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VOC Method Comparison EPA 524.2 and 524.3

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Changes in Method 524.2 to 524.3

- Comparison of eight changes: Method 524.2 to 524.3
  - BFB requirements
  - Purge and Trap parameter allowance
  - Preservatives
  - Autosampler cooling
  - Internal Standards / Surrogates
  - EI Scanning and Single Ion Monitoring (SIM)
  - Calibration requirements
  - Initial Demonstration of Capability requirements

BFB Requirements

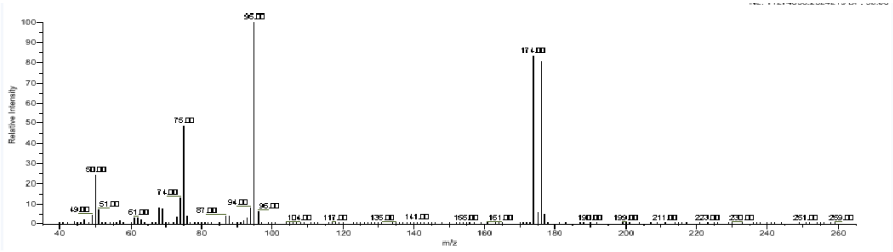
- Method 524.2 – MS Tune Check is required at the beginning of each work shift, but no less than every 12 hours.

- Method 524.3 The MS Tune Check must be performed:
  - prior to establishing and/or re-establishing an initial calibration
  - each time a major change is made to the mass spectrometer.
  - daily BFB analysis is not required.

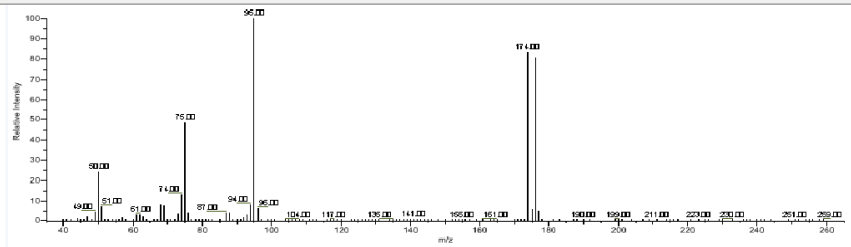
- 50 m/z and 75 m/z are not monitored in the 524.3 BFB criteria

BFB Requirements

- One less QC requirement for day to day operation
- The removal of 50 and 75 m/z makes tuning the MS for BFB easier.



m/z	Ion Abundance Criteria	% Relative Abundance	Pass/fail
50	greater than or equal to 15% AND less than or equal to 40% of m/z 95	24.1	Pass
75	greater than or equal to 30% AND less than or equal to 80% of m/z 95	48.4	Pass
95	equals 100% of Base Peak	100.0	Pass
96	greater than or equal to 5% AND less than or equal to 9% of m/z 95	6.4	Pass
173	less than 2% of m/z 174	0.4	Pass
174	greater than 50% of m/z 95	83.4	Pass
175	greater than or equal to 5% AND less than or equal to 9% of m/z 174	6.8	Pass
176	greater than 95% AND less than 101% of m/z 174	96.4	Pass
177	greater than or equal to 5% AND less than or equal to 9% of m/z 176	6.1	Pass



m/z	Ion Abundance Criteria	% Relative Abundance	Pass/fail
95	equals 100% of Base Peak	100.0	Pass
96	greater than or equal to 5% AND less than or equal to 9% of m/z 95	6.4	Pass
173	less than 2% of m/z 174	0.4	Pass
174	greater than 50% of m/z 95	83.4	Pass
175	greater than or equal to 5% AND less than or equal to 9% of m/z 174	6.8	Pass
176	greater than 95% AND less than 105% of m/z 174	96.4	Pass
177	greater than or equal to 5% AND less than or equal to 10% of m/z 176	6.1	Pass

Purge and Trap Parameters

- 524.2: Purge Time is set to 11 min and purge flow adjusted to 40 ml/min and desorb time for 4 minutes

