

Increasing Sample Throughput in Pesticide Residue Analysis Using A Geno/Grinder Extractor and LC/MS/MS Detection-Part II

Joseph P. McClory

Robert M. Henze

Crop Protection

E.I. DuPont de Nemours and Co., Inc.

Stine-Haskell Research Center

Newark, Delaware

OBJECTIVES

- **Use Geno/Grinder to double the number of samples analyzed per day.**
- **Verify with ^{14}C treated samples that extraction with Geno/Grinder is equivalent to tissuemizer probe.**
- **Share recent results from Independent Lab Validation, Animal Tissue and Bee Method transfers.**

Method Development For Experimental Compound, DuP-1

Extraction Procedure

- Extract twice with ACN/H₂O in Geno/Grinder for 2 minutes at 1200cy/min.
- Dilute 1ml of extract to 5ml with H₂O(pH 2.5)
Filter thru SAX SPE, Collect Extract.
- Dilute to 10.0ml, Filter thru PTFE Membrane into LC vial.
- Analyze by LC/MS/MS (API 5000)

Geno/Grinder



Check Out Under The Hood!



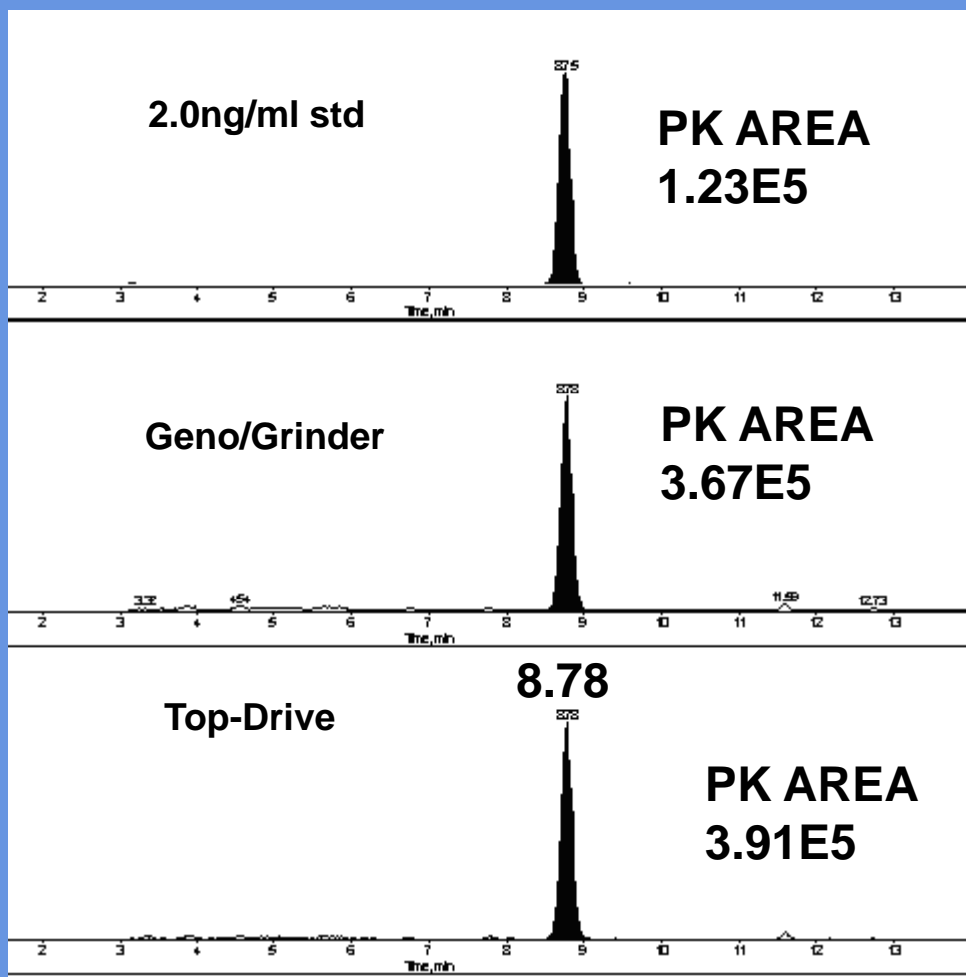
Minimize Contamination and Cleanup Time Between Sets



