

Understanding Intellidilution for use with a UV/Persulfate Analyzer

Abstract

In most instances, the task of routine instrument calibration and daily sample analyses for Total Organic Carbon (TOC) are uneventful. However, when there are samples that have elevated TOC levels outside of the calibrated range of the instrument, at least one of several processes are set into motion. These processes include but are not limited to halting the sample sequence, rinsing of the sample pathway to remove residue, dilution of the sample and reanalysis. These may be labor intensive and time consuming processes. This poster presents Intellidilution, which is a new and innovative way to automate the dilution and reanalysis of samples that are outside the calibrated range of a UV/ Persulfate TOC instrument.

Intellidilution Terminology

Below are some helpful definitions that will be used within this application note:

- ABS** – Units of measure that the detector output data uses and is an abbreviation for absorbance.
- Auto-Rinse** – The sample pathway rinse performed after detection of an over-range sample.
- Saturation Range** – The maximum value of the detector output data defined above 1000 ABS.
- Calibrated Range** – The range of values in ABS found in the calibration file.
- Calibration Target Range** – The dilution range determined by Intellidilution to fit samples into the calibrated range.
- Sample** – The detector output value in ABS of a sample run.
- Minimum Sample Volume** – This is the smallest sample volume that can be used due to the physical limitations of the syringe size.

The identification of sample results that are outside of the calibrated range of the instrument is performed by the Intellidilution feature of the TekLink™ software in a series of processes. The ABS of the highest point on the calibration curve is designated as the high limit for all samples. Sample results over this established high limit are regarded as exceeding the calibrated range and in need of dilution before proceeding. Intellidilution then performs a number of cleaning procedures. The number of cleaning steps performed before it continues with sample analysis is open to user input. The last three ABS values of the final cleaning procedure are averaged and used by Intellidilution to determine if the sample pathway is sufficiently clean to continue. This value is compared to the memorized ABS of the baseline prior to the analysis of the over-ranged sample. Only after Intellidilution determines that the baseline is within an acceptable limit of the memorized baseline, will the dilution of the over-ranged sample begin. Reanalysis begins with Intellidilution choosing the right dilution factor of the sample. The first attempts to calculate a dilution factor are based on 70% – 90% of the Calibrated Range. For instance, if the calibration range is 1 – 20 mg C/L, then the first attempt of a dilution for a 50 mg C/L sample would be 1:3. If not successful, it will broaden its parameters to 50% – 90% of the Calibrated Range. The final attempt will be based on 20% – 90% of the Calibrated Range. Intellidilution will use the first dilution factor that fits the criteria. Once the sample is successfully diluted and analyzed, the sample report flags the sample as having been over-range and analyzed with Intellidilution.

Intellidilution is simple to activate, saves time, reduces the need for manual dilutions, and provides user input as well and has pre-set parameters for multiple applications.



Figure 1. The analysis of a calibration curve is shown with the real-time display in the center.

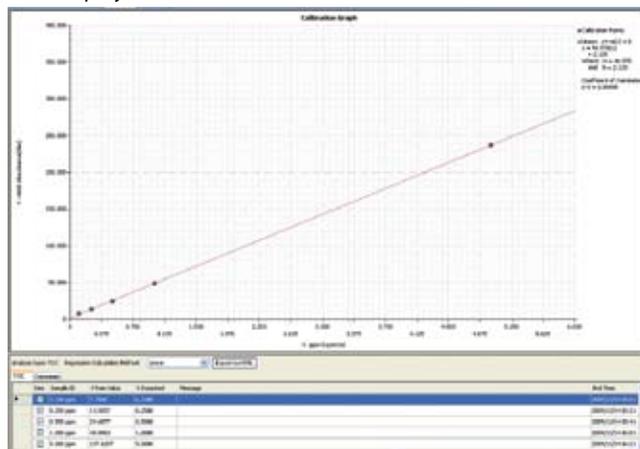


Figure 2. Graphical display of the calibration indicating excellent linearity with $R^2 = 0.99995$.

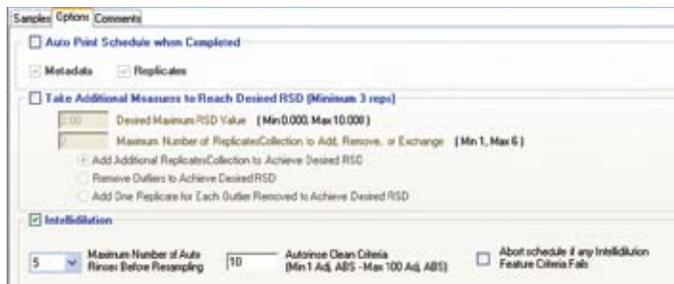


Figure 3. To activate the Intellidilution feature, located on the Options tab of the analysis schedule screen, check the Intellidilution box.



Figure 3A: Once selected, three options become available.

- **Maximum Number of Auto Rinses Before Resampling** – This feature allows for up to 5 sample path rinses [cleans] to be performed before continuing on with the schedule.
- **AutoRinse Clean Criteria** – This sets minimum absorbance value that “cleans” must be below before continuing on with the schedule.
- **Abort schedule if any Intellidilution Feature Criteria Fails** – This will stop the sample schedule completely if the “cleans” do not meet the absorbance criteria.

