Ensuring Quality Data for Organochlorine Pesticide Analysis by Using an Optimized SPE Cartridge for Sample Extract Cleanup

Jason Hoisington, Jason Thomas, Alexis Shelow, Colton Myers

Restek Corporation

NEMC 2025

EPA 8081 Pesticides Analysis Troubles

Problems resulting from complex sample matrices

- Quantitation inaccuracies
- Calibration interval reduction
- Frequent inlet degradation check failures

- Increased maintenance requirements
- Increased downtime
- Reduced throughput
- Diminishing profitability

EPA 8081 Pesticides Analysis Problems

Problems resulting from complex sample matrices

- **Chromatographic interferences**
  - Coelution from coextracted matrix compounds – e.g., chlorophenols
  - Massive chromatographic interferences – e.g., sulfur
  - Carryover/ghost peaks/crossover contamination – high boilers

- **System inertness effects**
  - Continuing calibration standards failure
  - Inlet degradation check failure

EPA 8081 Pesticides Analysis Problems

Problems resulting from complex sample matrices

- **Chromatographic Interferences**
  - **Coelution from coextracted matrix compounds – e.g., chlorophenols**

    Methods 3620/3610/3630
  - **Massive chromatographic interferences – e.g., sulfur**

    Method 3660
  - **Carryover/ghost peaks/crossover contamination - high boilers**

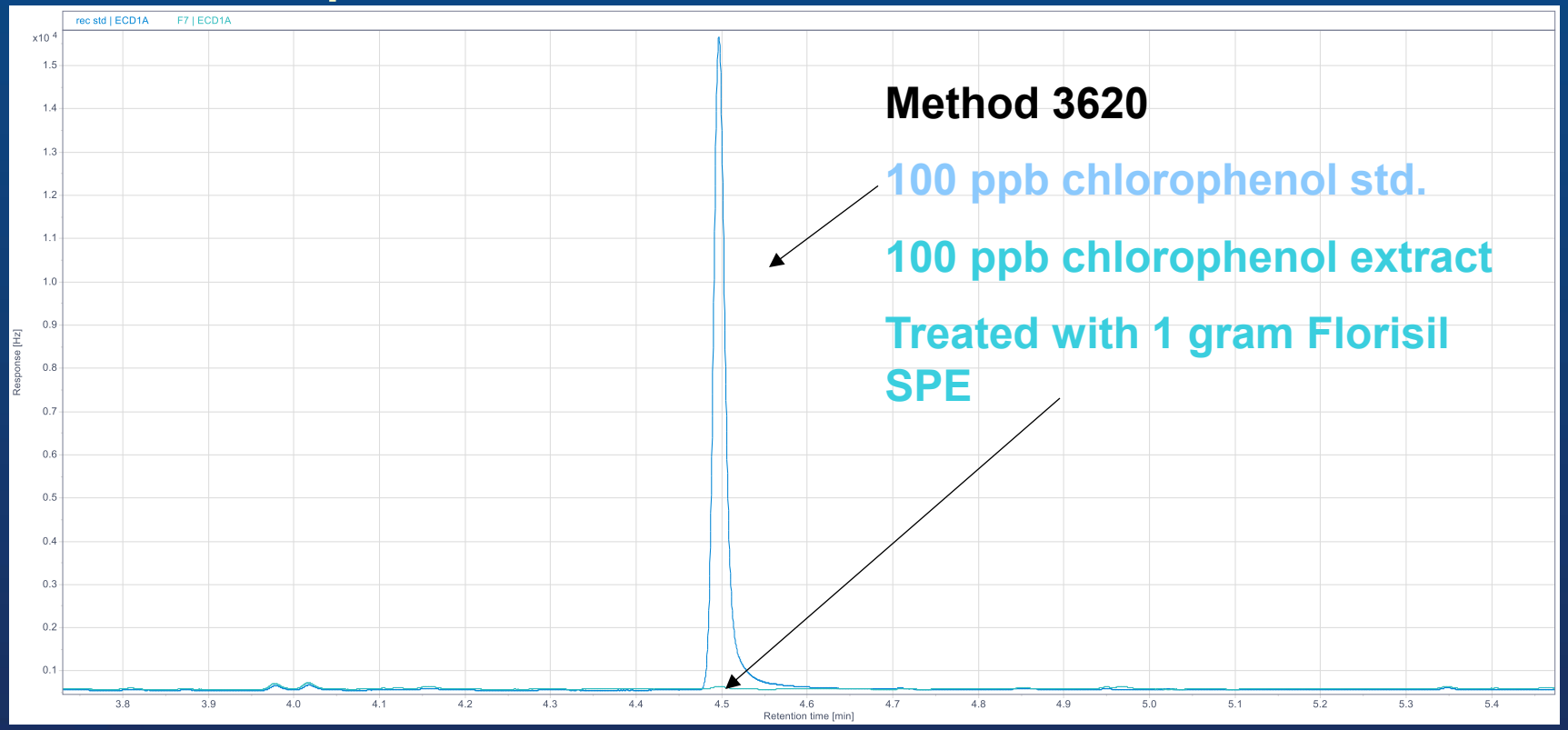
