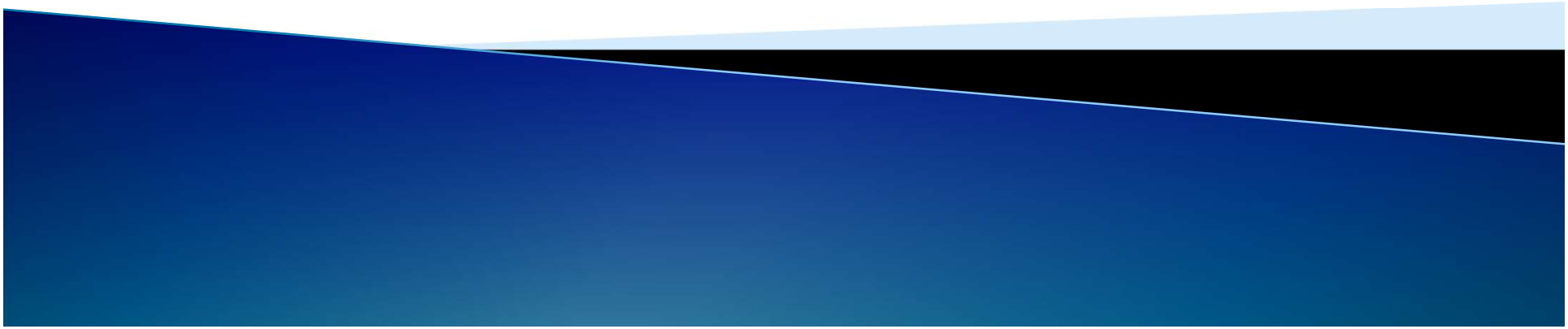
Measurement of Formaldehyde in Drinking Water Using Automated SPE & HPLC

Robert S. Johnson, Alicia J. Cannon and Michael Ebitson,
Horizon Technology, Inc., Salem, NH USA

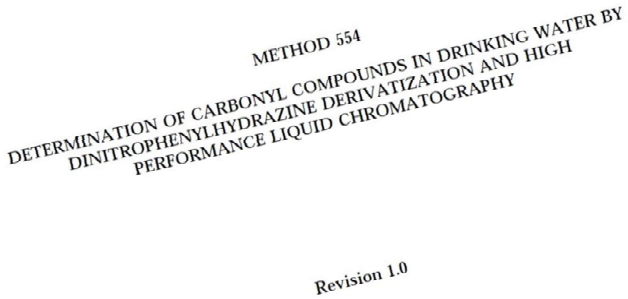


What is the Concern?

- Formaldehyde is found in many products including particle board , cabinets, and furniture
- It has also been reported in fracking fluids as a biocide or scale inhibitor
- Known to cause cancer
- Although not currently regulated in drinking water, it is included in draft Candidate Contaminant List-4 which will be monitored for occurrence and further evaluated for regulation in the next few years
- The EPA reason given for inclusion is “It is an ozonation disinfection byproduct, can occur naturally and has been used as a fungicide”

Analytical Methods

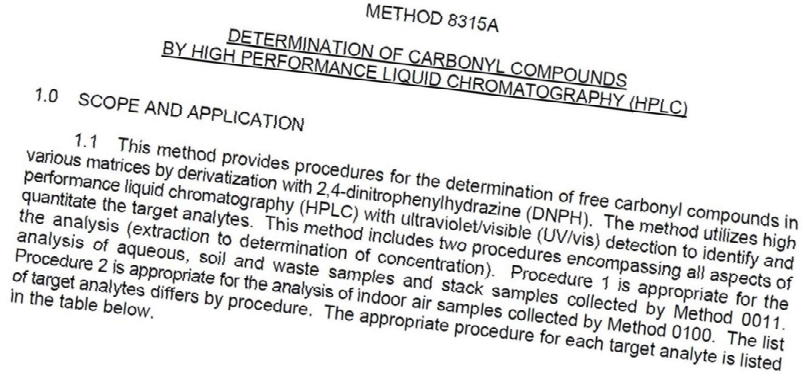
- Two EPA methods are available for preparation and analysis
  - US EPA Method 554 in drinking water program
  - US EPA Method 8315A in SW846
- Can use a C18 cartridge or disk. The sample is derivatized with 2, 4-dinitrophenyl hydrazine and detection with HPLC-UV is used for the analytical measurement.



