



## PT Grading & Formulation Requirements

*“The WI DNRLabCert program does not subscribe to the NELAC approach to scoring PT results, particularly for multi-component analyses certified as analyte ‘groups’ (e.g., VOCs, BNAs).”*

Wisconsin has its own specific rules for grading PT results, which are described below. Consequently, while a given PT result may be evaluated by the PT Provider as “Acceptable” for NELAC purposes, that same result may be deemed “Not Acceptable” in Wisconsin.

### The "50% Rule" (multiple technologies)

For each analyte or analyte group, laboratories need to pass more than 50% of the results reported for a given Technology—Analyte combination when multiple results are reported for the same analyte and technology in a given PT study in order to receive an evaluation of "Acceptable".

- Example: ACME Labs receives a “Not Acceptable” result for lead (Pb) by Standard Methods 3113B but an “Acceptable” result using EPA method 200.9 in a single PT study. In both cases, the “technology” is GFAA. Therefore we have two results for the same Technology—Analyte combination.

In this case, ACME passes by EPA 200.9 and fails by SM 3113B. Since both are GFAA methods, there is a 50% pass rate for the technology GFAA. Because this does not constitute "greater than 50%", the lab receives a grade of "Not Acceptable" (failure) for lead by GFAA.

*Note: this also can occur if a lab reports results for both PCBs in water and PCBs in Oil and fails one of the two.*

### The "80% Rule" (multiple analytes)

Laboratories need to pass 80% of the analytes present in (spiked into) a multi-analyte (GC, GC/MS, HPLC) PT sample to receive an evaluation of "Acceptable".

- Treatment of False Positive (and False Negatives)
  - **False positives** (reporting a result for an analyte which was not spiked) count as an analyte failure towards the “80% rule” .
  - **False negatives** (e.g. "<" X ) where the true value is greater than X count as a failure towards 80%.  
*If you report "< (LOD)" for any analyte present at a concentration greater than (LOD), your result will be scored as a failure.*
- Unreported & Undetected) Analytes
  - **Unreported analytes**(for analytes present in the sample) count as a fail towards 80%.
  - **Undetected analytes** (e.g. "<" X ) *where the true value is LESS than X* are NOT CONSIDERED in the accounting towards 80%.
- Analytes with an “Assigned Value” = 0 (Unspiked Analytes)
  - **Unspiked analytes** ARE NOT CONSIDERED in the accounting towards 80%.
  - **Unspiked analytes** ARE CONSIDERED as part of the minimum number of spiked analytes which the program has established.

*“Analytes that are not present in the sample, are not evaluated and do not ‘count’ towards the PT evaluation.”*

Minimum # of "Spiked" Analytes Required to Receive Credit	
"WP"- Aqueous/Solid Matrices	"WS" - Drinking Water Matrix
PAHs (12)	Trihalomethanes (4)
Organochlorine Pest. (15)	Haloacetic Acids [HAA] (5)
VOCs (20)	Unregulated VOCs (15)
BNAs (30)	Regulated VOCs (21)

## PT Formulation Requirements

### PAHs by HPLC

- The concentrations of PAH analytes in PT samples submitted for polynuclear aromatic hydrocarbons (PAHs) by High Performance Liquid Chromatography (HPLC) technology must be representative of the lower concentration ranges detectable by HPLC.
- PAH PT samples with higher concentrations representative of the ranges detectable by GC or GC/MS will not be accepted for certification under the HPLC technology.
- When ordering reference samples for PAHs by HPLC, request PT samples in the concentration range appropriate for HPLC analysis by the State of Wisconsin.

### Underground Storage Tank (UST) Parameters

There are many different PT formulations available for underground storage testing. Wisconsin requires PTs for GRO and DRO to mirror the formulation of standards as described in its unique methodologies. 'Real world' PTs composed of a specific oil or gasoline formulations are not acceptable.

### Diesel Range Organics (DRO)

Requires a PT sample containing the even-numbered alkanes from C-10 to C-28.

Analysis using the Wisconsin specific DRO method is required.

### Gasoline Range Organics (GRO)

Analysis using the Wisconsin specific GRO method is required.