    Method 3640

EPA 8081 Pesticides Analysis Problems

Problems resulting from complex sample matrices

➢ Chromatographic Interferences

- **Coelution from coextracted matrix compounds – e.g., chlorophenols**



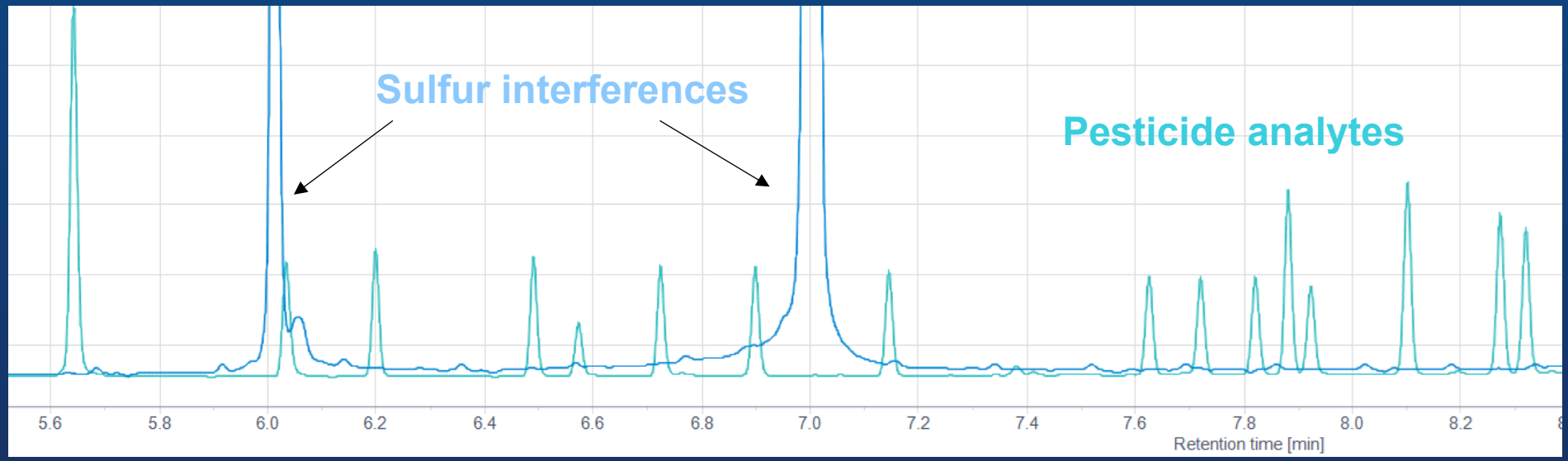
EPA 8081 Pesticides Analysis Problems

Problems resulting from complex sample matrices

➢ Chromatographic Interferences

- **Massive chromatographic interferences – e.g., sulfur**

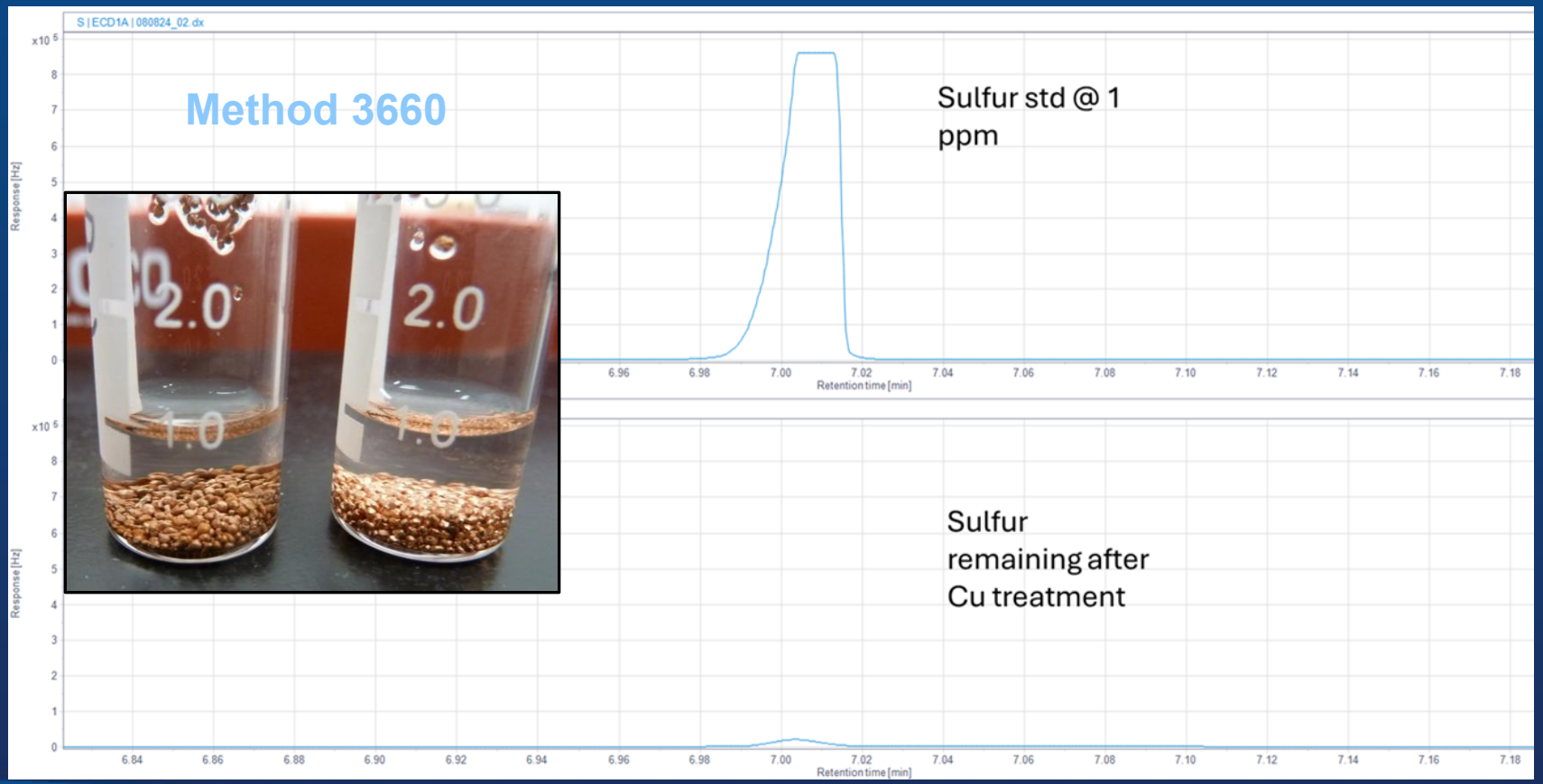
  Method 3660



EPA 8081 Pesticides Analysis Problems

Problems resulting from complex sample matrices

- **Chromatographic Interferences**
  - **Massive chromatographic interferences – e.g., sulfur**