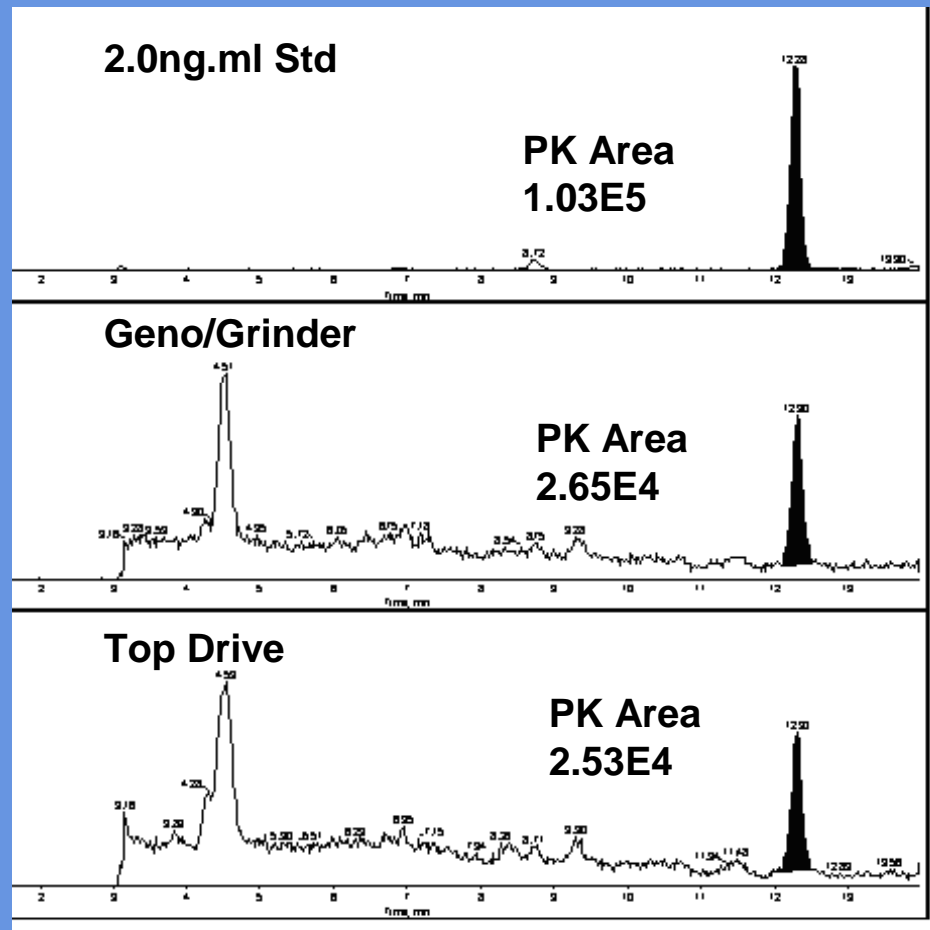
Comparison of Counts Between Residue and Metabolism Methods

COMMODITY	% EXTRACTED		RESIDUE/ METABOLISM (%)
	TOP DRIVE (METABOLISM)	GENO GRINDER® (RESIDUE)	
Lettuce	95	95	100
Beet Foliage	93	89	96
Wheat Grain	67	60	89
Wheat Hay	83	79	94

