# MXSUSUOUSUO(5)

## Optimal Separation of Polar Anionic Pesticides From Fruits and Vegetables with Unique HPLC Column Selectivity

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## Introduction

Analysis of polar pesticides presents multiple challenges including adequate retention, separation of critical pairs, and reproducibility, to name a few. In addition, food matrices can add additional challenges due to the presence of complex matrix components including pigments, fats, and sugars that can interfere with the analyte of interest.

Often, polar, anionic analytes like Glyphosate will utilize QuEChERS or QuPPE sample preparation techniques, followed by HILIC LC-MS/MS methods for chromatographic retention and separation. Historically, these methods are not user friendly, and lack reproducibility necessary for a commercial application.

In this study, we are presenting a unique HPLC selectivity that provides optimal separation of various anionic polar pesticide classes including Glyphosate, Chlorate, Perchlorate, Ethephon, Phosphoric Acid-based pesticides, and N-Ac-Glu pesticides. The study demonstrates robust polar pesticide analysis from real sample matrix.

## **Materials and Methods**

### **Sample Preparation: LC-MS/MS Conditions QuPPE-PO Method Column:** Venusil® 3 µm HILIC Weigh Sample Homogenate into 50 mL Centrifuge Tube Dimension: 100 x 2.1 mm Fresh fruits and vegetables (with high water content): 10 g ± 0.1 g Part No.: VH931002-0 reviously re-hydrated dry fruit: e.g. 13.5 g ± 0.1 g (containing 5 g sample Dry commodities (e.g. herbs): 2 g ± 0.02 g Injection: A: 0.2 % Formic Acid in Water Adjust Water Content of Sample to 10 mL **Gradient: Time (min)** (Mandatory for matrices w. <80 % water. If no IL-IS used mandatory for ALL matrices) . +10 mL water to 2 g of dried mint; +2 mL water to 10 g potato +3.5 mLwater to 10 g garlic Add 100 µL Isotopically-labeled Internal Standard (IL-IS mix) Add Extraction Solvent (10 mL Methanol containing 1 % Formic Acid) Flow Rate: 0.3 mL/min Shake Thoroughly for 1 min to 15 min for Dry Commodities Injection: 0.5 or 1 µL Preferably Freeze-out Extract until Completely Frozen **Temperature:** 40 °C e.g. >90 min at -18 °C or ca. 30 min at -80 °C **Detector:** SCIEX® 7500 Centrifuge (5 min at >3,000 g but Preferably >10,000 g);

Preferably cryogenic centrifugation (e.g. at -10 °C)

centrifuge not refrigerated, proceed with centrifugation and following step to avoid redissolvation of matrix)

dSPE to Remove Lipids for High Oil Content Samples:

at  $\leq$  -10 °C and  $\geq$  20 min)

Transfer 4 mL raw extract into a tube containing 200 mg

3-sorbent, shake for 1 min and centrifuge (>3,000 g for 5 n

Withdraw Supernatant and Filter in into a Plastic Autosampler Vial

(Use syringe filter of 0.2 µm pore size; e.g. H-PTFE)

(Plastic vials are recommended as some compounds tend to interact with glass) (Withdraw cold supernatant quickly after centrifugation to avoid that matrix components redissolve)

LC-MS/MS and IC-MS/MS Analysis

## Sample Details

1. Matrix Extracted following QuPPe Method: Grain\*, Kiwi\*, Zucchini\*, Rocket\*\*, Soy\*\* 2. Raw Matrix, 10ppb Spike, 100ppb Spike

B: 0.2 % Formic Acid in Methanol

Different Matrices Dilution depending on matrix composition (1:4\* or 1:10\*\*)