METHOD 554

DETERMINATION OF CARBONYL COMPOUNDS IN DRINKING WATER BY DINITROPHENYLHYDRAZINE DERIVATIZATION AND HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

Revision 1.0



METHOD 8315A

DETERMINATION OF CARBONYL COMPOUNDS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

1.0 SCOPE AND APPLICATION

1.1 This method provides procedures for the determination of free carbonyl compounds in various matrices by derivatization with 2,4-dinitrophenylhydrazine (DNPH). The method utilizes high performance liquid chromatography (HPLC) with ultraviolet/visible (UV/vis) detection to identify and quantitate the target analytes. This method includes two procedures encompassing all aspects of the analysis (extraction to determination of concentration). Procedure 1 is appropriate for the analysis of aqueous, soil and waste samples and stack samples collected by Method 0011. Procedure 2 is appropriate for the analysis of indoor air samples collected by Method 0100. The list of target analytes differs by procedure. The appropriate procedure for each target analyte is listed in the table below.

SPE Cartridges

- SPE Cartridges were used for this work
- When cartridges are used, inconsistent flow rates or flow rates faster than specified can affect the recovery and precision. Performance using an automated system can provide more consistent recovery
- Development of an automated cartridge procedure will be explored and performance reported.

Apparatus and Materials

- Horizon SmartPrep Extractor (6 mL plunger set up).
- In-line 3.1 µm syringe filters (in sample lines)
- 1 g C18 6 mL Phenomenex Cartridge
- Heating oven at 40 ºC
- Manual Cartridge vacuum block
- Chemical Reagents- Water, acetonitrile, 6 N HCl, 40 mM Dilute Citrate Buffer, DNPH reagent, Formaldehyde Standard
- HPLC Shimadzu LC-2040C i Series
- HPLC Column- Phenomenex Kinetex C18 100 x 4.6mm

SmartPrep Cartridge Extractor

- Fully automates the extraction process
- Precise flow rate control gives better recoveries and consistency
- More efficient method development
  - Multiple methods
  - Fraction collection to screen load, wash and elution steps to determine breakthrough and optimal elution volumes

