

APPLICATIONS

Trace Glyphosate Analysis in Drinking Water by LC-Fluorescence Post-Column Derivatization, EPA Method 547

David Schiessel¹ and Scott Krepich²

¹BABCOCK Laboratories, Inc, 6100 Quail Valley Court, Riverside, CA 92507 USA

²Phenomenex, Inc., 411 Madrid Avenue., Torrance, CA 90501, USA



Scott Krepich
Senior Field Application
Scientist

Scott Krepich is a chess enthusiast, enjoying both sides of unsound gambits, such as the Smith-Morra, Budapest, and Danish. His favorite player is Viswanathan Anand.

Introduction

While LC-MS can be used for the determination of glyphosate in drinking water, and is often expanded to include the degradant and metabolite profiles at low levels, there are currently only two established methods for glyphosate approved by the EPA for the analysis of drinking water¹; EPA Method 547 and Standard Methods 6651². Both methods utilize LC followed by post-column derivatization and fluorescence detection. Because of the chemical nature of glyphosate, the separation method required to chromatograph glyphosate is ion exchange or ion-exclusion which introduce a different set of challenges. The RezexTM RFQ Fast Acid ion-exclusion column, allows this analysis to be done in about 15 minutes without the need for column regeneration after each injection. AMPA is not included here, however AMPA will elute at approximately 15 minutes. Additionally, the RFQ Fast Acid column dimensions that were chosen reduce band broadening which substantially improves the sensitivity of the method. Most typical methods in this realm yield a glyphosate peak that is about 3 minutes wide. Conversely, the Rezex RFQ Fast Acid method generates a peak width of about 1 minute.

While the current California regulation of glyphosate in drinking water requires labs to meet a reporting limit of 25 µg/L, some states including Arizona, Oregon, and New York require a reporting limit of 6.0 µg/L. Using the Rezex RFQ method, this criteria can be easily met and with robustness that meets the demands of the EPA method requirements.

Experimental Conditions

Sample Preparation

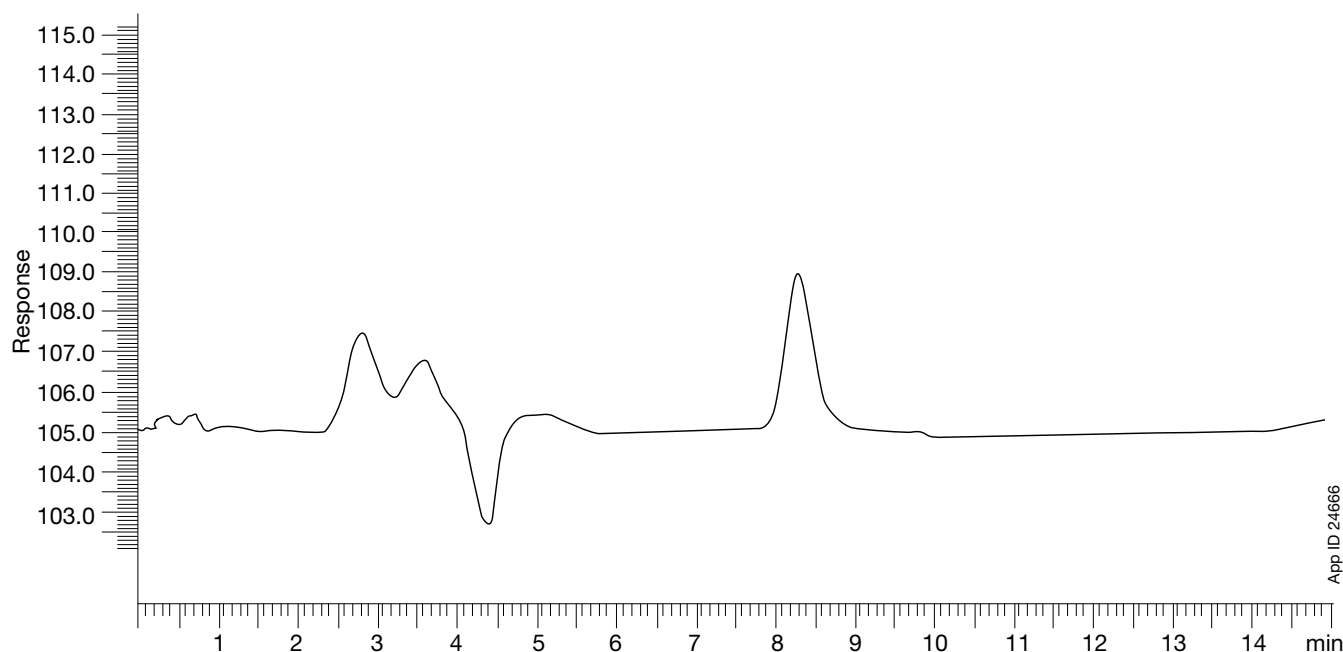
Samples are collected in 40 mL VOA vials preserved with a sodium thiosulfate dechlorinating agent according to EPA Method 547. A 50 µL aliquot of Pickering RESTORETM (50 mM Potassium Phosphate buffer) is added to a 1.5 mL sample aliquot.