- 524.3: Five key Purge and Trap parameters restricted to prescribed ranges:

Parameter	Recommended		Allowable	
	Minimum	Maximum	Minimum	Maximum
Sample temperature	Ambient	40 °C	Ambient	60 °C
Purge flow rate	40 mL/min	80 mL/min	20 mL/min	200 mL/min
Purge volume	360 mL	520 mL	240 mL	680 mL
Desorb time	1 min	2 min	0.5 min	4 min
Purge volume + dry purge volume	360 mL	720 mL	240 mL	880 mL

9.1

Purge and Trap Parameters

- 20 m x 0.18 mm x 1.0 u Film columns have caused the Purge and Trap process to be the limited factor in Drinking Water GCMS analysis
  - All compounds easily elute with in 12 minutes with separation acceptable for GCMS integration
- Applying new purge volume changes from Method 524.3 can help improve sample efficiency
- Using Purge Volume (360 ml) 6 min purge time at 60 ml/min flow rate and 0.5 min dry purge time
  - Purge 6.0 min
  - Dry Purge 0.5 min
  - Desorb: 0.5 min
  - Bake 3.5 min

Total Purge and Trap Cycle time with out trap cool down of 10.5 minutes

Preservatives

- 524.2: 1:1 HCl for each 40 mL of sample
- If sampling only for the THMs, you may preserve samples with sodium thiosulfate

- 524.3: Maleic acid and ascorbic acid added to each sample vial, preservative must be added to all prepared standards
- If sampling only for the THMs, you may preserve samples with sodium thiosulfate

8.1

Preservatives

- Picture of sample purging with 524.3 preservatives Maleic acid and ascorbic acid

Autosampler Cooling and Sample Heater

- 524.3: requires temperature control on samples in the Autosampler:

- When resident in the autosampler, samples must be held at 10 °C or lower. Samples must not be frozen.

- Requirement results in the need for a Autosampler with cooling and sample heater.

8.4

Autosampler Cooling and Sample Heater

- Autosamplers with cooling require a recirculation bath to either:
  - Chill a plate that the samples rest on
  - Or the area where the samples reside is sealed and the temperature is maintained by circulating air
  - Or the tray to hold samples is cooled
- Sample Heating is required to bring the samples back to ambient temperature.
- Expect condensation if the lab in humid in the summer months.

Internal Standards / Surrogates

- 524.2
- Fluorobenzene IS
- 4-Bromofluorobenzene Surrogate
- 1,2-Dichlorobenzene-d4 Surrogate

- 524.3
- 1,4-Difluorobenzene IS
- Chlorobenzene-*d5* IS
- *1,4*-Dichlorobenzene-d4 IS
- methyl-t-butyl-ether-*d3* Surrogate
- BFB Surrogate
- 1,2-Dichlorobenzene-*d4* Surrogate