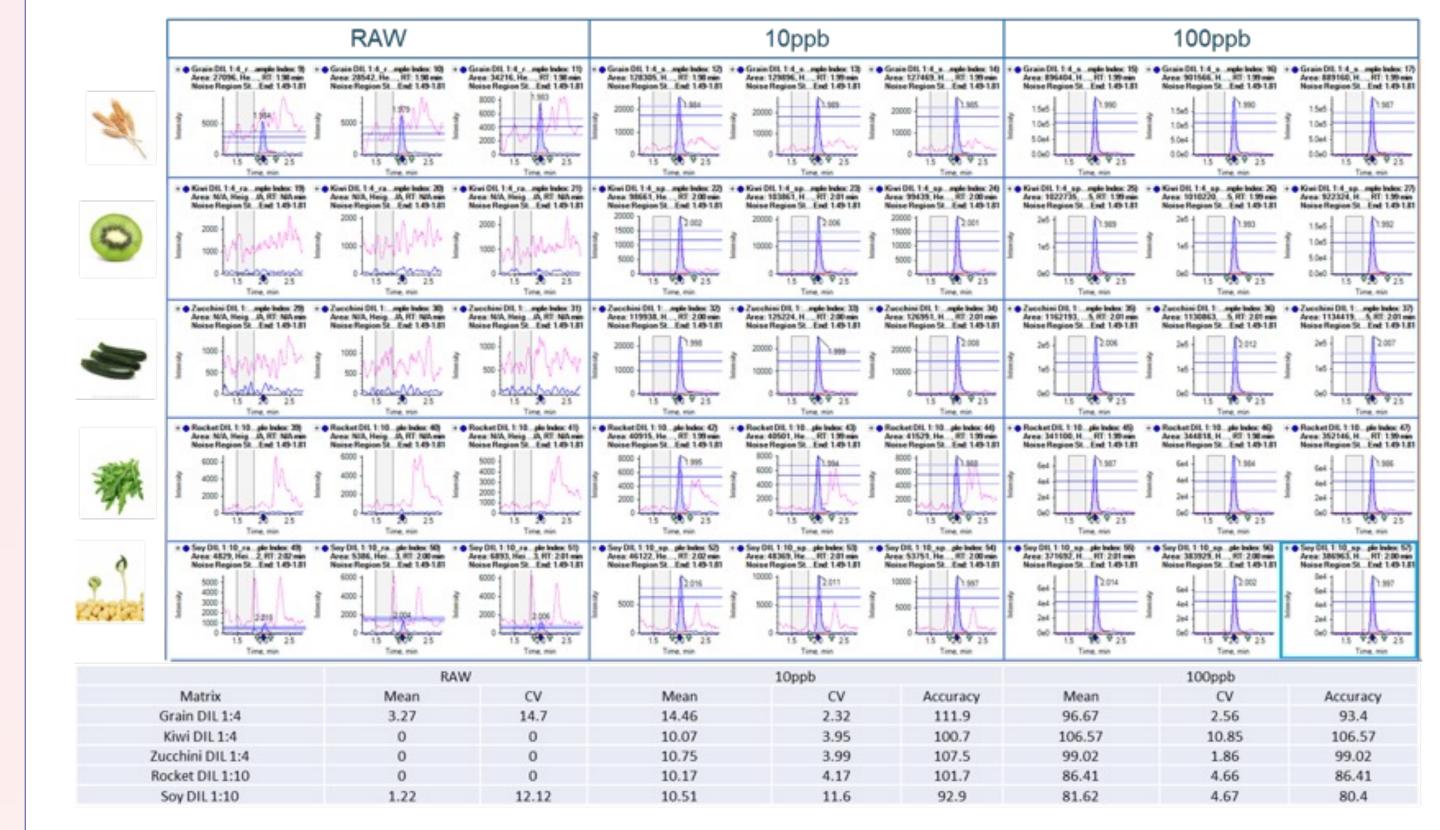
4. Each sample injected in triplicate

## Results

Figure 2. Real Matrix Analysis of Polar Pesticides.