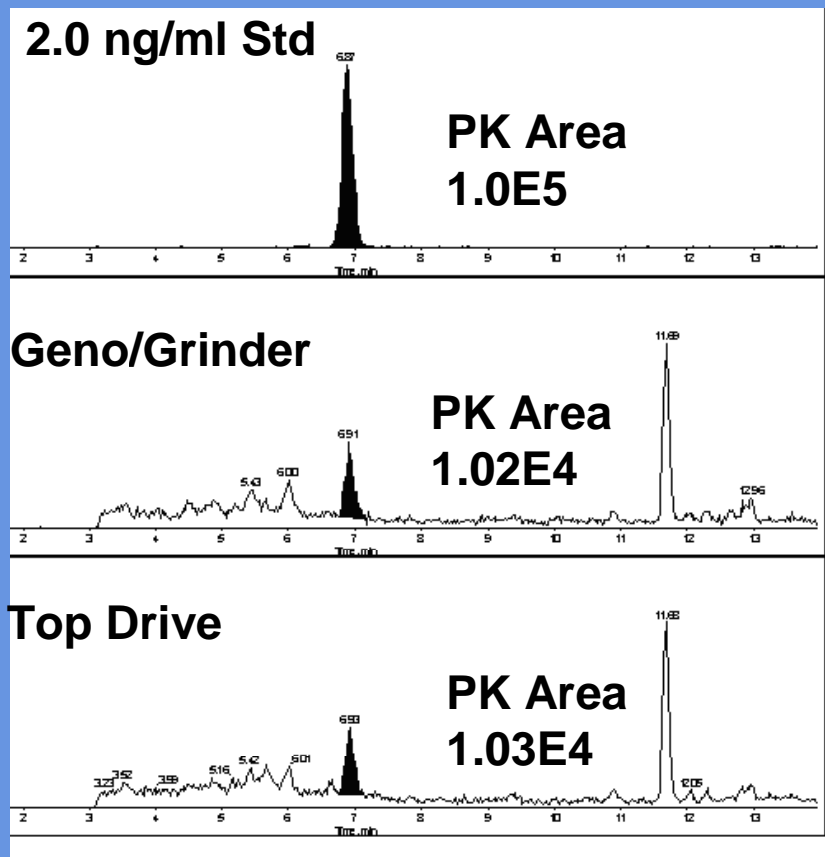
DuP-1 WHEAT GRAIN



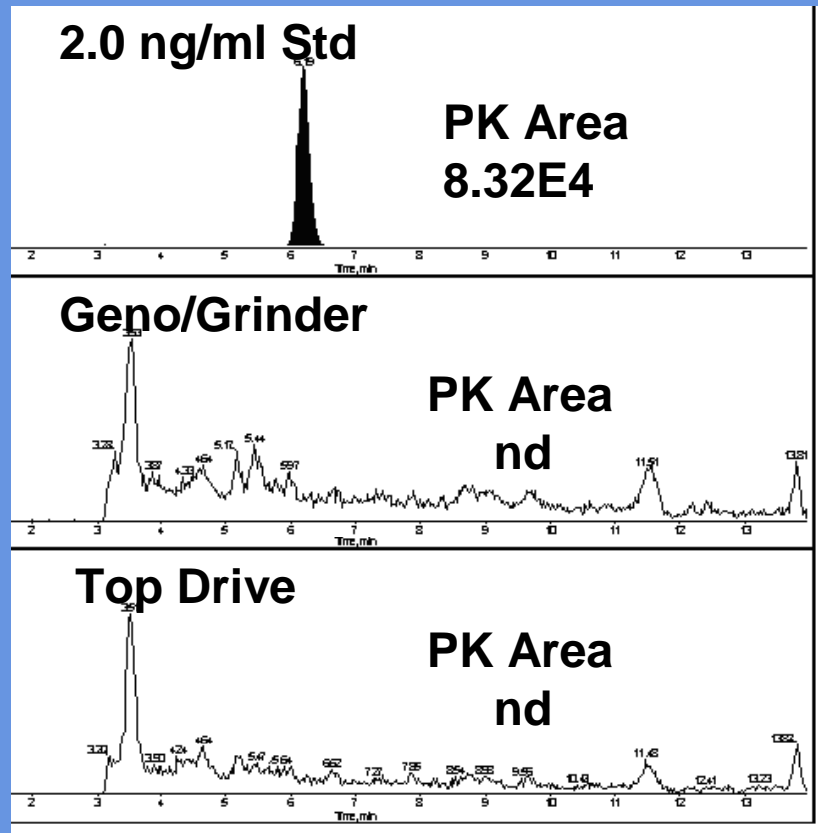
MET-D WHEAT GRAIN



Met-B WHEAT GRAIN



Met-A WHEAT GRAIN



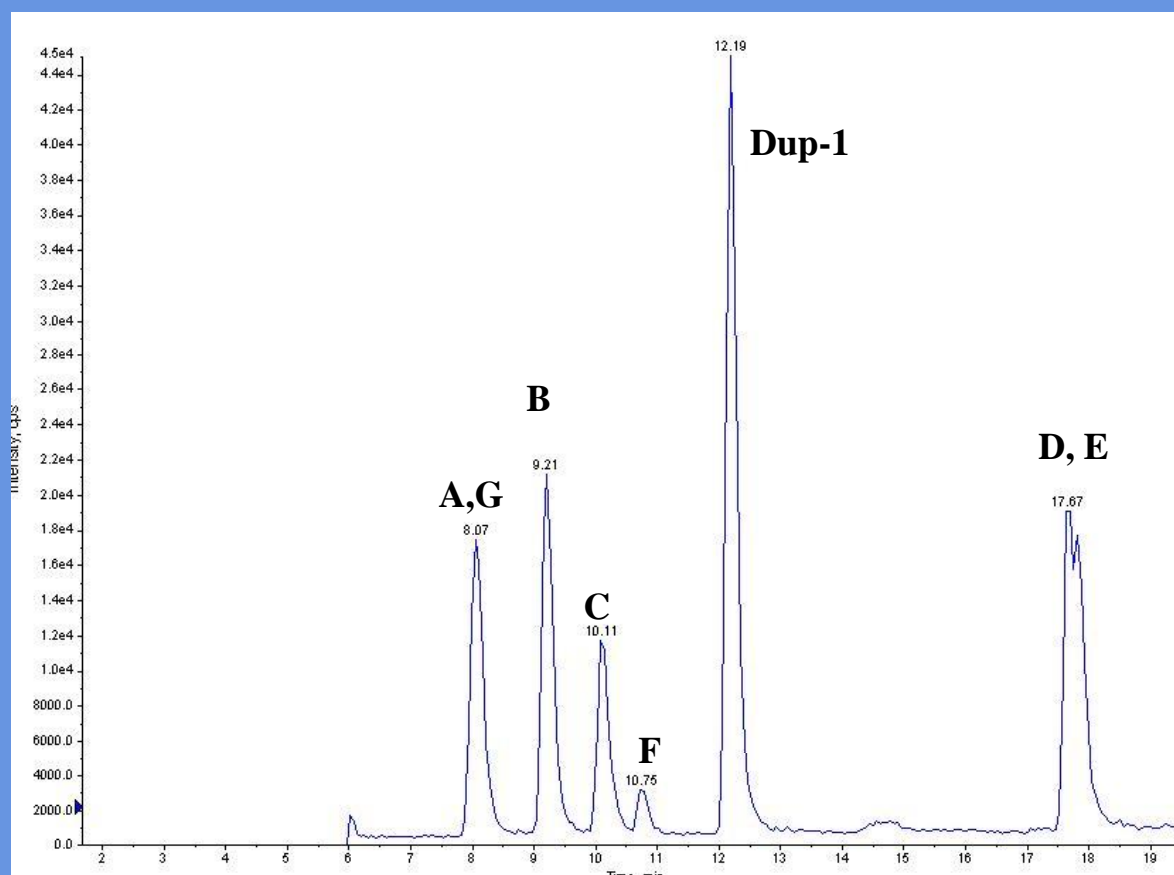
Crop and Processed Fractions ILV

MATRIX	MET -A	MET -B	MET -C	MET -F	DUP -1	MET -D	MET -E
ALMOND							
Average	100	111	105	94	106	95	98
Std Dev	6.3	8.6	6.3	11	5.9	14	6.0
Tomato Paste							
Average	83	84	91	92	88	97	90
Std Dev	3.7	3.9	6.3	4.2	2.0	8.2	5.5

DuPont Recoveries Animal Tissues

MATRIX	MET -A	MET -G	MET -B	MET -C	MET -F	DUP -1	MET -D	MET -E
MUSCLE								
Average	90.0	92.5	92.2	92.5	94.2	94.7	89.1	91.5
Std Dev	4.71	4.67	4.96	6.28	5.37	3.30	3.18	4.38
LIVER								
Average	99.5	91.5	91.4	94.3	97.1	90.4	86.8	81.0
Std Dev	5.72	2.55	2.55	3.30	5.49	2.63	7.93	2.75
WHOLE MILK								
Average	88.4	100.	99.6	88.6	97.1	96.6	88.5	86.8
Std Dev	3.20	5.72	3.24	12.1	7.05	4.65	6.00	5.61
EGGS								
Average	83.1	87.3	89.6	89.6	93.6	85.2	90.7	87.7
Std Dev	2.96	7.26	21.2	9.22	14.8	4.61	11.2	15.0