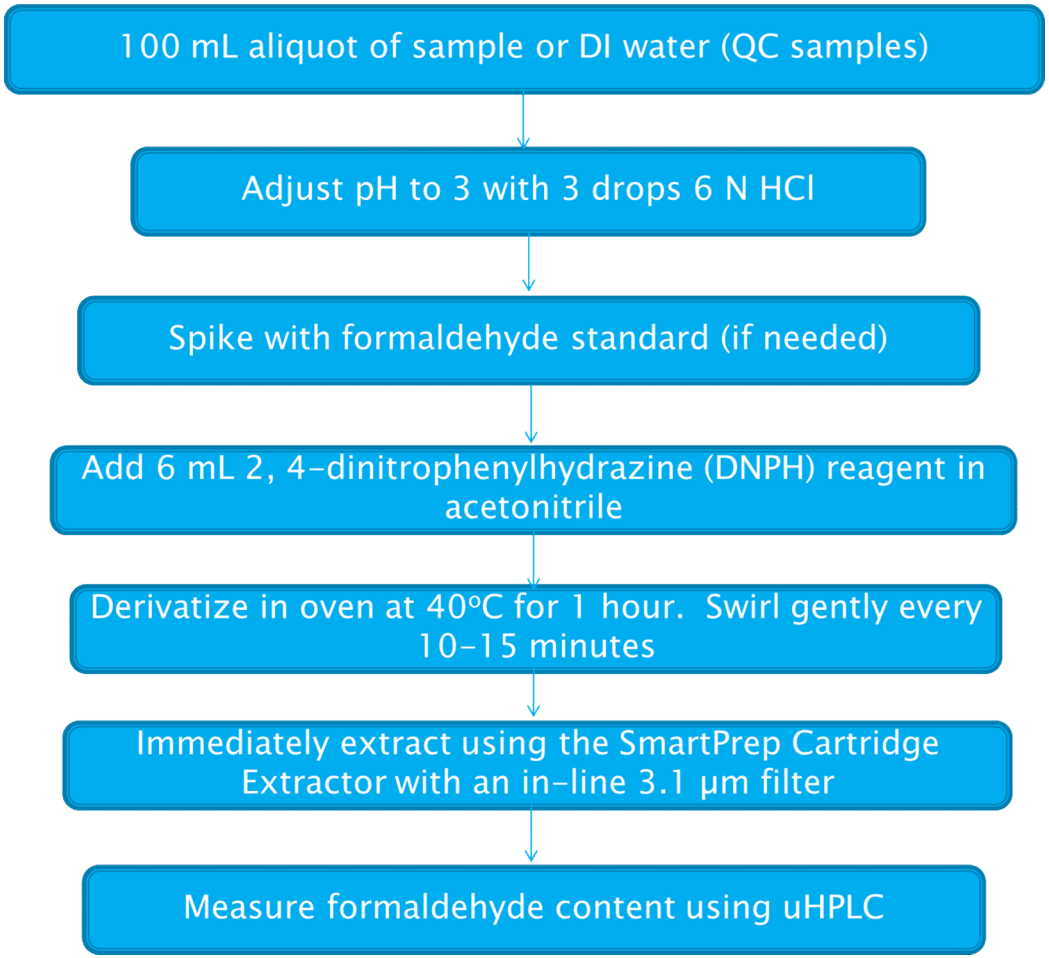
Sample Preparation Process

1) 100 mL aliquot of sample or Di H2O (QC Samples)
2) Adjusted to pH 4 with 3 drops 6 N HCl
3) Spiked with formaldehyde standard
4) Add 6 mL 2,4-ditnitrophenylhydrazine (DNPH) reagent in acetonitrile
5) Derivatize in oven 40°C for 1 hour. Gently swirl every 10-15 minutes.
6) Immediately extract on SmartPrep
7) Determine formaldehyde content by HPLC.

Extraction Procedure Comparison

EPA Method 8315 (Procedure 1)	SmartPrep Extraction
Vacuum manifold extraction	Automated extraction with filter
Condition with 10 mL dilute citrate buffer	Condition with 10 mL dilute citrate buffer
Load sample at 3–5 mL/min	Load sample at 5 mL/min
Pull vacuum additional 1 minute	Purge with nitrogen 1 minute
Maintain vacuum, elute with 9 mL acetonitrile in a 10 mL volumetric flask	Elute with 10 mL acetonitrile at 5 mL/min

Automated Method Overview



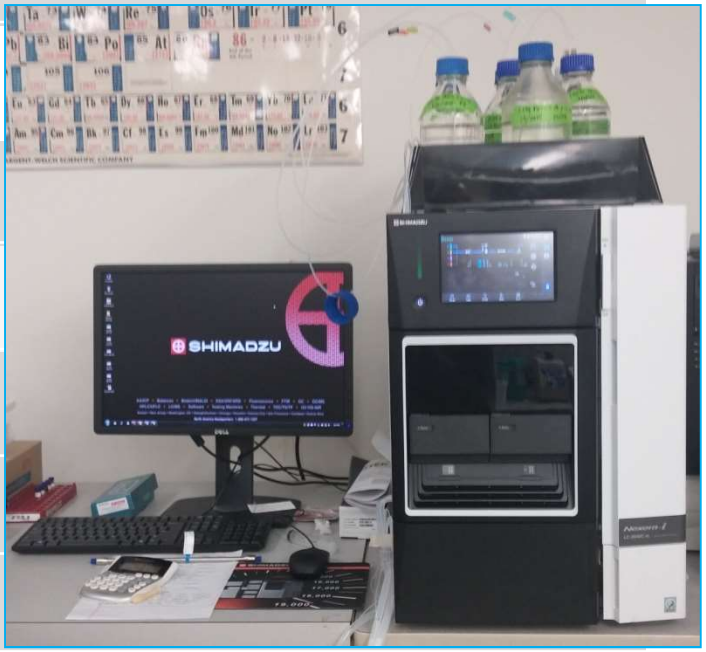
SmartPrep Extraction Method

Method Name: 8315 Extn_XC_10_V_C
Cartridge: C18
Cartridge Size: 6
Number of Steps: 17