LC-Fluorescence Method Parameters

Column:	Rezex RFQ-Fast Acid H ⁺ 8 µm
Dimension:	100 x 7.8 mm
Part No.:	00D-0223-K0
Mobile Phase:	20% Pickering K200 and 80% Water (1.0 mM KH ₂ PO ₄)
Flow Rate:	0.8 mL/min
Injection Volume:	250 µL
Post-Column Reactor:	Pickering Vector PCX
Reagent 1:	0.2 mL/min Hypochlorite Diluent (Pickering GA116)
Reagent 2:	0.2 mL/min OPA Diluent (Pickering GA104), 2 g/L Thiofluor, 100 mg/L o-phthalaldehyde
Reactor 1 Temp:	36 °C
Reactor 2 Temp:	Ambient
Detector:	Waters 474 Fluorescence with 16 µL flow cell
Emission:	465 nm
Excitation:	330 nm
Gain:	10
Attn:	16
Response:	3 sec
Mode:	Normal

Figure 1.

Chromatogram of a 5.0 µg/L calibration standard



App ID 24666



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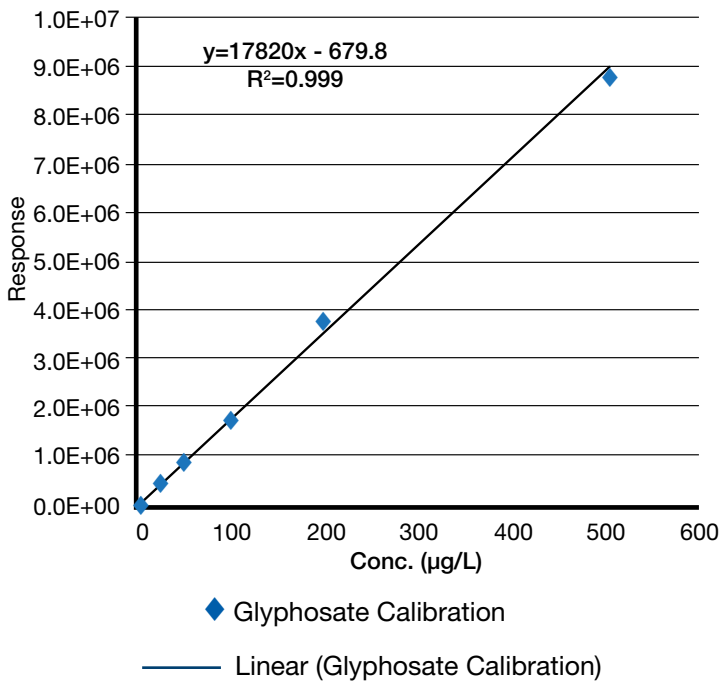
Table 1.
Replicate analysis of reagent water spiked at 5.0 µg/L

Rep1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Mean	SD	T factor	MDL _s
5.6981	4.9674	4.9631	4.9261	4.4762	4.6429	4.7779	4.921671	0.38805	3.14	1.21

Table 2.
Replicate analysis of Blank reagent water

Rep1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Mean	SD	T factor	MDL _b
ND	0.6534	ND	ND	ND	ND	ND	0.6534	#DIV/0!	3.14	0.65

Figure 2.
Calibration of Glyphosate



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Results and Discussion

The system was calibrated from 5.0-500 µg/L using a 6-point external calibration. An MDL study was performed per 40 CFR Part 136 (rev. 2017) using 7 spike replicates and 7 blank replicates performed over 3 days. This data is presented in **Tables 1 and 2** respectively. The final MDL was determined to be 1.21 µg/L which was the higher value of the MDL determined from the spiked and blank replicates.

Conclusion

The Rezex RFQ-Fast Acid ion-exclusion column can be utilized within the parameters of EPA Method 547 and Standard Methods 6651 to achieve below the 6.0 µg/L reporting limits in a flexible and user-friendly workflow.