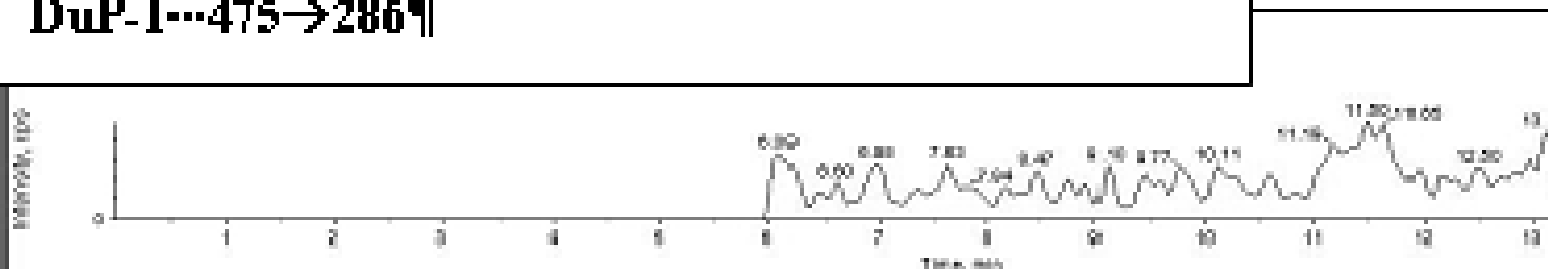
Method Development For Experimental Compound, DuP-1