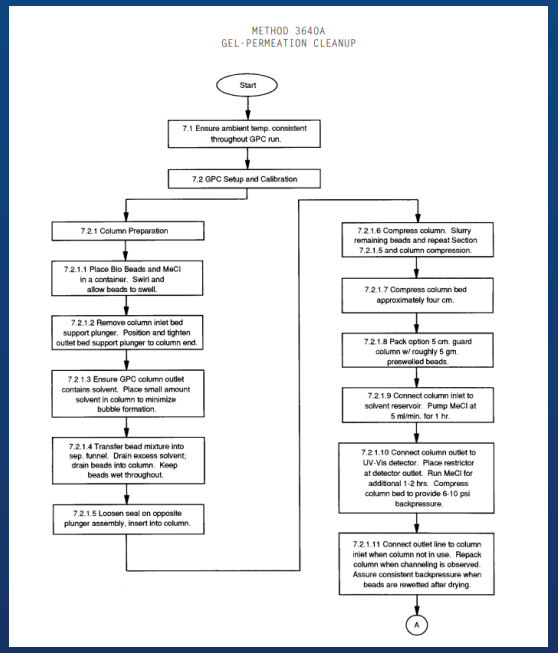


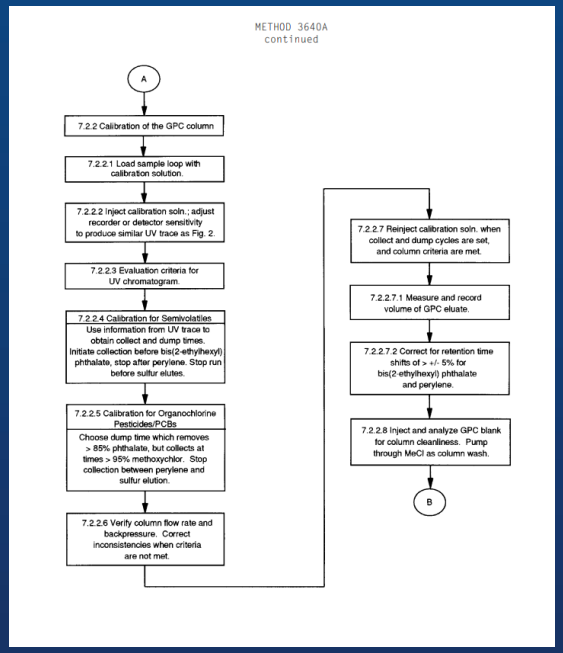
EPA 8081 Pesticides Analysis Problems

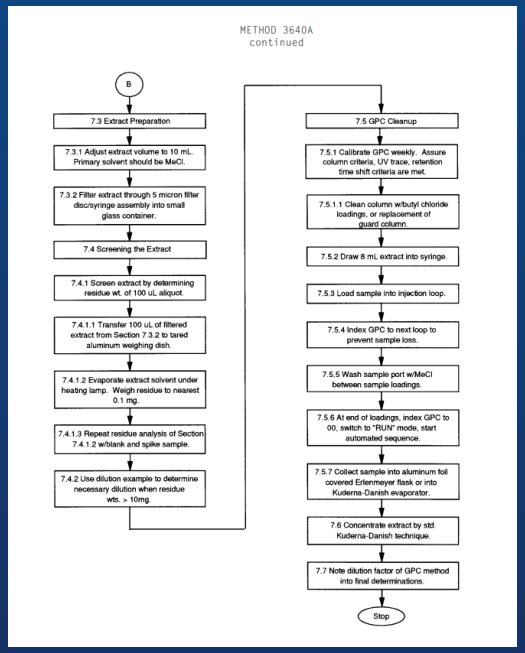
Problems resulting from complex sample matrices

- **Chromatographic Interferences**
  - **Carryover/ghost peaks/crossover contamination - High Boilers**

Method 3640 GPC costly and cumbersome process







Method 3640A: Gel-Permeation Cleanup, part of Test Methods for Evaluating Solid Waste, Physical/Chemical Methods

EPA 8081 Pesticides Analysis Problems

Problems resulting from complex sample matrices

- **System inertness effects**
  - **Continuing calibration standards failure**
  - **Inlet degradation check failure**

9.3.3 DDT and endrin are easily degraded in the injection port. Breakdown occurs when the injection port liner is contaminated with high boiling residue from sample injection or when the injector contains metal fittings. Check for degradation problems by injecting a standard containing only 4,4'-DDT and endrin. Presence of 4,4'-DDE, 4,4'-DDD, endrin ketone or endrin indicates breakdown. If degradation of either DDT or endrin exceeds 15%, take corrective action before proceeding with calibration. Unless otherwise specified in an approved project plan, this test should be performed even when DDT and endrin are not target analytes for a given project, as a test of the inertness of the analytical system.