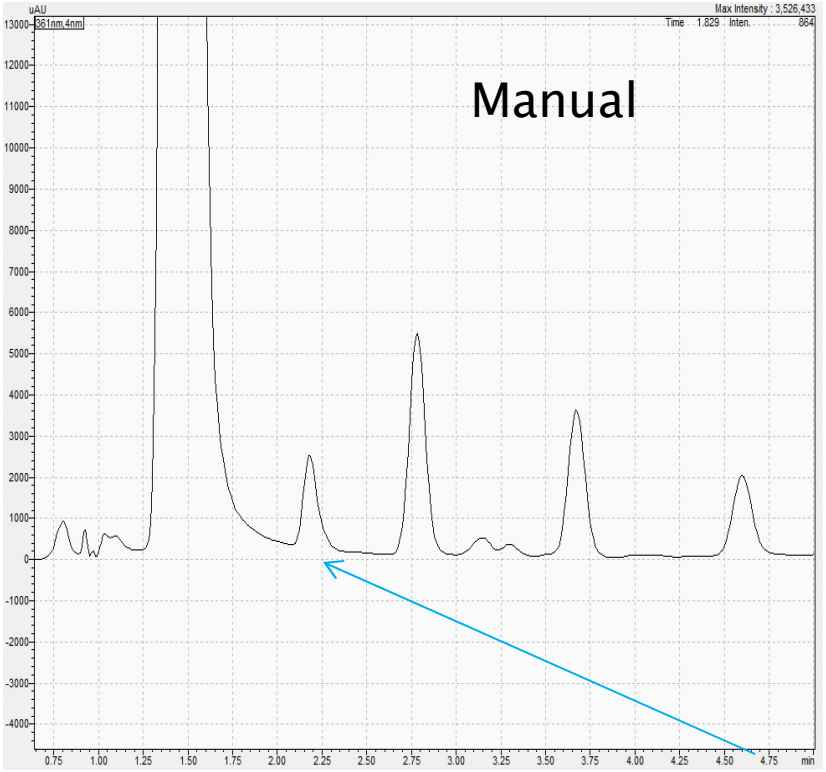
1. Clean plunger using 6 mL of Dilute Citrate Buffer at 30 mL/min
2. Condition cartridge using 5 mL of Dilute Citrate Buffer at 5 mL/min Soak 15 sec
3. Condition cartridge using 5 mL of Dilute Citrate Buffer at 5 mL/min Soak 15 sec
4. Load 110 mL of Sample at 10 mL/min. Deliver at 5 mL/min.
5. Dry for 1 minutes
6. Elute cartridge using 5 mL of Acetonitrile at 15 mL/min into 1st Collection Tube Soak 5 sec
7. Elute cartridge using 5 mL of Acetonitrile at 15 mL/min into 1st Collection Tube Soak 5 sec Dry 10 sec
8. Elute cartridge using 6 mL of VENT at 10 mL/min into 1st Collection Tube Dry 10 sec
9. Clean plunger using 6 mL of Acetonitrile at 20 mL/min Soak 2 sec
10. Clean plunger using 6 mL of Acetonitrile at 20 mL/min Soak 2 sec Dry 10 sec
11. Clean plunger using 6 mL of Reagent Water at 20 mL/min Soak 2 sec
12. Clean plunger using 6 mL of Reagent Water at 20 mL/min Soak 2 sec Dry 10 sec
13. Clean system tubing using 6 mL of Acetonitrile at 20 mL/min
14. Clean system tubing using 6 mL of Acetonitrile at 20 mL/min Dry 10 sec
15. Clean system tubing using 6 mL of Reagent Water at 20 mL/min
16. Clean system tubing using 6 mL of Reagent Water at 20 mL/min Dry 10 sec
17. Clean system tubing using 6 mL of VENT at 20 mL/min Dry 10 sec