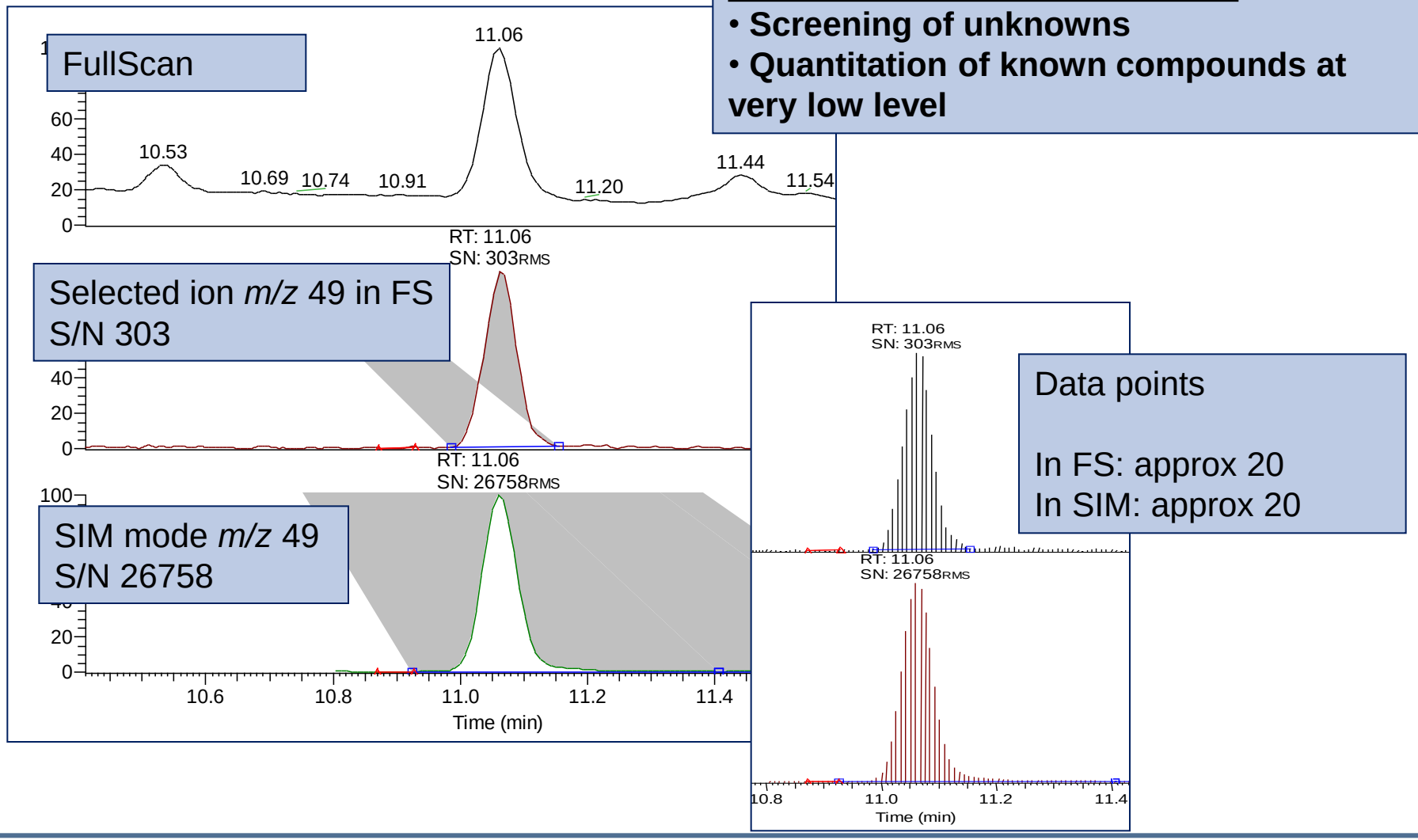
EI Scan range and Single Ion Monitoring (SIM)

- 524.2: is a EI Full Scan only method 35- 260 m/z

- 524.3 :
- Mass range can be altered for the early eluting compounds: 45 -260 m/z and then returned to 35 – 260 m/z for the rest of the analysis
- SIM (Single Ion Monitoring) analysis is permitted for determining selected analytes that are monitored at levels too low for the full scan detection mode.
  - 1,2-dibromoethane (EDB)
  - 1,2-dibromo-3-chloropropane (DBCP)

Flexibility with Simultaneous FS and SIM

Simultaneous FullScan and SIM
- **Screening of unknowns**
- **Quantitation of known compounds at very low level**



Data points

In FS: approx 20
In SIM: approx 20

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Calibration Standards -

- 524.2: The number of CALs needed depends on the calibration range desired. A minimum of three CAL solutions is required to calibrate a range of a factor of 20 in concentration. For a factor of 50, use at least four standards, and for a factor of 100 at least five standards.

- 524.3: Seven levels are shown as examples to create a calibration curve

CAL[a] Level	Final CAL Std. Conc. (µg/L)
1	0.50
2	1.0
3	2.0
4	5.0
5	10
6	20
7	40

7.4

QC Requirements – Calibration

- 524.2

- Initial Calibration - Calculate a response factor (RF) for each analyte and isomer pair for each CAL solution using the internal standard Fluorobenzene.