## **Glyphosate**

Chlorate



Ethephon



			RAW			10ppb		100ppb		
17)		* • Grain DH. 1-4 r. ample Index 3) Area: 593319, H, RT 2:90 min Noise Region St. End 3:30-4:21	Grain DH. 1:4 r mple belox: 10) Area: 571554, H RT: 2:90 min Noise Region St End 3:93-4:21	Grain Dil. 1:4_r_asple Index: TI) Area: 553413, H RT: 2:91 min Noise Region St. End: 3:50-4:21	+ • Grain Dil. 1-4, sngle Index: 12) Area: 602346, H RT: 2-90 min Noise Region St End: 330-421	Grain DIL 1:4, smple Index: 13)     Area: 644916, H, RT: 2:30 min     Noise Region St End 3:33-4:21	Grain DIL 1:4, s spic leder: 14)     Arex: 581055, H RT: 2:30 min     Noise Region St End: 1:33-4:21	+ • Grain DIL 1-4 anple ledex: 15) Area: 1077016,5.RT: 2:89-sin Noise Region St. End: 330-421	Noise Region St., End 3:50-4:21	Grain OH. 1-4 s. reple index: 17)     Avex: 1183850, S. RT: 2.89 min     Noise Region St. End 3:30-4:21
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13				Kwi DIL 1:4_ns_mple index: 21)     Area: NA, Heig_ JA, RT: NA.min     Noise Region St. End: 3:90-4:21			Kiwi DH. 1:4 npmple Index: 24) Area: 758113, He, RT: 2:89 min Noise Region St End: 3:93-4:21	+ • Kiwi Dil. 1:4, spngle Index: 25) Area: 624663, it, RT: 2.88 min Noise Region StEnd: 3:50-4.21		Wiwi DR. 1:4, apmple Index: 27) Area: 634544, H, RT: 2.88 min Noise Region StEnd 3:90-4.21
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13		Area: 11809, He, RT 2.89 min Noise Region St., End 3:33-4.21	◆ Zucchini DH. 1: .mple Index 303 Area: 13505, He RT 2.83 min Noise Region St. End 133-4.21	Zucchini DB, 1:mpln Index: 31)     Area: NIA, Heig:D, RT NIA.min     Noise Region StEnd: 3.90-4.21	+ • Zucchini DB, 1:mple Index: 32) Area: 77165, He, RT 2.89 min Noise Region St., End: 330-421	+ • Zucchini Dtl. 1 . mgle Index 33 Area 74984, He RT 238 min Noise Region St. End 333-421	+ © Zucchini Dtl. 1 reple Index 36) Acres 82924, He RT 2.89 min Noise Region St. End 133-4-21	Area: 642130, H, RT 2.89 ean Noise Region St. End 3.50-4.21	+ • Zucchini DE. 1mpln Index: 30) Area: 617105, H, RT 250 min Noise Region St. End: 350-421	+ © Zucchini Dt. 1: .mple index: 37) Area: 599851, H RT 2:90 min Noise Region StEnd 3:93-4:21
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	<b>李</b>	2e5 1e5 0e0 2472 25 V0.09 15 Time, min	2485 040 23 V 10 35 Time, min	245 2574 2574 35 Time, min	265 165 060 25 9 35 Time, min	265 165 260 25 V 10 15 Time, nin	3e5 3e5 0e0 25 90 19 15 Time, min	1.5e5 1.0e5 5.0e4 0.0e0 2.5 V 5 3.5 Time, min	286 286 286 286 286 Time, nin	2852 0e0 25 9 59 15 Torse, min
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		cchini DIL 1:4	2.12	10.61	12.63	3.43	105.1	99.37	4.45	97.25
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## **Phosphonic Acid**

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	+ © Rocket Dt. 1: 10 ple Index: 20) Area: 61354, He RT: 2:87 min Noise Region St. End 3:33-4:21	Rocket Dt. 1: 10 ple ledex: 40)     Area: 63068, He RT 2:85 min Noise Region St. End: 333-4-21	<ul> <li>Rocket Dfl. 1:10 _ple index: 41)</li> <li>Area: 60213, HeRT; 2.57 mm</li> <li>Noise Region St. End: 350-421</li> </ul>	+ • Rocket Dil. 1:10 gle Index 43) + Area: 91712, No RT 2.88 ean Noise Region St End 330-421	Rocket Dt. 1: 10. ple Index: 43)     Area: 89504, He RT 2:88 min     Noise Region St. End 3:30-4:21	Rocket DIL 1: 10 ple licke: 46) Area: 94410, He RII 2:88 min Noise Region St., End 3:93-4:21	+ • Rocket Dll. 1:10. ple index: 45) Area: 272972; H. RT: 2.06 min Noise Region St. End: 333-421	+ • Rocket Dll. 1:10 _ple index 40) Area: 260622, HRT 2:36 min Noise Region StEnd 3:30-421	Rocket Dil. 1: 10 ple Inde Area: 263373, H, RT: 2:1 Noise Region St. End 3:1
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0	<ul> <li>Soy Dil, 1:10, na., ple Index; 48)</li> <li>Acce; 23473, He., 80: 2:30 min</li> <li>Noise Region St., End; 3:33-4:21</li> </ul>	<ul> <li>Soy Dill, 1:10_ra_ple Index 50)</li> <li>Area N/A, Heng_JA, RT. N/A min Noise Region St. End 133-4.21</li> </ul>	<ul> <li>Soy Dil, 1: 10_ra_ple tuber 51)</li> <li>Area: 18214, NoRT: 2:90 min</li> <li>Hoise Region St. End: 3:90-421</li> </ul>	Area: 47277, Re RT: 231 min Hoise Region St. End: 330-421	<ul> <li>Soy DR, 1 10, sp., ple Index SS;</li> <li>Area: 37175, He., RT 2:31 min</li> <li>Noise Region St. End 3:34:421</li> </ul>	<ul> <li>Soy Dil, 1:10, sp., ple Index: 54)</li> <li>Area: 45753, He., 80: 2.89 min</li> <li>Noise Region St., End: 3:33-4:21</li> </ul>	<ul> <li>Soy DH. 1: 10_spple Index: 50)</li> <li>Area: 232976, H RT: 2:90 min</li> <li>Hoise Region St. Entl 3:90-421</li> </ul>	Soy Dtl. 1: 10 sp. ple teles: 50)     Area: 250499, H RT: 2:90 min.     Noise Region St. End: 3:90-4:21	Area: 232864, H., RT 22 Noise Region St., End 33
especial and the second	20000 2964 0 25 <del>V 1</del> 00 35 Tene, min	15000 10000 5000 0 25 \$10 35 Time, min	20000 2500 25 Time, min	20000 25 00 35 Time, min	20000 2508 35 Time, min	3ed 2852 (ed 25 V 15 GP 15 Tens, min	10e5 50e4 2900 25 P 65P 35 Time, min	1545 1045 235 104 25 35 Time, min	5.0e4 2.00 0.0e0 2.5 0 1.0e Time, min
		0.0	w		10ppb			100ppb	
		TO-			CV	Accuracy	Mean	CV	Accuracy
	Matrix	Mean	CV	Mean					
	Grain DIL 1:4	Mean 101.2	2.39	111.49	5.31	102.9	202.46	3.69	101.26
	Grain DIL 1:4 Kiwi DIL 1:4	Mean 101.2 1.76	2.39 45.7	111.49 11.69	5.31 3.88	102.9 99.3	98.34	5.01	96.58
Z	Grain DIL 1:4	Mean 101.2	2.39	111.49	5.31	102.9			