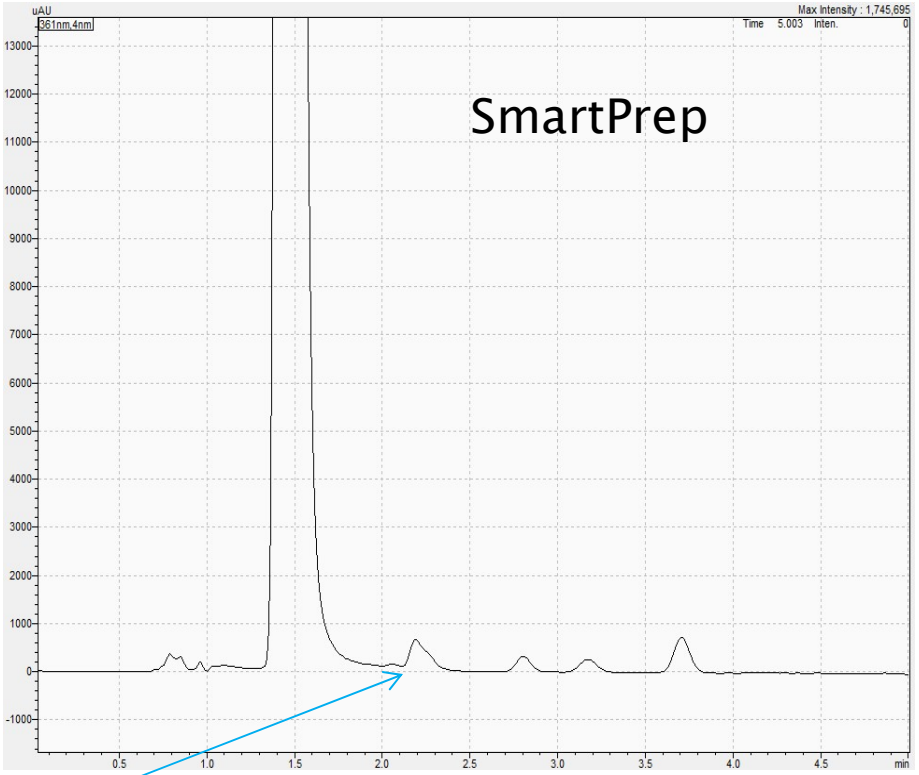
Analysis Conditions–Shimadzu UHPLC

Column	Phenomenex Kinetex C18, 100 x 4.6 mm
Mobile phase	45:55 HPLC Grade Water: Acetonitrile
HPLC System	Shimadzu HPLC iSeries
Flow rate	1.0 mL/min
Run Time	5 minutes
Injection Volume	10 µL
Detection	360 nm
Calibration Levels	10 µg/L, 25 µg/L, 50 µg/L, 100 µg/L, 250 µg/L, 500 µg/L