- Calculate the mean RF from analyses of CAL solutions. Calculate the standard deviation (SD) and the relative standard deviation (RSD) < 20 %

.

$$RF = \frac{(A_x)\ (Q_{is})}{(A_{is})\ (Q_x)}$$

QC Requirements – Calibration

- 524.3

- Initial Calibration – Percent Difference calculation:
  - Calculation of the difference between theoretical and calculated concentration

  - Any regression or average response factor calculation that provide 50 % difference of lowest standard and 30 % difference of all other standards.

QC Requirements – Calibration

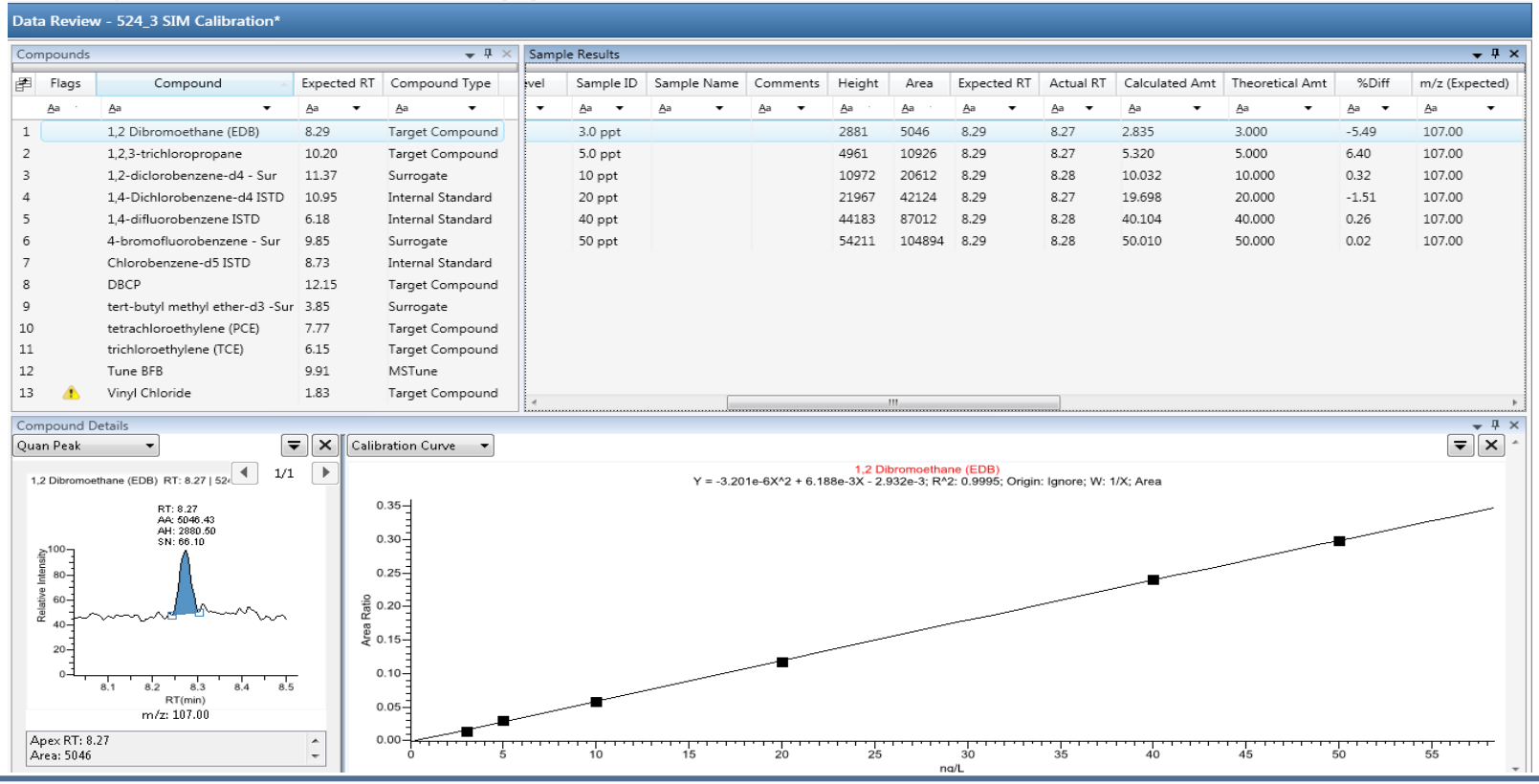
- GCMS Software needs to be able to calculate a single point back against the calibration an calculate a percent difference.