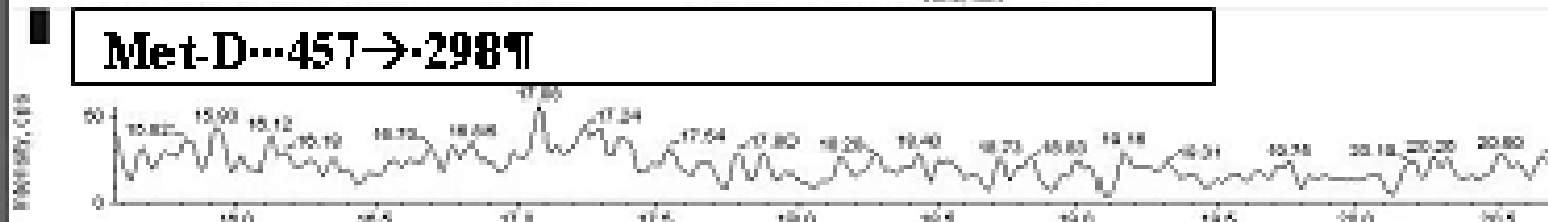
Control Muscle

||

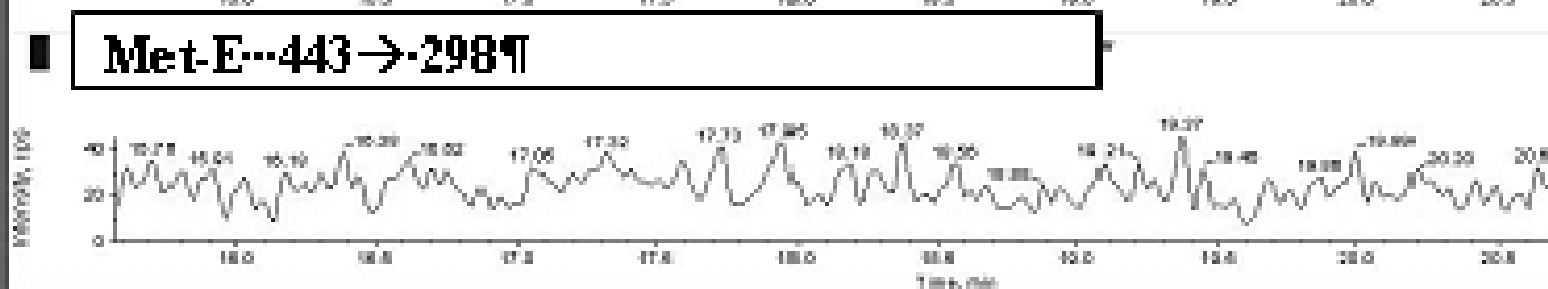
DuP-1...475 → 286



Met-D...457 → 298

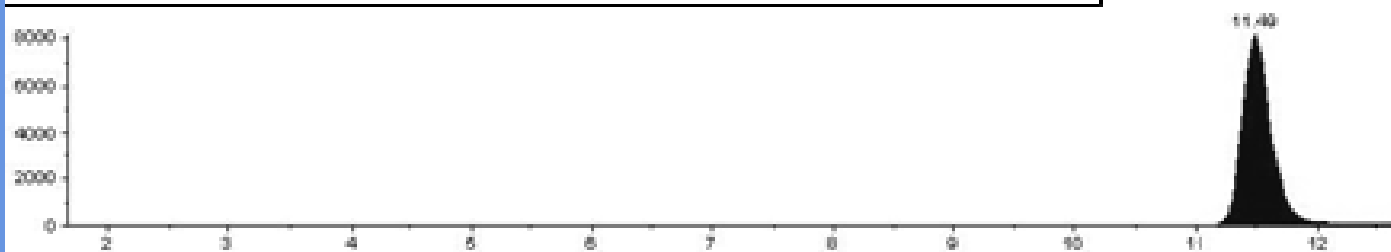


Met-E...443 → 298

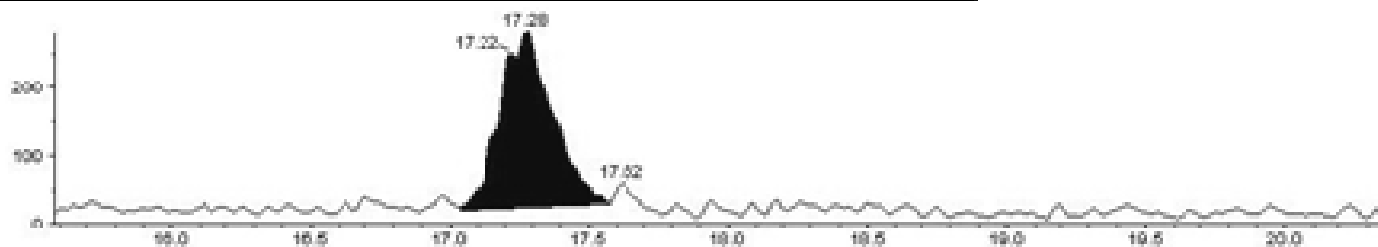


LOQ MUSCLE

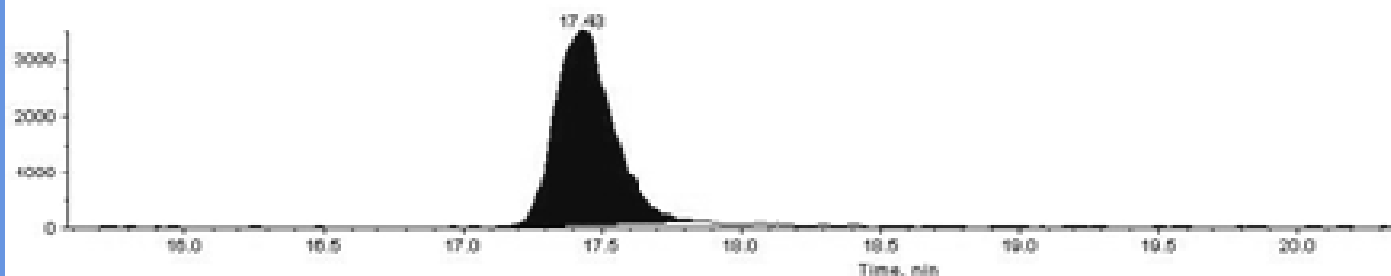
DuP-1...475 → 286 ¶



Met-D...457 → 298 ¶



Met-E...443 → 298 ¶



CRL Recoveries Animal Tissues- Method Validation

MATRIX	MET -A	MET -G	MET -B	MET -C	MET -F	DUP -1	MET -D	MET -E
WHOLE MILK								
Average	91.8	98.7.	87.5	85.1	86.4	86.0	82.4	74.2
Std Dev	5.0	5.2	4.7	5.1	5.5	4.8	3.3	3.4

