TURBIDITY CALIBRATION STANDARDS EVALUATED  
FROM A DIFFERENT PERSPECTIVE

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ABSTRACT

History: Formazin was established as the first calibration standard for turbidimeters in the 1950's. Machine performance and Environmental Protection Agency (EPA) approval for turbidimeters was structured around formazin as the calibration standard. The EPA method 180.1 also outlined design parameters for turbidimeters used for testing surface source drinking water. The design parameters include a white light source and photodetector(s) positioned at 90° to the light source. The nephelometric design was to optimize the detection of sub-micron particulate. Refer to Brumberger et al, Light Scattering is a Function of Light Wave Length and Particle Size. That is, the characteristics of a given particle depend on its refractive index, shape, and size. Sub-micron particles scatter short wavelengths light (white light) at optimally 90°.

Current EPA Approved Standards: Today the scenario is unchanged except for additional EPA approved calibration standards. Besides "scratch" formazin, there is formazin concentrate (4000 NTU – Nephelometric Turbidity Units), stabilized formazin and submicron polymer suspensions.

The polymer suspensions are unique among the approved standards in several ways:

- non-toxic
- ready to use
- accurate +/- 1% of stated value lot to lot
- submicron in particle size distribution
- size, shape, and particle size distribution is always the same, regardless of lot.

It has been argued that since real world water samples have a wide distribution of particle shapes and sizes; the perfect turbidity standard should be of the same matrix. Perhaps true if the filtered final water still consisted of that composition, however, this is not the case. The large particles have been removed. Remember that turbidity reporting is done on finished water.

Particle Size / Light Scatter of Approved Standards: See Figure 1 of the three particle sizes. Figure 1(A) most closely resembles the remaining particulate in finished treated water. The size 1/10th the wavelength of white light; less than 60nm = 0.06µ. White light wavelength is 400 to 600 nm = 0.4 to 0.6microns. Again to emphasize the fact, the EPA protocol of nephelometric turbidimeter design optimizes detection of submicron particulate that scatters light in a 90° direction. Formazin is represented by Figure 1(C), 6000nm = 6.0µ. Formazin is outside the box; too large in size by several factors to equate to the particles that are analyzed. Does Formazin represent real world samples?
Formazin can be reproduced +/- 1% batch to batch. This is true under ideal conditions; which involves quality chemicals, precise volumetric glassware, ultra pure water and excellent laboratory technique. The formulation process is tedious and timely. The final diluted standards are time sensitive and it is commonly recommended not to prepare standards below 2.0 NTU. The EPA requires turbidity values not to exceed 0.3 NTU for surface source drinking water.

**Turbidimeter Design Versus Particle Size of Standards:** To demonstrate the relationship of machine design on formazin and the polymer calibration standards, three different lots of stock formazin data (1,2) and instrument specific polymer standards were tested in four different turbidimeters. The difference in this analysis is that the machines are calibrated with both types of calibration standards instead of just formazin and compared against each other.

Each machine employs a different optical and photo detector design. Analyzing the test results demonstrates several key points.

The different formazin lots do not stay within the 1% variance that is claimed by the manufacturer. The importance of the variance relates to the premise that it is reproducible by any end user.

Evaluating the data sheets for the HF Micro 100 and the McVan 160 probe, the worst case variance is 6.8% per NTU value. Discarding the outliers (2) the average variance is 1.56%. The machines do not change into ratio mode above 40.0 NTU. The polymer calibration standards are instrument specific due to the wavelength of the light sources, which are extremely different; HF 400-600nm and McVan 870 nm. The light source wavelength for the McVan is almost twice that of the HF. The impact of the difference is realized in what the two machines see. Imagine two wire mesh screens; one sized 0.4 \( \mu \) and the other size at 0.82 \( \mu \), which one is going to trap smaller particles? Remember the EPA turbidimeter design criteria for filtered drinking water wavelength? The white light HF machine with its shorter wavelength, 400-600nm, will strike more small particles than the McVan machine. Visualize ping-pong balls verses basketballs.

The two Hach machines data sheets are the most complex to decipher. First, only the Hach 2100 AN instrument specific polymer calibration standards were used in the testing of both machines. At the 20 NTU reading, overall variance is 1.45%. At the 200 NTU value, variance is 3.7%. At the 1000 NTU value, the variance is 10.43%. Lastly, the variance is 4.38% at the 4000 NTU calibration point. The percent error is large for both machines at the 1000 NTU and 4000 NTU polymer standard, why?
One, the polymer standards are specific for the 2100AN machine. Two, the machines are in the ratio mode at the 200 NTU, 1000 NTU, and 4000 NTU calibration points. Thus, multiple detectors at different angles other than 90° are being used, and transmitted light is also measured. These additional detectors are not seeing as much of the polymer suspension as with the 90° photo detector. Three, the ISO machine uses an infrared light source, 860 nm, as opposed to a white light source, 400-600 nm. Four, when calibrating the AN machine with the polymer suspension, the formazin standards read high in the ratio mode. The additional detectors are seeing the formazin therefore, inflating their turbidity readings. Also, more polymer suspension is needed to read matching formazin values at 200 NTU, 1000 NTU, and 4000 NTU. This is demonstrated in the ISO machine where the polymer suspension standards are not instrument specific. Once the ISO machine is calibrated with the non-instrument specific standards the calibration points are undervalued. This is shown by low formazin readings.

Is that a flaw in the polymer standard? No, because in the ratio mode the machines are "tuned" to measure large particles and to compensate for color. Neither of which is a parameter in the analysis of finished drinking water.

**Polymer “Generic” Standards:** The last test results demonstrate the variance of the generic EPA formulated polymer calibration standard in six different design parameter machines. The term generic is defined as the standard to be used to calibrate any turbidimeter that meets the EPA design parameters.

A criticism of the polymer calibration standards is that the turbidity values are established by comparing point to point against formazin, down to 0.1 NTU. Discard the outliers and factor this into the variance from 0.1 to 1000 NTU, then deduct 5% for the expected accuracy of formazin. The compared deviation is 3.37%!

Obviously, machine design can make radical differences in readings but they are outside of the EPA design parameters. Reverse the standard comparison. Let the polymer calibration standards be the gauge. Consider the benefits:

A. The polymer concentrate is formulated in batches that could be a 10 - 20 year supply. Batch to batch particle size variance +/- .001%.
B. Retention samples that could last indefinitely.

**Defining New Turbidity Units:** Realizing that turbidimeter design relates to its performance it is appropriate to define new application specific turbidity units.

**Independent Study:** Syracuse University under the sponsorship of AwwaRF conducted a one-year study of the performance of the calibration standards and turbidimeters. All of the EPA approved calibration standards were evaluated. On Page 76 of the study it states “the calibration method does not seem to have a significant effect on the agreement or lack of agreement between instrument-modes.”

**In summation**
- The polymer calibration standards being instrument specific reveals a deviance of machine design as opposed to a shortcoming of the standard.
- Factoring in the machine design variance regardless of application, the generic polymer calibration standards on average are well within the tolerance of formazin (+/-5%).
- The final consideration is safety.