Requires a PT sample containing each of the following 10 analytes:

Benzene	1,2,4-Trimethylbenzene
Ethylbenzene	1,3,5-Trimethylbenzene
Toluene	MtBE (Methyl tert-butyl ether)
m-Xylene	Naphthalene
p-Xylene	
o-Xylene	

### Petroleum Volatiles (PVOC)

Essentially a GRO PT excluding Naphthalene. A GRO PT sample can usually be analyzed for both GRO and PVOC simultaneously. Requires a PT sample containing each of the following 9 analytes (same as GRO minus Naphthalene):

Benzene	1,2,4-Trimethylbenzene
Ethylbenzene	1,3,5-Trimethylbenzene
Toluene	MtBE (Methyl tert-butyl ether)
m-Xylene	
p-Xylene	
o-Xylene	

### PT Grading: VOC Example

At first glance, the following VOC PT data may look to be worthy of an "Acceptable" evaluation for the VOC analyte group. 47 analytes are "Acceptable"; only 6 are "Not Acceptable". That appears to be a passing rate of 47/53 or 88.7%

**Unfortunately, by our grading protocol, it is not acceptable.** The number of spiked analytes is 26. Four (4) analytes that were spiked were scored "Not Acceptable". In addition, there were two (2) false positives receiving an evaluation of "Not Acceptable". That leaves us with  $(26-4-2) \div 26$ , which simplifies to  $20 \div 26$ , or 76.9%. A passing score for "analyte groups" is 80%.

At the heart of this issue lies a difference between Wisconsin's PT requirements, and the NELAC requirements adopted by approved PT Providers. Under the NELAC rules, one or more analytes for multi-component analyses may be considered "negative challenge" analytes. These analytes are not "spiked" (assigned concentration value =0) in the PT sample, and the challenge is to correctly identify that these analytes are not present. Any lab that correctly reports one of these analytes as being < LOD, receives a grade of "Acceptable".

Wisconsin, however, requires an analyte to be spiked in a PT sample in order to obtain credit. Our program requires successful identification and quantitation for each analyte requiring a PT. In addition, labs are penalized for false positives (*reporting an analyte to be present above the LOD when it's assigned value is zero*) and false negatives (*reporting an analyte as not detected, when its assigned value is greater than the lab's LOD*).

Here's how we scored the VOC example on the next page. This is a software subroutine applied to uploaded PT provider files.

Step 1 counts the number of "spiked" analytes (assigned value>0) = **26**

Step 2 counts the spiked analytes for which "Acceptable/Check for Error" results were obtained = **22**

Step 3 subtracts any "penalties" for false positives or false negatives = **- 2**

Step 4 adjusts the number of correct analytes and calculates a percentage.  $(22-2) = 20$  correct out of 26 = **76.9%**

**The program then applies the "80% rule"...meaning that a passing grade for the PT requires a score of at least 80%.**

The bottom line is that NELAC gives labs "credit" for every unspiked analyte (*about 27 in this case*) correctly identified as "ND" or not reported. We don't do that. Our requirements for an acceptable PT results are accurate identification and quantitation for each spiked analyte.