ample Results

Sample Name	Comments	Height	Area	Expected RT	Actual RT	Calculated Amt	Theoretical Amt	%Diff
0_25voastd1		914439	1118995	2.33	2.32	0.28	0.250	11.18
1voastd3		2014305	2553329	2.33	2.33	0.91	1.000	-9.01
2voastd4		3091922	3918603	2.33	2.33	2.20	2.000	9.92
5voastd5		6068206	7358997	2.33	2.33	4.41	5.000	-11.83
10voastd6		12017999	14497940	2.33	2.33	9.32	10.000	-6.83
20voastd7		27626729	33999925	2.33	2.33	21.39	20.000	6.96
40voastd8		51380612	66756541	2.33	2.33	39.97	40.000	-0.07
50voastd9		62755820	83820950	2.33	2.33	49.94	50.000	-0.12
100voastd10		105324308	151251427	2.33	2.33	99.83	100.000	-0.17

SIM Analysis by 524.3

- Here is (EDB) 1,2-dibromoethane
- 5 ml purge
- Calibrated from 3.0 to 50 ppt
- Integration of the 3.0 ppt standard



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QC Requirements – Check Standards

- 524.2

- Continuing Check Standard (CCC) Verify the initial calibration at the beginning of each 12-hour work shift

- The RF for each analyte and surrogate must be within 30% of the mean value measured in the initial calibration.