CRL Recoveries Animal Tissues- Method Tryout

MATRIX	MET -A	MET -G	MET -B	MET -C	MET -F	DUP -1	MET -D	MET -E
MUSCLE								
Average	89	103	87	97	92	92	79	71
LIVER								
Average	89	106	92	97	95	96	54	46

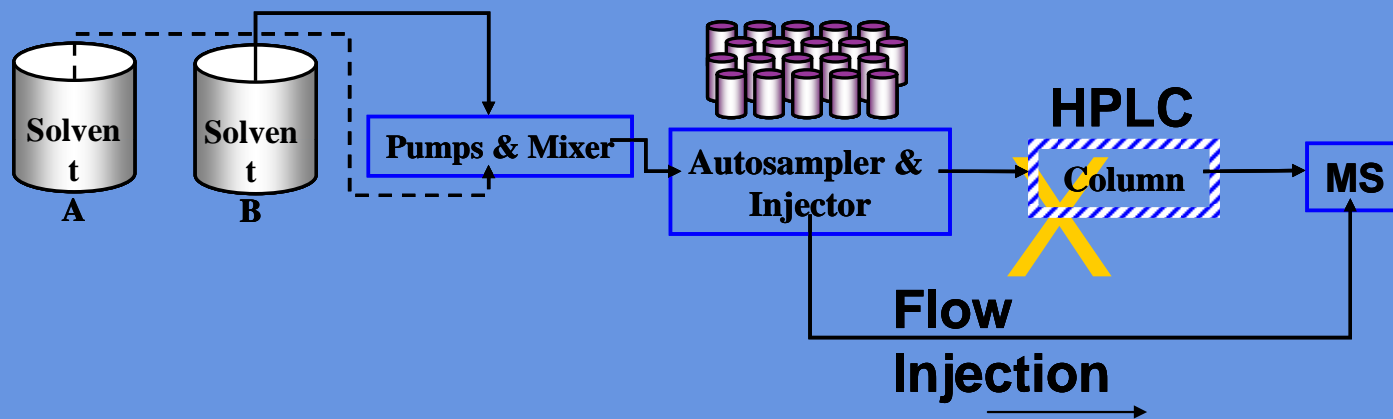
CRL Recoveries Pollen- Method Tryout

MATRIX	MET -A	MET -G	MET -C	MET -F	DUP -1	MET -D	MET -E
POLLEN							
Average	87	82.	81	82	83	80	70

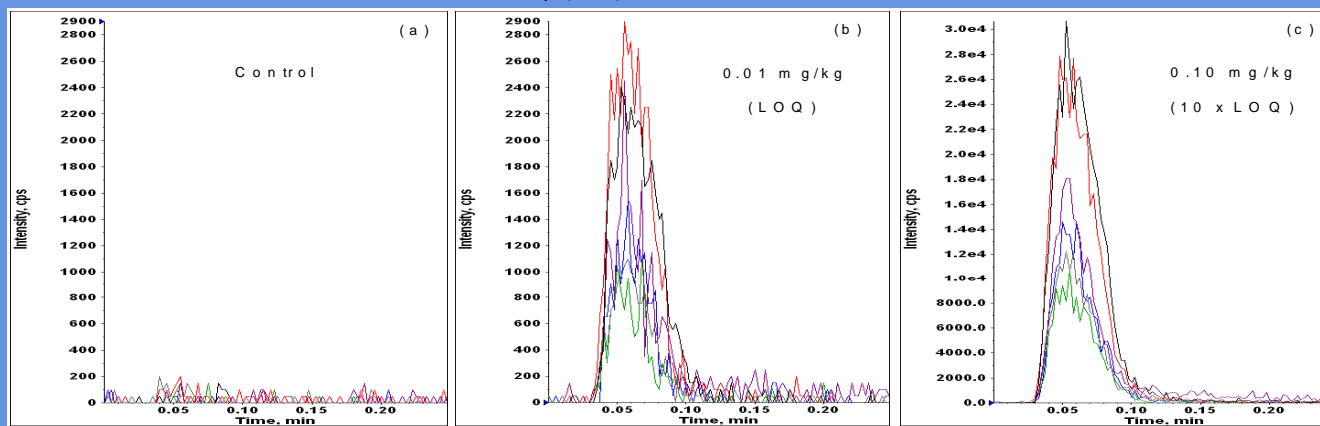
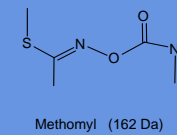
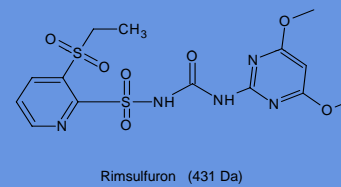
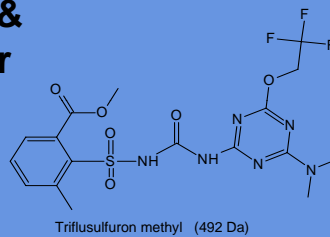
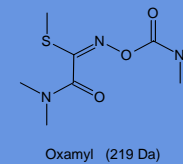
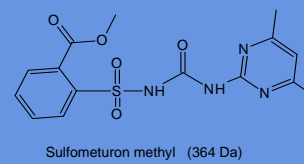
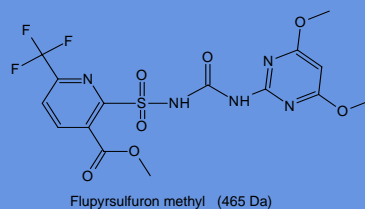
S.C. Nanita, A.M. Pentz, F.Q. Bramble