EPA 8081 Pesticides Analysis Problems

Problems resulting from complex sample matrices

- **Inlet degradation check failure**
  - Endrin – metal activity, lack of deactivation
  - DDT – accretion of high molecular weight material in inlet and head of column, ex: humic/fulvic acids

EPA 8081 Pesticides Extract Cleanup

- **GPC costly and cumbersome process**
  - **Florisil only, no HMW**
    - chlorophenols
  - **CPP only, no TCP**

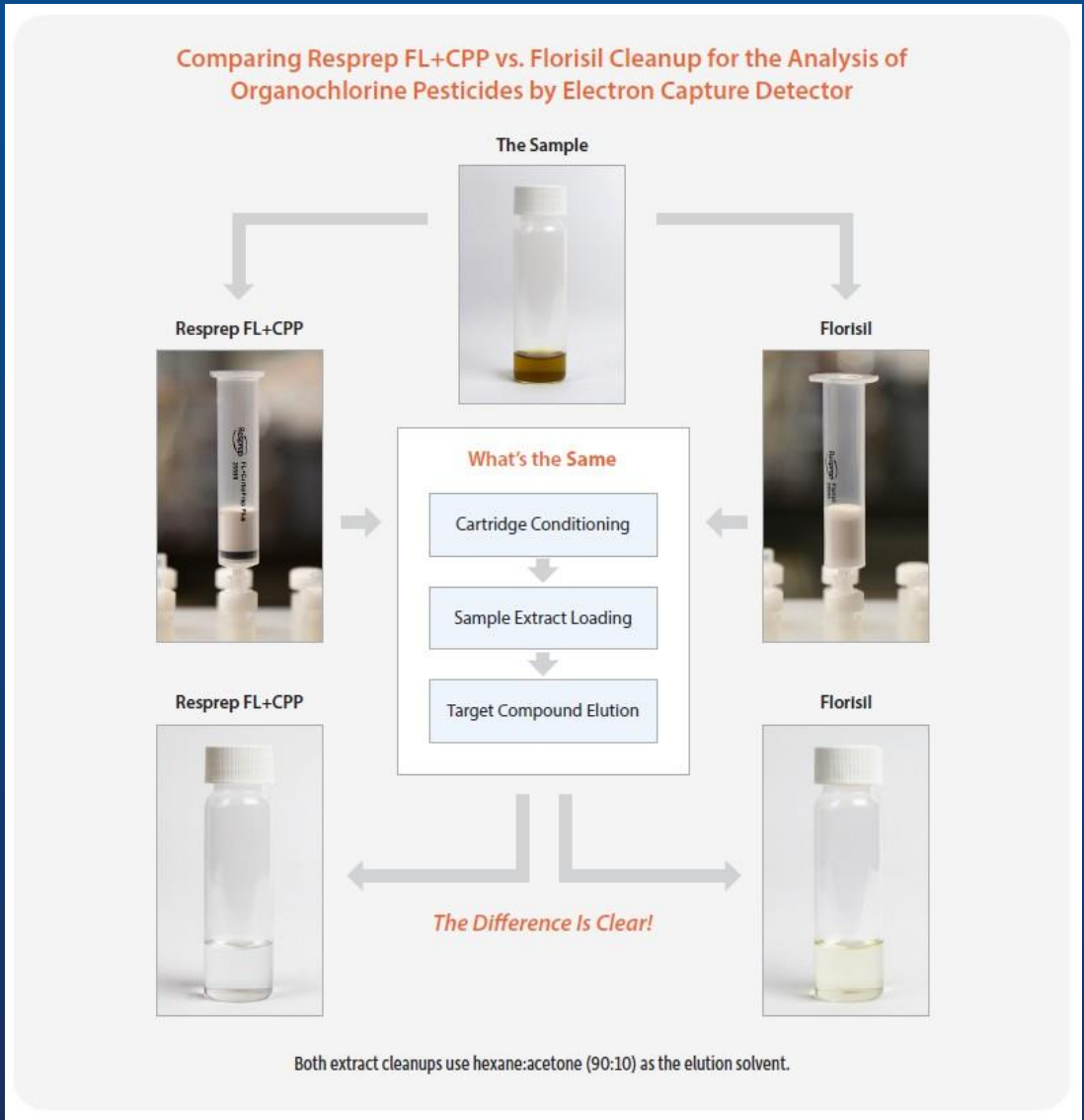
EPA 8081 Pesticides Extract Cleanup

- **Combined orthogonal sorbents**
  - no cumulative effects of combined strong retention
- **GCB with tempered affinity for planars**
  - High variation and high retention (HCB) reigned in
- **Florisil with moisture control**
  - Commonly encountered high moisture levels causing > 5% TCP @ 10 mls elution