Conclusion

Results

RT Stability

Discussion

Figure 3. Retention Time Stability of Glyphosate.

pesticides. Reproducible retention, optimal selectivity, and precise and accurate results prove that the Venusil HILIC column is the ideal choice for polar pesticide analysis. In addition to providing consistent retention, the Venusil HILIC column offers short run time of less than 6

Venusil HILIC is a versatile HPLC column selectivity that provides enhanced retention and selectivity for polar

minutes for high throughput analysis.

00 <del>|</del>

2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35

Column selectivity plays an important role in providing enhanced chromatographic resolution for critical pairs. In

addition, retention of extremely polar analytes are very challenging. In this study, we present optimal separation of polar pesticides on a Venusil HILIC HPLC Column, which is a versatile selectivity with amide functionality

that can be run in normal, reverse and HILIC mode. In this study, we have utilized the polar interactions in the

Venusil HILIC stationary phase in reverse phase mode to obtain enhanced retention of polar pesticides. The chromatogram of standards on a SCIEX 7500 shows excellent retention and selectivity for polar pesticides

Optimal concentration of 0.2% Formic Acid in the mobile phase provided a great balance of peak shape and retention. Traditional reverse phase columns do not retain analyte like Glyphosates, which can fall in the ion suppression zone in real samples and hence can show false positive or negative. With the Venusil HILIC column,

enhanced polar selectivity from the un-endcapped silica base and from the Amide ligand provides excellent retention which is evident from retention factor for polar pesticides that ranges from 0.7 to 6.6.

Real samples like Grains, Kiwi, Zucchini, Rocket, and Soy were analyzed with this method followed by spiking them with a known concentration of polar pesticides. The method proved to be precise, robust, and accurate for

the polar pesticides (**Figure 2**). In addition, retention time stability of Glyphosate is presented as a representative in **Figure 3**. Consistent and robust retention of Glyphosate proves that the Venusil HILIC column is a robust

Unlike traditional HILIC methods, the method demonstrated here provides stable retention in reverse phase by utilizing polar interactions from the stationary phase. Thus, the developed method is easy to adopt in labs running routine polar pesticide analysis.

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stationary phase selectivity for the analysis of polar pesticides by LC-MS/MS.

Comparative separations may not be representative of all applications.