Anal. Chem. 2009, vol. 81, pp. 3174-3786

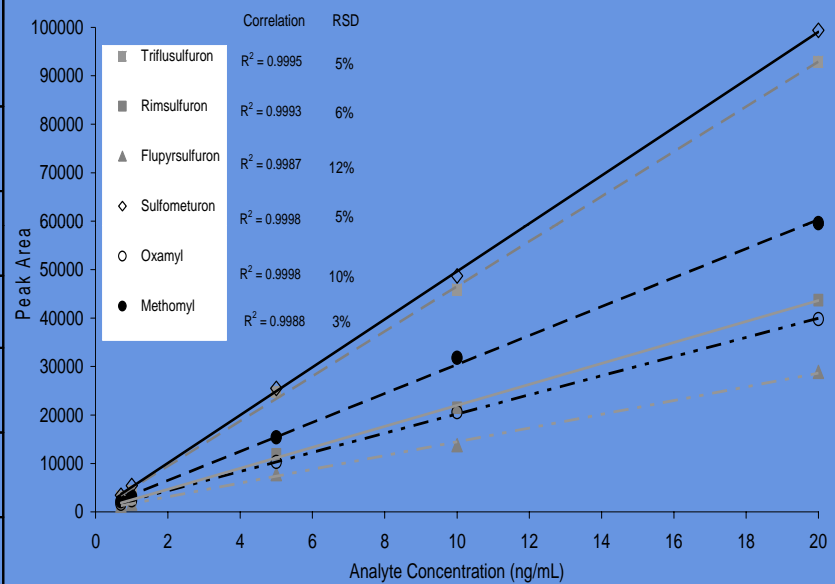
Flow Injection (FI)



Compounds tested & ion chromatograms for corn samples



ALL CROPS MATRICES TESTED		
ANALYTE	% RECOVERY	SAMPLES
Triflusulfuron-methyl	113 ± 13	14
Rimsulfuron	103 ± 9	14
Flupyrsulfuron-methyl	106 ± 12	14
Sulfometuron-methyl	109 ± 12	14
Methomyl	99 ± 13	14
Oxamyl	99 ± 15	14



- SPE purification performed with ENV cartridges
- Instrumental analysis throughput: ~ 55 injections per hour

CONCLUSIONS

- Extraction with Spex Geno/Grinder versus tissuemizer probe increased the typical set size from 8 to 24 samples.
- Extraction efficiency experiment with ^{14}C radio-labeled crops verified that Geno/Grinder is equivalent to tissuemizer probe.
- Method development is not over until the method is transferred and the Independent Laboratory Validations (ILV) are complete.

ACKNOWLEDGEMENTS

DuPont- John May, Sergio Nanita, Jim Stry

SPEX- Keith Tucker

Charles River Laboratories (Scotland)

Scott Cairns, Joseph Kinney, Chris Lowrie, Clive Ward

ABC Laboratories (Missouri)

A.G. Gant, Del Koch, Carol Rodgers, Emily Shepherd