EPA 8081 Pesticides Extract Cleanup

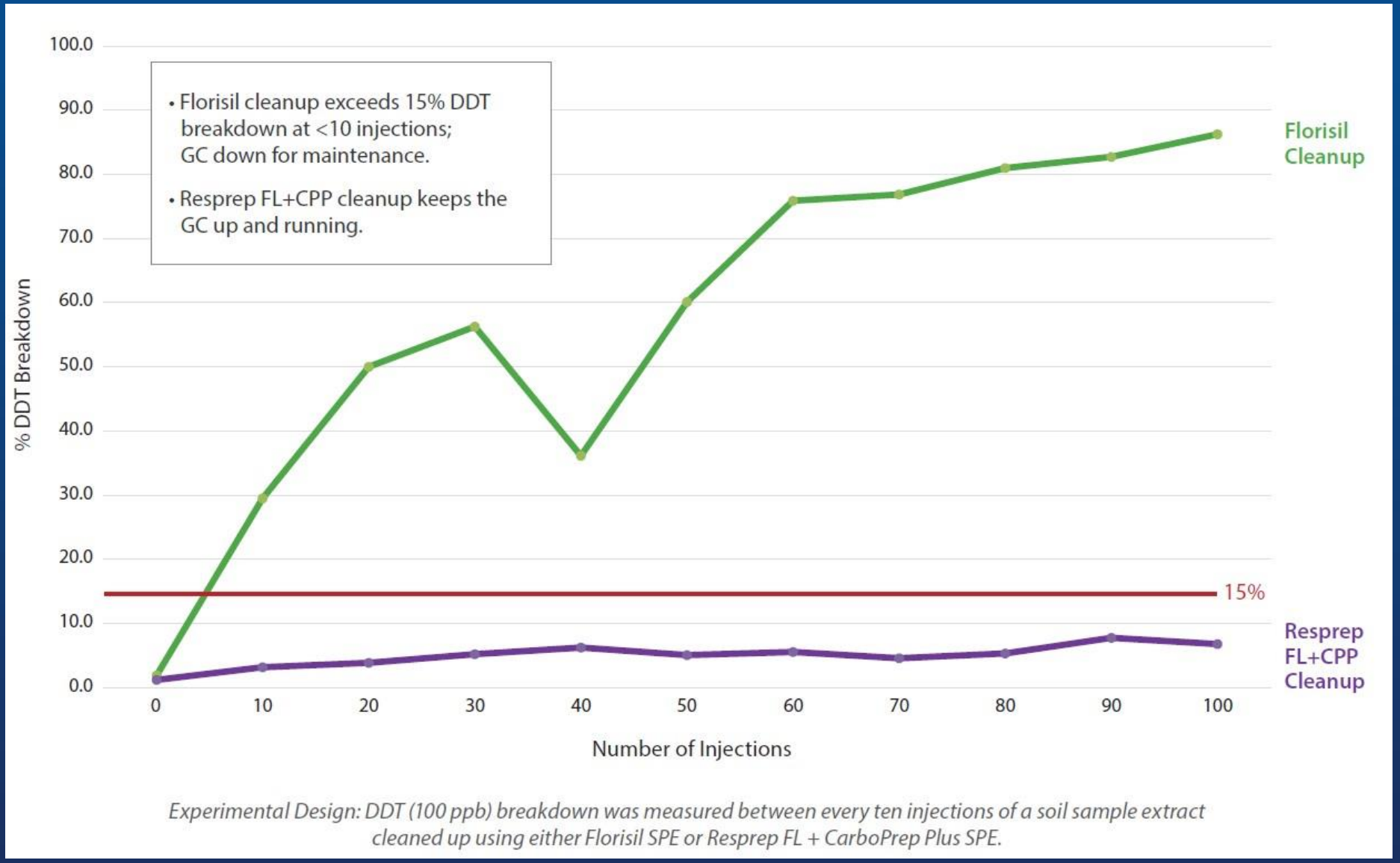
Visual difference in cleanup efficacy

(note: colorless does not always mean it's free from activity problems, nor does a colored extract guarantee problems)



EPA 8081 Pesticides Extract Cleanup

Comparison of DDT breakdown check standard results checked successively after repeated sets of 10 injections of a soil extract cleaned by Florisil only cartridge versus that of GCB stacked with Florisil



Experimental Design: DDT (100 ppb) breakdown was measured between every ten injections of a soil sample extract cleaned up using either Florisil SPE or Resprep FL + CarboPrep Plus SPE.