Blanks-Manual Vs SmartPrep

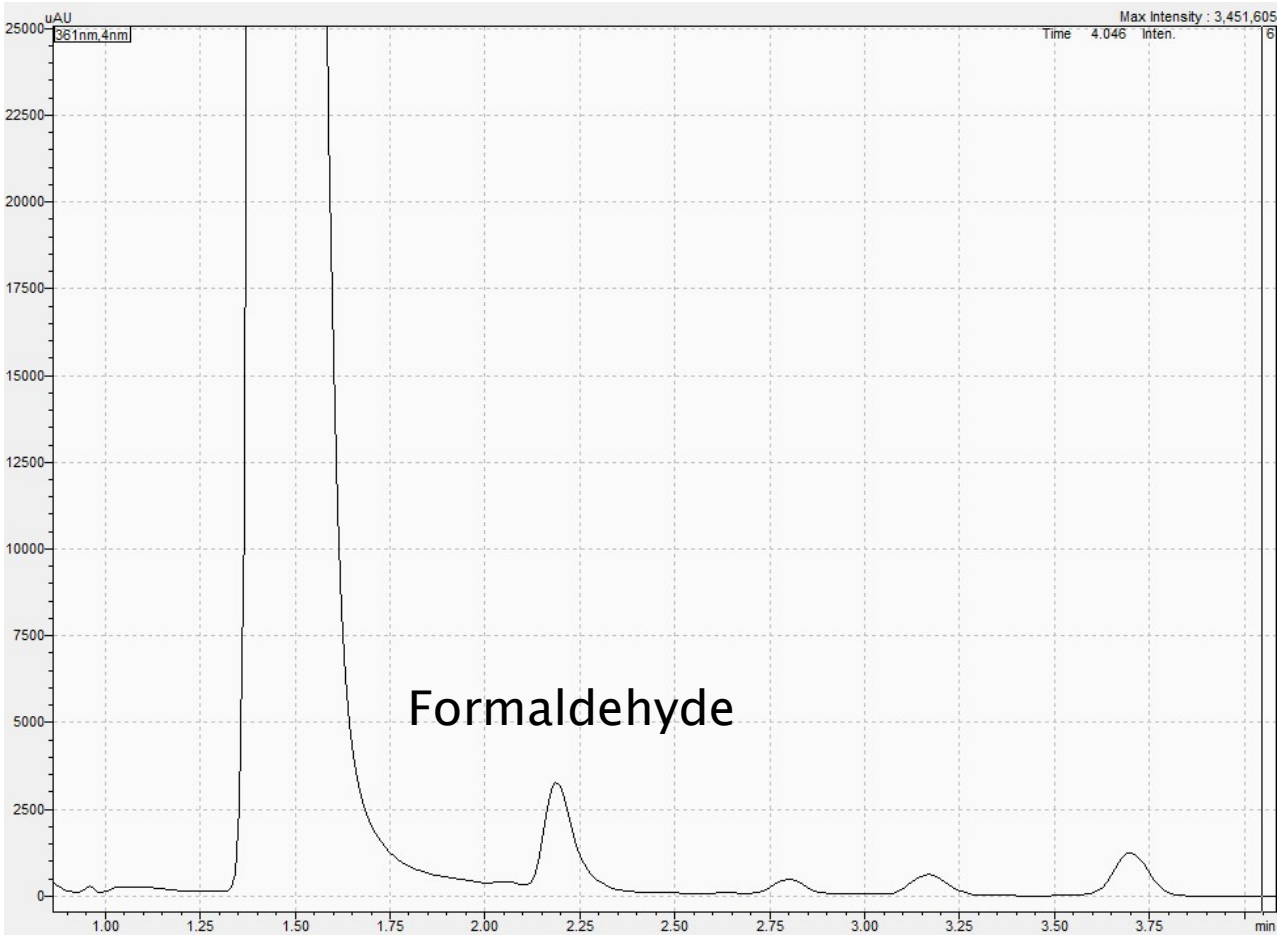




Formaldehyde

Automated background is consistently cleaner than manual Background.

Formaldehyde Chromatogram Di Water Spike at 100 µg/L



Recoveries for Automated Extraction-Acetonitrile (Method 8315)

Sample Type	Sample Conc. (µg/L)	Recovery
Automated Blank	0	ND
Manual Blank	0	65 µg/L
Automated LCS	100	97.9 %
Automated LCS	100	74.3 %
Automated LCS	100	119 %
Automated LCS	100	87.3 %

Average Automated Recovery 94.6 %
SD 18.8 %

Recoveries for Automated Extraction-Ethanol (Method 554)

Sample Type	Spike Conc. (µg/L)	Recovery (%)
Automated LCS	100	76.3
Automated LCS	100	64.6
Automated LCS	100	66.4
Automated LCS	100	64.2
Automated LCS	100	84
Average Recovery		71.1
Standard Deviation		8.7

Results/Discussion

- Average recovery over 4 replicates is 94.6 %, for ACN and 71.1 % for 5 ethanol extractions, meeting recovery criteria of 39-153 % (method 8315)
- Standard deviation over 4 replicates is 18% for ACN and 8.7 for ethanol extraction, both meeting the criteria of less than 30
- Benefit of SmartPrep over manual mode is liquid delivery rates are more consistent and blanks are cleaner
- SmartPrep extraction method includes system clean-up steps to clean system in between sample runs

Conclusion

- Separation and detection of formaldehyde was achieved, however this is a difficult method due to compound volatility and environmental interferences
- While the automated technique is cleaner, the method needs further optimization to improve reproducibility
- Time savings of 55 minutes was demonstrated even with a method requiring further optimization
- Ethanol extractions were more consistent on the SmartPrep than the acetonitrile extractions. Both methods had the same steps prior to the elution step
- Though still within the range of recovery there is room for improvement with both extraction methods
- The use of a 6-mL SPE cartridge with additional sorbent of 1.5g-2g of C-18 will be explored in future testing, since stacking is not possible