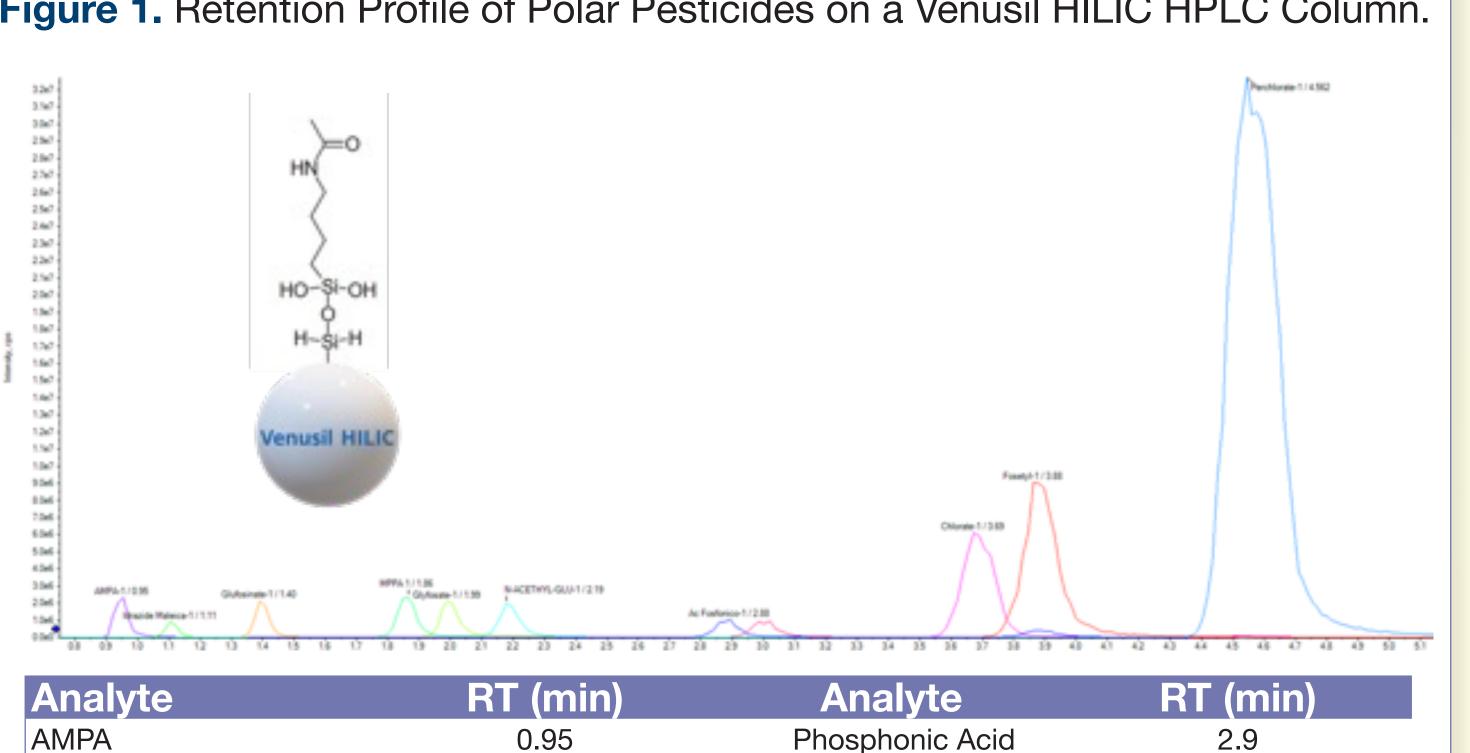
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## Results

Glyphosate

N Acetyl Glu

Figure 1. Retention Profile of Polar Pesticides on a Venusil HILIC HPLC Column.



