeness of the lab sample needs to be defined in the method.
   c) There may be differences in results due to holding time and sample preservation.

Number 6 above is the most crucial for demonstrating the on-line results are equivalent to approved laboratory methods. Acceptance criteria must be established. Figure 3 is an example of a comparison between on line total phosphorus and laboratory total Kjeldahl phosphorus. Because there is no acceptance criteria it is not possible for a laboratory to establish whether these data are the same.

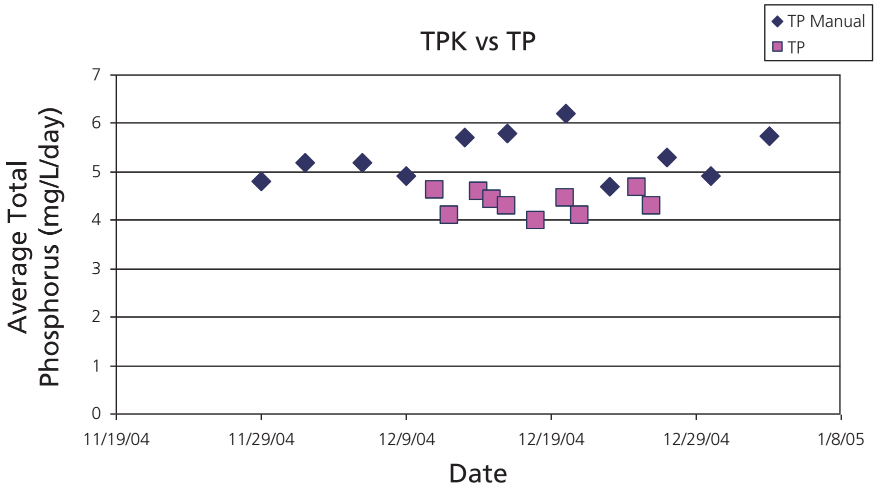

Figure 3 Comparison of TKP and on-line TP

Conclusion

The US EPA requires that methods used for CWA compliance have defined accuracy and precision. With few exceptions, currently approved CWA methods are laboratory methods. It is possible to claim that an on-line analyzer measures a parameter by the same technique as an approved method, however, all approved nutrient methods are laboratory methods. Laboratory methods analyze samples as a batch bracketed by QC. It is the QC criteria that needs to be defined before an on-line method can be approved. This poster presented six suggestions for QC that, if followed, could guarantee on-line analyzer methods collect legally defensible data. None of the requirements are difficult and could be easily implemented. On-line analyzer results should be periodically compared to existing, approved, laboratory methods. New on-line methods need to define sample collection and comparability data.

References

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