## WI DNR Multi-Analyte PT Grading Example (VOCs)

		Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method/Description
<b>WP Volatiles (cat# 830)</b>							
4315	Acetone	µg/L	2.21	0.00		Not Acceptable	EPA 8260B
4320	Acetonitrile	µg/L	0	0.00		Acceptable	EPA 8260B
4325	Acrolein	µg/L	0	0.00		Acceptable	EPA 8260B
4340	Acrylonitrile	µg/L	0	0.00		Acceptable	EPA 8260B
0065	Benzene	µg/L	13.9	17.7	11.9 - 23.5	Acceptable	EPA 8260B
0060	Bromodichloromethane	µg/L	21.6	27.2	18.9 - 36.6	Acceptable	EPA 8260B
0062	Bromoform	µg/L	29.7	34.7	21.6 - 47.4	Acceptable	EPA 8260B
4950	Bromomethane	µg/L	0	0.00		Acceptable	EPA 8260B
4410	2-Butanone (MEK)	µg/L	6.46	24.8	7.22 - 38.7	Not Acceptable	EPA 8260B
5000	tert-Butyl methyl ether (MTBE)	µg/L	18.0	20.0	11.6 - 29.7	Acceptable	EPA 8260B
4450	Carbon disulfide	µg/L	1.50	0.00		Not Acceptable	EPA 8260B
0058	Carbon tetrachloride	µg/L	18.1	26.5	14.9 - 36.5	Acceptable	EPA 8260B
0064	Chlorobenzene	µg/L	23.1	28.2	20.3 - 35.7	Acceptable	EPA 8260B
0061	Chlorodibromomethane	µg/L	32.6	38.2	26.0 - 50.6	Acceptable	EPA 8260B
4485	Chloroethane	µg/L	0	0.00		Acceptable	EPA 8260B
4500	2-Chloroethylvinylether	µg/L	0	0.00		Acceptable	EPA 8260B
0055	Chloroform	µg/L	16.2	19.8	13.6 - 26.6	Acceptable	EPA 8260B
4960	Chloromethane	µg/L	0	0.00		Acceptable	EPA 8260B
4570	1,2-Dibromo-3-chloropropane (DBCP)	µg/L	0	0.00		Acceptable	EPA 8260B
4585	1,2-Dibromoethane (EDB)	µg/L	0	0.00		Acceptable	EPA 8260B
4595	Dibromomethane	µg/L	0	0.00		Acceptable	EPA 8260B
0094	1,2-Dichlorobenzene	µg/L	33.3	48.4	33.4 - 63.0	Not Acceptable	EPA 8260B
0096	1,3-Dichlorobenzene	µg/L	25.8	37.2	24.8 - 47.7	Acceptable	EPA 8260B
0095	1,4-Dichlorobenzene	µg/L	41.3	64.9	43.9 - 81.4	Not Acceptable	EPA 8260B
4625	Dichlorodifluoromethane (Freon 12)	µg/L	0	0.00		Acceptable	EPA 8260B
4630	1,1-Dichloroethane	µg/L	0	0.00		Acceptable	EPA 8260B
0054	1,2-Dichloroethane	µg/L	33.3	39.5	27.4 - 52.4	Acceptable	EPA 8260B
4640	1,1-Dichloroethylene	µg/L	19.5	24.8	13.1 - 36.3	Acceptable	EPA 8260B
4645	cis-1,2-Dichloroethylene	µg/L	14.1	16.9	11.0 - 22.7	Acceptable	EPA 8260B
4700	trans-1,2-Dichloroethylene	µg/L	34.8	44.2	26.2 - 62.3	Acceptable	EPA 8260B
4655	1,2-Dichloropropane	µg/L	0	0.00		Acceptable	EPA 8260B
4680	cis-1,3-Dichloropropylene	µg/L	0	0.00		Acceptable	EPA 8260B
4685	trans-1,3-Dichloropropylene	µg/L	0	0.00		Acceptable	EPA 8260B
0066	Ethylbenzene	µg/L	41.5	61.4	42.3 - 78.0	Not Acceptable	EPA 8260B
4835	Hexachlorobutadiene	µg/L	0	0.00		Acceptable	EPA 8260B
4860	2-Hexanone	µg/L	0	0.00		Acceptable	EPA 8260B
0063	Methylene chloride	µg/L	16.4	21.6	13.0 - 31.3	Acceptable	EPA 8260B
4995	4-Methyl-2-pentanone (MIBK)	µg/L	0	0.00		Acceptable	EPA 8260B
5005	Naphthalene	µg/L	21.3	33.7	11.3 - 43.6	Acceptable	EPA 8260B
5100	Styrene	µg/L	0	0.00		Acceptable	EPA 8260B
5105	1,1,1,2-Tetrachloroethane	µg/L	21.4	25.3	16.4 - 34.1	Acceptable	EPA 8260B
5110	1,1,2,2-Tetrachloroethane	µg/L	0	0.00		Acceptable	EPA 8260B
0059	Tetrachloroethylene	µg/L	26.2	42.0	23.0 - 55.0	Acceptable	EPA 8260B
0067	Toluene	µg/L	26.2	33.8	23.5 - 42.8	Acceptable	EPA 8260B
5155	1,2,4-Trichlorobenzene	µg/L	19.6	41.8	7.61 - 53.3	Acceptable	EPA 8260B
0056	1,1,1-Trichloroethane	µg/L	25.2	33.8	21.2 - 45.0	Acceptable	EPA 8260B
5165	1,1,2-Trichloroethane	µg/L	0	0.00		Acceptable	EPA 8260B
0057	Trichloroethylene	µg/L	28.7	39.7	25.2 - 52.3	Acceptable	EPA 8260B
5175	Trichlorofluoromethane	µg/L	0	0.00		Acceptable	EPA 8260B
5180	1,2,3-Trichloropropane (TCP)	µg/L	0	0.00		Acceptable	EPA 8260B
5225	Vinyl acetate	µg/L	0	0.00		Acceptable	EPA 8260B
5235	Vinyl chloride	µg/L	0	0.00		Acceptable	EPA 8260B
5260	Xylenes, total	µg/L	67.9	98.0	55.8 - 133	Acceptable	EPA 8260B