QC Requirements – Check Standards

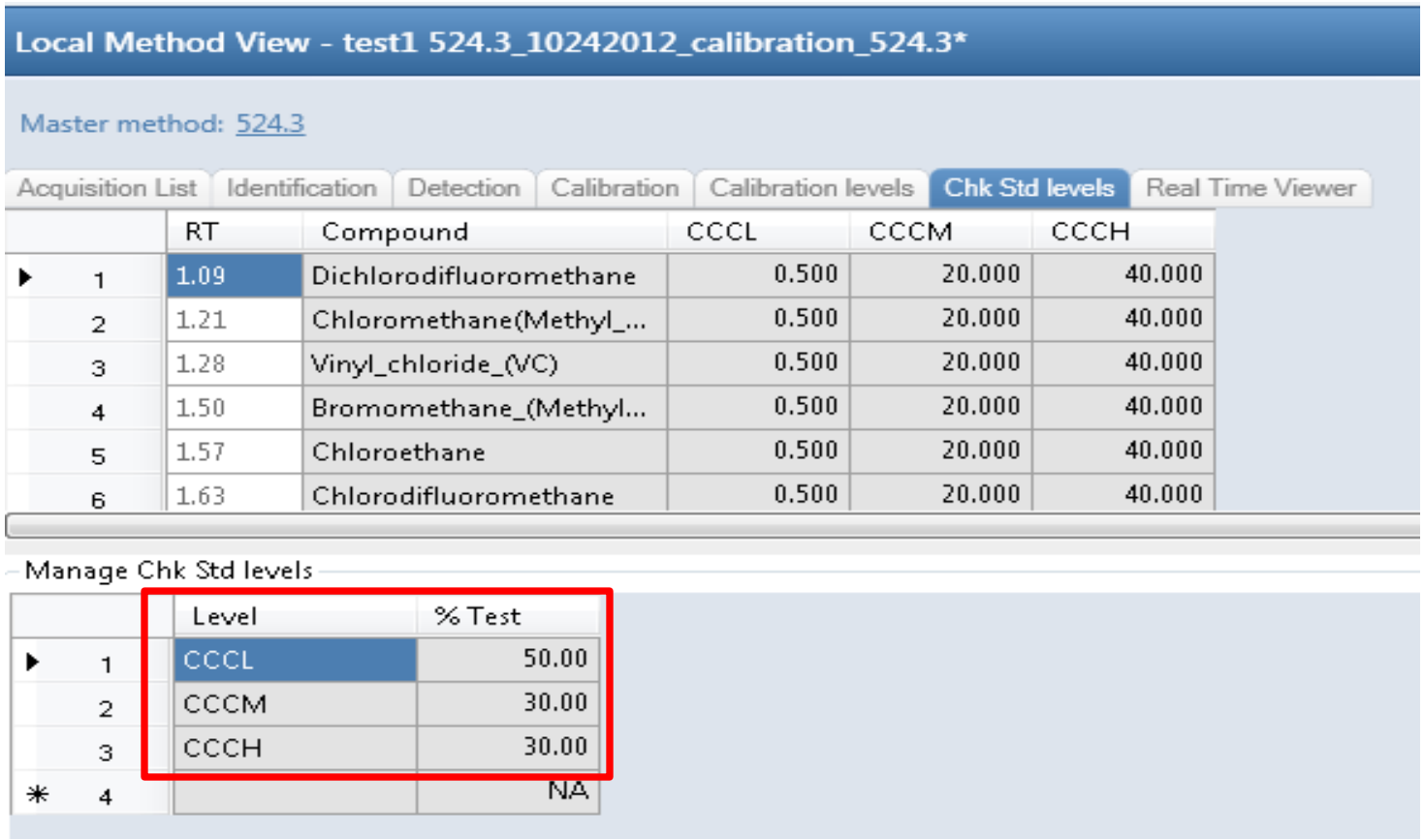
- 524.3

- Check Standard after every 10 samples
  - Low Level CCC standard 50 %
  - Mid Level CCC Standard 30 %
  - High Level CCC Standard 30 %

- Requires more time to dedicated to daily QC.

QC Requirements – Check Standards

- GCMS Software needs to be able to calculate different limits for calculated concentrations of Check Standards



QC Requirements: 524.2 Method Detection Limit

- Method Detection Limits - To determine the MDL, analyze a minimum of seven LFBs prepared at a low concentration. MDLs in Table 5 were calculated from samples fortified from 0.1-0.5 µg/L .
- Calculate the mean accuracy and standard deviation for each analyte. Calculate the MDL using the equation

$$MDL = S\ t_{(n-1,\ 1-alpha\ =\ 0.99)}$$

QC Requirements: 524.3 Method Reporting Limit

- Minimum Reporting Limit (MRL) - Confirm the MRL following the procedure outlined below
- Fortify and analyze seven replicate
- *Calculate - Half Range Predicition of Interval Results HRPIR = 3.963S*

The Upper PIR Limit must be ≤150% recovery.

$$\frac{Mean + HR_{PIR}}{Fortified\,Concentration} \times 100 \leq 150\%$$

The Lower PIR Limit must be ≥50% recovery.

$$\frac{Mean - HR_{PIR}}{Fortified\,Concentration} \times 100 \geq 50\%$$

- The MRL is validated if both the Upper and Lower PIR Limits meet the criteria described above. If these criteria are not met, the MRL has been set too low and must be confirmed again at a higher concentration.

Summary of Comparison of 524.2 and 524.3

- Daily BFB is no longer required
- Recommend and Allowable Purge Parameters allow for optimization
- Preservatives may show foaming during the Purge Cycle
- Investment in cooling Purge and Trap Autosamplers
- More Internal Standards and Surrogates to track
- Both Full Scan and SIM analysis is acceptable
- Calibrations require more points and use % Difference Calculations
- Check Standards are required every 10 samples and vary in concentration
- Calculations of IDC requires more calculations out side of the GCMS software for MRL Validation

Thank you!

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