Ethephon

Perchlorate

## **Percholrate**

		RAVV			10ppb			100ppb	
	+ • Grain DE, 1-4_r angle below 3) Area: 384185; M., RT 4-54 min Noise Region St. End 2.82-3.06	Grain DE. 1.4 r. agle Index: 10) Area: 342728, H., RT 4.54 min Noise Region St., End 2.82-3.06	Area: 336601, H RT 4.55 min Noise Region St End 2.82-3.06	Area 8610731 6 RT 4.54 min Noise Region St. End 2.52-3.06	Area: 8509763,6, RT: 4.55 min Noise Region St. End 2.82-3.06	+		+ • Grain Dtt. 1:4. s. replic below: 10) Area: 75577083 RT: 4:50 min Noise Region St. End: 2:82:106	Grain DH. 1-4 s. angle Index: 17 Anna: 75277435
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	+	Avea 476624, H., RT 457 min None Region St., End 2,823.06	+ • Kiwi Dtl. 1:4 ranple Index 21) Area 436362 HRT 456-nie Moise Region StEnd 232-306	+ • Kiwi Dtl. 1-4 ap. mple Index: 22) Area: 1946(2988, RT 4.57 min Noise Region St. End 2.82-1.06	+ • Kiwi Dit. 1 4. spepie Index 23) Area: 10366879, RT 4.57 min Neise Region St. End 2.62-3.06	+ • Kiwi DIL 1-4 np. mple Index: 20 Area: 10355527 RT 4.57 min Name Region St. End 2.82-3.00		+ • Kwi DIL T-4 ppmpin Index: 20) Area: 85934655, RT: 4.56 min Noise Region St End: 2.82-3.06	+ • Kimi Dil. 1-4 np. argle Index 27 Area 81029876. RT 456 min Noise Region St. End 2.82-3.0
0	2e4 2e4 4D Time, min	5ed 2566 3e4 3e4 3e4 3e4 3e4 3e4 3e4 5e0 4.0 Q 950 Time, min	5e4 4564 3e4 3e4 40 40 40 Time, min	1.0e6 5.0e6 0.0e0 4.0 4.9 90 Time, min	1.0e6 5.0e6 0.0e0 4.0 V 4.9 V0 Time, min	1.0e6 5.0e5 0.0e0 4.0 V 4 V V V V V V V V V V V V V V V V V	5e6 49 49 90 Time, min	5e6 0e0 49 49 96 Time, min	5e6 49 49 90 Time, min.
	* • Zucchini DE, 1: _mple Index: 29) + Area: 823302, H, RT: 4.57 min	Area: 815510, H, RT: 4.56 min	Area: 812136, H RT: 456-min	Area: 10317363 RT: 4.57 min.	Area: 10852632, RT: 4.57 min	Area: 10419705,, RT: 4.58-min		Area: 86728533, RT: 4.58 min	* • Zucchini Dtl. 1 ngle buku: 37) Area: 83299193 RT: 4.57 min
*	Noise Region St. End 2.82-3.06 1 0-6 5 5-64 0 5-0 4.9 40	Sed 40 40 40 Tome, min	Noise Region St. End 280-306	Noise Region St. End 2.80-3.06	1.5e6 6.5e6 0.5e0 4.506	1.0e6 1.578 0.0e0 4.0 4.0 50 Time, min	Noise Region St. End 2.83-106	Noise Region St. End 280-306	Noise Region St. End 2.83-3.00
	Area: 9065834,5, RT: 4.51 min	Rocket Dil. 1:10 ple loder 40) Area: 9043334 5 RT 4:50 mm	Pocket DIL 1:10 ple leder 41) Area: 8343547 5 RT 4.50 mm	Area: 11372373,, RT: 452 min	Area: 11352982,, RT: 4.51 min	+ • Rocket Dtl. 1:10ple Index: 44) Area: 11445289RT 4.51 min	Area: 30113374 RT-451min	Area: 30380037 RT: 450 mm	+ • Rocket DIL 1:10. ple ledec 47) Area: 29718714. RT 4:51 mm
獭	Hoise Region St. End 2.82-3.86	Neine Region St. End 2.82-3.00 865 665 665 665 665 665 665 665	Moise Region St. End 230-306 Sec. Sec. Sec. Sec. Sec. Sec. Sec. Sec.	Noise Region St. End 2.82-3.06 1.066 5.060 4.0 9 4.9 9.0 Time, min	S De5 0 250 40 9 4 9 90 Time, min	Noise Region St. End 2.523.06	Noise Region St. End 2.82-3.06	Noise Region St. End 280-106	2e6 4.508 1e6 5e0 4.0 9 4.9 90 Time, min
٨	* • Soy Dil. 1: 10 na. ple leder. 48) * Area: 48641, No RT: 456 min Noise Region St. End 2:52-3:06	<ul> <li>Soy Dil, 1: 10_raple leder 50)</li> <li>Area: 74255, He, RT: 4.56 min</li> <li>Naine Region St. End 2:ID-3:I6</li> </ul>	<ul> <li>Soy Dtl. 1:10, ra., ple Index: 57)</li> <li>Area: 54303, He., 911:456-min</li> <li>Noise Region St., End 2:82-3.06</li> </ul>	* • Sey DR, 1:10_apple Index: S2) Area: 37471785, RT: 4:50 min Noise Region St. End: 2:82-3:06	<ul> <li>Soy Dil, 1:10 sp. ple Index SB Area: 3787248, 5.117:450 mm Noise Region St. End 232-306</li> </ul>	<ul> <li>Soy Dil, 1:10, sp., ple Index: 50;</li> <li>Area: 3729432,5, RT: 458 min.</li> <li>Noise Region St. End: 232-336.</li> </ul>	Area: 31140000, RT: 4.58 min	* • Sey Oil, 1:10 np. ple leder; 50) Area: 31591530 RT: 4:58 min Noise Region St. End 2:82-3:06	*
explai	4000 4000 2000 0 40 0 4 % 0	5000 4.0 % %0 Time, min	5000 40 9 4 9 9 50 Time, min	365 365 365 365 365 365 365 365 365 365	465 365 365 365 365 460 4.0 4.0 9.0 Time, min.	265 365 365 365 365 365 365 365 365 365 3	3e6 26 265 1e6 0e0 43 4 90 Time, min	366 266 166 166 1776 Time, min	365 366 366 000 40 94 90 Torse, min
-	-		RAW		10ppb			100ppb	
	Matrix	Mean	CV	Mean	CV	Accuracy	Mean	CV	Accuracy
	rain DIL 1:4	0.44	8.59	10.96	0.64	105.2	101.29	2.49	100.85
	iwi DIL 1:4	0.47	5.75	11.01	1.98	105.4	104.04	1.03	103.57
	chini DIL 1:4	0.9	0.98	11.56	2.61	106.6	101.71	2	100.81
	:ket DIL 1:10 by DIL 1:10	33.24 0.14	2.34 18.04	41.72 8.8	0.69 0.52	84.8 86.6	112.44 73.98	0.23 2.8	79.2 73.84
30	Jy DIL 1.10	0.14	10.04	0.0	0.52	00.0	73.30	2.0	73.04