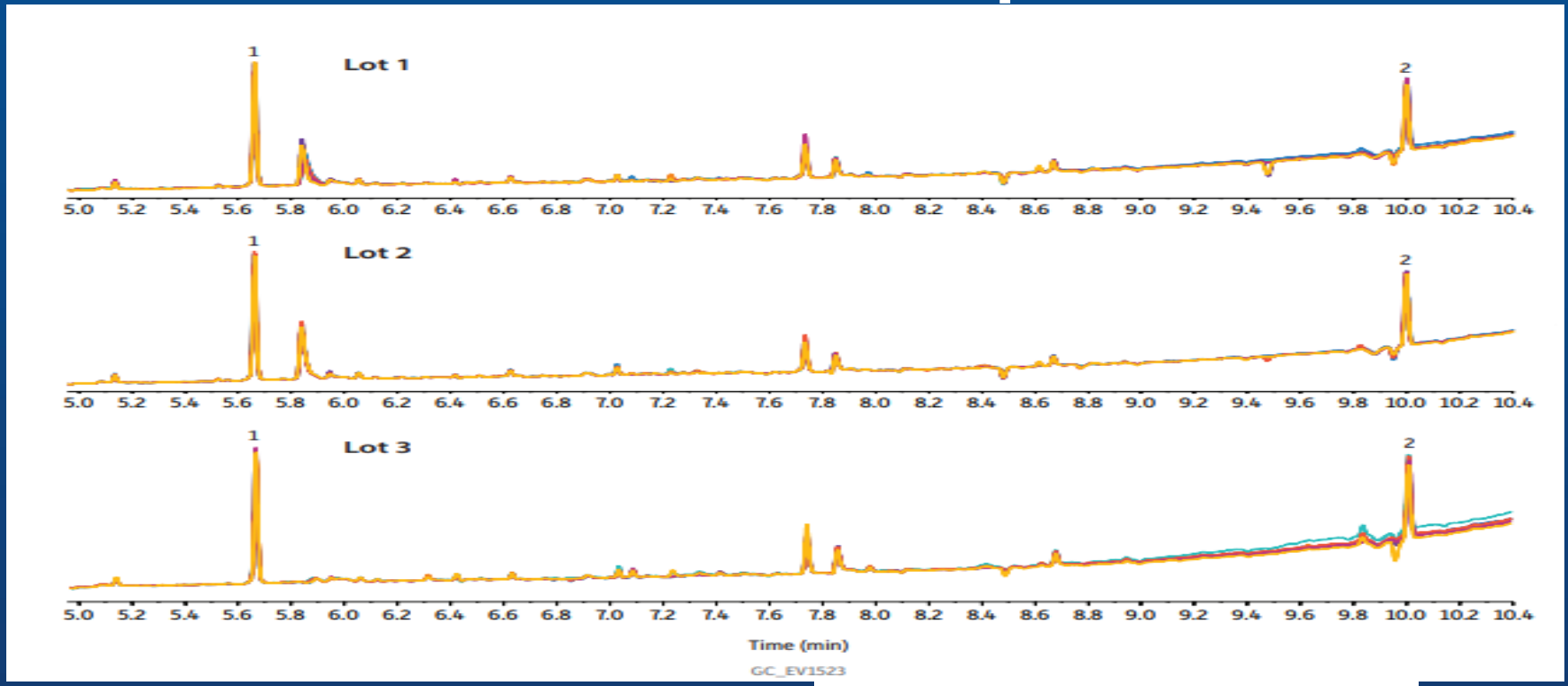
EPA 8081 Pesticides Extract Cleanup

Notice easy pass for trichlorophenol breakthrough requirement

Compound	Concentration (ng/mL)	Average Recovery (%)	%RSD
TCP	100	<1*	-
TCMX	20	98	1.8
Hexachlorobenzene	5	89	1.3
alpha-BHC	5	100	1.4
gamma-BHC	5	99	1.3
beta-BHC	5	102	3.6
delta-BHC	5	103	4.6
Heptachlor	5	91	4.1
Aldrin	5	98	1.8
Heptachlor epoxide	5	103	1.1
gamma-Chlordane	5	105	3.4
alpha-Chlordane	5	96	2.0
4,4'-DDE	10	99	1.6
Endosulfan I	5	101	2.3
Dieldrin	10	98	2.6
Endrin	10	97	5.1
4,4'-DDD	10	97	2.9
Endosulfan II	10	99	3.9
4,4'-DDT	10	97	2.2
Endrin aldehyde	10	92	4.6
Methoxychlor	50	95	4.1
Endosulfan sulfate	10	100	2.1
Endrin ketone	10	98	1.3
DCB	20	101	2.4

*Meets requirement of <5% breakthrough.

EPA 8081 Pesticides Extract Cleanup



Overlay of eight samples for each lot

Peaks	tR (min)
1. 2,4,5,6-Tetrachloro-*m*-xylene	5.65
2. Biphenyl, decachloro-	10.00

Column	Rtx-CLPesticides, 30 m, 0.32 mm ID, 0.32 µm (cat.# 11141)
Standard/Sample	2,4,5,6-Tetrachloro-meta-xylene (cat.# 32027) Decachlorobiphenyl (BZ #209) (cat.# 32029)
Diluent:	Hexane
Conc.:	5 ng/µL
Injection	