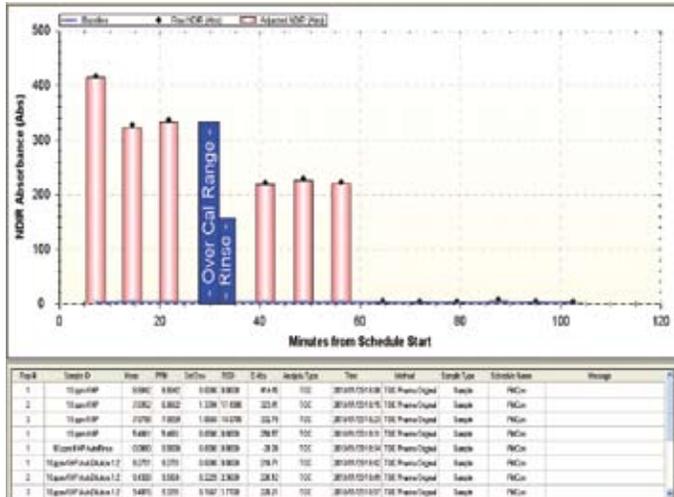


Figure 4. The first three replicates are the analysis of a hand-made 10ppm C sample that is analyzed in triplicate not using Intellidilution. The sample absorbance values were applied directly to the calibration curve without dilution. The analysis falls outside of the Calibrated Range and the maximum absorbance range for the method.



Figure 5. The sample run screen depicts the analysis of a 10ppm C sample using Intellidilution. In Figures 5 – 6 and Figure 3A, the process of analyzing over-ranged samples using Intellidilution is shown and occurs in the following manner.

1. The software analyzes the first replicate and determines that its absorbance is out of the Calibrated Range by comparing the sample ABS to that of the highest point in the calibration curve.
2. The replicate ABS is flagged as Over Cal Range and the graphical display is in blue [Figure 5].
3. The AutoRinse function then cleans the sample pathway based upon the user requirements chosen in the Options Tab [Figure 3A]. If the AutoRinse ABS meets the requirements then the sample schedule continues. If the AutoRinse ABS does not meet requirements then the schedule will either halt or continue with the next sample based upon user input in the Options Tab.

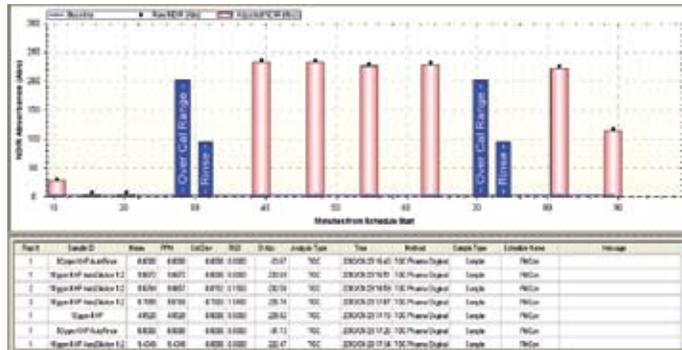


Figure 6. The original analysis of the 10ppm C sample is shown at far left in blue, followed by the AutoRinse. Three 10ppm C replicates using Intellidilution are analyzed along with the analysis of another 10ppm C sample using Intellidilution.

4. The ABS for the AutoRinse was below the 10 absorbance limit set by the user. Therefore, the analysis of the sample using Intellidilution continues [Figure 6].
5. A dilution of the sample will be made based upon its ABS. TekLink estimates a dilution factor so that the sample ABS will fall within the Calibrated Range. Intellidilution first attempts to calculate a dilution factor based on 70% – 90% of the Calibrated Range. If not successful, it will broaden its parameters to 50% – 90% of the Calibrated Range. The final attempt will be based on 20% – 90% of the Calibrated Range. Intellidilution will use the first dilution factor that fits the criteria.
Calibration Target Range attempts within the Calibrated Range:
1st: 70% – 90%
2nd: 50% – 90%
3rd: 20% – 90%
6. For the calibration curve of 1 – 25ppm C, the 25ppm calibration standard returned an ABS of 48.1983. The dilution calculations are as follows:
1st: $[48.1983 * 0.90] = 43.3785\text{ppm C}$ // $[48.1983 * 0.70] = 33.7388\text{ppm C}$
2nd: $[48.1983 * 0.90] = 43.3785\text{ppm C}$ // $[48.1983 * 0.50] = 24.0992\text{ppm C}$
3rd: $[48.1983 * 0.90] = 43.3785\text{ppm C}$ // $[48.1983 * 0.20] = 9.6397\text{ppm C}$
7. The first replicate of the 50ppm C sample returned an over-range absorbance of 98.6190 [Figure 7]. Since a 1:3 dilution is acceptable within the 90% to 50% range, TekLink™ continues with the analysis and uses this dilution factor. The final result has better accuracy and precision than the original undiluted sample.

Summary

Often during schedules, unknown samples fall outside of the upper range of the calibration curve. The Intellidilution feature of the TekLink™ software, which is available on several preloaded methods, automatically detects the sample as being outside the upper calibration limit. Intellidilution accomplishes this by selecting the highest ABS point on the calibration curve as its high limit. Results over this limit are regarded as exceeding the calibrated range and Intellidilution then performs a number of cleaning procedures. The cleanliness of the sample pathway is verified by the average of the last three ABS values of the final clean. This is compared to the memorized ABS of the baseline prior to the analysis of the over-ranged sample. Only after Intellidilution verifies the baseline is within an acceptable limit of the memorized baseline, will the dilution of the over-ranged sample begin. Once the sample is successfully diluted and analyzed, the sample report flags the sample as having been over-ranged and analyzed with Intellidilution. This feature is simple to activate, saves time, reduces the need for manual dilutions, and provides user input as well having pre-set parameters for multiple applications.