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		RAW			10ppb			100ppb	
M	+  Grain DIL 1:4 s. angle Index 3) Area: NAA, Heig. IB, RT NAI nin. Noise Region St. End: 1:27-2:08  Sed 464 204 204 207 207 25		Grain DH, 1:4 r. myle ledec 11) Area MM, Heig. Jh, RT MA nin Noise Region St. End 1.87-2.00  fed  ded  2nd  2nd  20  25	+ • Grain DR. 1.4. s. regio Indoc. 12) Area: 131112; H. , RT; 2:38-sin Nume Region St. , End: 1.87-2.08  465 265 265 265 265 265 2181		+	# Grain DIL 1:4 amale bules: 15) Area: 1323831 5, 92 2:18 min Noise Region St. End: 187-208 245 165 060 28 \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$	- • Grain DH. 1:4 smyle Index: 16) Area: 12/70655, S. PIT 2:10-nin Noise Pergion St. End 1.87-206 2e5 2e5 2e5 2e5 2e6 2e7	+ • Grain DEL 1-4 smgle below. Area: 1400583 . 5, RT 2 19+ Noise Region St. End 187-2 265 29 9 95
0	Time, min  Fee: 20933, He. HT: 2.17 min  Hoise Ringion St. End 1.87-2.08  4000  2000  1000  2000	Ace: 15135. He RT 2.16 min Noise Region St. Eart 1.87-2.86	Area: 15736. He RT 2.18 rate Noise Region St. East 1.67-2.06 2000 2000 2000 0 25 Feb. 2.177 2 177 2 177 2 177 2 177	Area: 132922 H. HT 2 19 min Hoise Region St. End 1.67 208 20000 10000 2 194 95	Miner DIII, 1-4, sp. myler index: 230 Aces: 1330 13, H. , HT -2 19 min Noise Region St. End 1.67-206	Area: 132284, H 807 2 19-min Moise Region St. East 1.87-2.06	Firm, min  * • Kiwi Dili, 1:4, sp., mple belov, 25) Area: 1155833,5, KT 2:18 min Hoise Region St., East 1:57-2:08  245  145  145	Area: 1158624. 5 RT: 2 18-nin Noise Region St. End: 1.87-2.06 245 145	* • Kiwi Oil, 1:4, spegde belor. Avez. 1124964. 5, 171: 2-18 Noise Region Sz. End 1,67-3 2065 1,565 1,565 1,566 5,064 0,060 2,77 T.5
*	Area: NAA, Heig. JR, ST 160 min. Noise Region St. End 187-208	Torse, min  Zucchini DII, 1 mple Index 30) Acear NIIA, Heing. JA, HT. NIIA.min Noise Region St. End 1.67-266  2000 2000 200 25 Torse, min	Tone, min  - Zucchini DH, 1	Time, min  * • Zuschimi DB, 1: .mple Index 32)  Area: 120741, H HT 2:19 min  Noine Region St. End 1.87-208  20000  2100  2106  Time, min	Tome, min  Acea: 109959, M., RT 2.19-min Noise Region St. End 1.67-206	Time, min  * * Zuechimi DII, 1mple Index: 34) Area: 1090006, H 807 2.20 min Moine Region St Evet 1.87-2.06 20000	Time, min  * © Zucchimi (Ht. 1mple Index 20) Area: 11805255, RT 2,20 min Noine Region St. End: 1,87-2,08  2e5 2e5 2e5 2e5 2e5 75 Time, min	Time, min  * • Zucchini DH, 1: .mple luder; 30) Area: 1147924. 5, RT: 221 min Noise Region St. End: 1.67-2.66  2e5  1e5  1e5  Time, min.	Tone, nin  Zucchini Dtl. 1ngle Index Area: 1131738. 5, RT: 2,30 Noise Region St. Ext 1.87-2 265 295 2107  1e5 297 75 Tone, nin
-attained of			Rocket DIL 1: 10. ple telex: 41)     Avex: 20763, He 62: 2:17 min     Noise Region St. End 1:87-2:08			+ © Rocket Dtl. 1-10 _pin index 44) Area: 64966, No _ 87 2 19-min Noise Region St. End 187-208		The second secon	+ © Rocket DIL 1: 10. ple Index: 4 Area: 449421, H, 82: 2: 10 Moise Region St End 1:82-3 2: 5e4