Inj. Vol.:	4 µL pulsed splitless
Liner:	Topaz single taper inlet liner w/wool (cat.# 23303)
Inj. Temp.:	250 °C
Pulse Pressure:	35 psi (241.3kPa)
Pulse Time:	0.74 min
Purge Flow:	50 mL/min
Oven	
Oven Temp.:	70 °C (hold 0.5 min) to 320 °C at 25 °C/min (hold 2 min)
Carrier Gas	He, constant flow
Flow Rate:	3.5 mL/min
Detector	Micro-ECD @ 330 °C
Make-up Gas Flow Rate:	60 mL/min
Make-up Gas Type:	N_2
Data Rate:	50 Hz
Instrument	Agilent 7890B GC
Sample Preparation	Conditioned a Resprep FL + CarboPrep Plus SPE cartridge (cat.# 28899) by adding one cartridge volume of hexane:acetone (90:10) and letting it stand for five minutes before drawing the solvent down to frit level. Then, 1 mL of sample extract was loaded onto the cartridge and eluted with 9 mL of hexane:acetone (90:10).

Conclusion

The combined effects of both Florisil and GCB in a serial format provide remarkably increased removal of performance deteriorating coextracted matrices while still retaining the attributes and solvent elution ability of a standard Florisil cartridge thereby enabling better quality data and greater profitability

Questions?