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RADIA	# Soy Dil. 1:10, ra. pie ledoc 40) Area: NAA, Heig. Ji, Riff NAA min Noine Region St. Cad 1:87-2:08 2000 2000 2000 200 25 Time, min	Sory DR. 1:10, na., ple leder 50) Area Nill, Heing JA, HT: Nill, min Noise Region St East 1.87-2.00  2000 2000 2000 2000 2000 2000 200	Sery DRI. 1:10, rspic bridex: 51] Area: NiA, Mining. JA, RT: NiA-men Noise Region StEnd 1.87-2.00  2000 2000 200 25 Tome, min  RAW  CV	5000 2 (949 2 )5 Time, min  + • Soy Dil. 1: 10 ap. pie Index S2) Avea: 53547, No III: 2.22 min Noise Region St. End 1:07-208  2 294 295 Time, min  Mean	5000 26 Torus, min  - Soy Dill, 1: 10, pp. pic index 500 Area: 42359, No RT 221 min Noise Regions St. East 1.67-2.08  - 2209  5000 - 2209  Torus, min  10ppb  CV	5000 2 9 1 1 10 pp. ple Index 54) Area: 40919, its. 801 2 20 min Moise Region St. East 187-208  2 197 2 5 Time, min  ACCUITACY	294 Ys. Time, min  4 Soy 001, 1: 10, np. ple belox 90 Area: 413135 H 817: 221 min Noise Regime St End: 147-208  Sel	Soy Dill. 1:10, sp. ple badec 500 Area: 4304105, H RT 2.20 min Noise Region St. End 1.87-2.00  feel 2200  feel 2200  feel 2200  Time, min  100ppb  CV	Soy Dil. 1-10 sp. gle hole: Area: 413945, H 87: 2:19 Noise Region St End 1.E7 Soil del 2:19 Accuracy  Accuracy
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G Zu Ro	# Soy DIL 1:10, ra. pie beloc 40) Area: NIA, Heig. Ji, RT NiA min Noine Region St. Cad 187-208 2000 2000 2000 200 25 Time, min  Matrix Grain DIL 1:4  Kiwi DIL 1:4	Sory Dil. 1: 10, ra. ple heler 50) Area Nill, Heig. Ji, HT: Nill-min Noise Region St. Led 1.87-200  2000  2000  300 28 Time, min  Mean  0  1.76	Sery DRL 1:10, rsple belox 51) Area NiA, Reig JA, RT. NiA-me Noise Region St. Text 1.87-2.00  2000 2000 2000 2000 2000 200 2000	5000 2 5000 2 500 2 500 Aver: 53547, No III: 2.22 con Noise Region St End 1.67-208 22% Time. Tron  Mean 15.53 13.26	5000 78 PV 25 Time, min  - Soy Dill, 1: 10, ap., dis index 50) Area: 42359, No RT 221 min Noise Region St. End 1.87-208  - 2209  5000  - 2209  5000  - 2209  - 5000  - 2209  - 5000  - 2308  - 2309  - 2308  - 2309  - 2308  - 2309  - 2308  - 2309  - 2308  - 2309  - 2309  - 2309  - 2309  - 2309  - 2309  - 2309  - 2308  - 2309	\$5000 294-925 Time, nin  + \$500 081,110, pg. nin dex 54) Area: 40919, lie. 801 220 min Moise Region St. End 187-208  \$5000 2107 \$5000 2107 \$5000 ACCUITACY \$55.3 \$115	294 Ys. Time, min  + • Sey 041, 1: 10, sap. ple belox 90; Avez: 413135, H 87: 221 min Noise Region St. End 1,87: 208  feel 201 201 201 201 201 201 201 201 201 201	500 C 28 9 5 Terra, min  * Soy Dill. 1:10 sp. ple below 50 Area: 430410, 14 IET 2.20 min Noise Region St. End 1.87-280  500 289 95 Terra, min  100ppb  CV  6.33  7.52	Del 29 95 Torse, min  - Soy Dill, 1:10, sp., ple index Area: 413945; H., 87: 2:19 Noise Region St., End: 1:17 Sel 2:19 Sel 2:19 Sel 2:19 Torse, min  Accuracy 143.63 122.01