Acknowledgements

We would especially like to thank David Schiessel and BABCOCK Laboratories for developing and contributing this application.



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References

1. EPA Method 547 – Approved Drinking Water Analytical Methods, <https://www.epa.gov/dwanalyticalmethods/approved-drinking-water-analytical-methods>
2. Standard Methods 6651 <http://www.standardmethods.org/store/Product-View.cfm?ProductID=171>

Rezex Ordering Information

Columns					Guards		SecurityGuard™ Cartridges (mm)
Description	Part No.	Cross Linkage	Ionic Form	Size (mm)	Part No.	Size (mm)	4 x 3.0" 10/pk
RCM-Monosaccharide	00D-0130-K0	8 %	Calcium	100 x 7.8	03B-0130-K0	50 x 7.8	AJ0-4493
RCM-Monosaccharide	00F-0130-K0	8 %	Calcium	150 x 7.8	03B-0130-K0	50 x 7.8	AJ0-4493
RCM-Monosaccharide	00H-0130-K0	8 %	Calcium	300 x 7.8	03B-0130-K0	50 x 7.8	AJ0-4493
RHM-Monosaccharide	00H-0132-K0	8 %	Hydrogen	300 x 7.8	03B-0132-K0	50 x 7.8	AJ0-4490
RAM-Carbohydrate	00H-0131-K0	8 %	Silver	300 x 7.8	—	—	AJ0-4491
RSO-Oligosaccharide	00P-0133-N0	4 %	Silver	200 x 10.0	03R-0133-N0	60 x 10.0	—
RNO-Oligosaccharide	00P-0137-N0	4 %	Sodium	200 x 10.0	03R-0137-N0	60 x 10.0	—
RPM-Monosaccharide (for USP procedure)	00H-0135-K0	8 %	Lead	300 x 7.8	03B-0135-K0	50 x 7.8	AJ0-4492
	00D-0135-K0	8 %	Lead	100 x 7.8	03B-0135-K0	50 x 7.8	AJ0-4492
RNM-Carbohydrate	00H-0136-K0	8 %	Sodium	300 x 7.8	03B-0136-K0	50 x 7.8	—
ROA-Organic Acid	00F-0138-E0	8 %	Hydrogen	150 x 4.6	—	—	AJ0-4490
ROA-Organic Acid	00G-0138-E0	8 %	Hydrogen	250 x 4.6	—	—	AJ0-4490
ROA-Organic Acid	00F-0138-K0	8 %	Hydrogen	150 x 7.8	03B-0138-K0	50 x 7.8	AJ0-4490
ROA-Organic Acid	00H-0138-K0	8 %	Hydrogen	300 x 7.8	03B-0138-K0	50 x 7.8	AJ0-4490
RKP-Potassium	00H-3252-K0	8 %	Potassium	300 x 7.8	—	—	—
RFQ-Fast Acid	00D-0223-K0	8 %	Hydrogen	100 x 7.8	03B-0223-K0	50 x 7.8	AJ0-4490
RCU-USP Sugar Alcohols	00G-0130-D0	8 %	Calcium	250 x 4.0	03A-0130-D0	30 x 4.0	AJ0-4493

for ID: 3.2-8.0 mm

*SecurityGuard Analytical Cartridges require universal holder Part No.: KJ0-4282

guarantee

If you are not completely satisfied with the performance of any Rezex column, as compared to a competing product of the same size and phase, simply return the Rezex column with your comparative data within 45 days for a FULL REFUND.



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Australia

t: +61 (0)2-9428-6444
 f: +61 (0)2-9428-6445
 auiinfo@phenomenex.com

Austria

t: +43 (0)1-319-1301
 f: +43 (0)1-319-1300
 anfrage@phenomenex.com

Belgium

t: +32 (0)2 503 4015 (French)
 t: +32 (0)2 511 8666 (Dutch)
 f: +31 (0)30-2383749
 beinfo@phenomenex.com

Canada

t: +1 (800) 543-3681
 f: +1 (310) 328-7768
 info@phenomenex.com

China

t: +86 400-606-8099
 f: +86 (0)22 2532-1033
 phen@agela.com

Denmark

t: +45 4824 8048
 f: +45 4810 6265
 nordicinfo@phenomenex.com

Finland

t: +358 (0)9 4789 0063
 f: +45 4810 6265
 nordicinfo@phenomenex.com

France

t: +33 (0)1 30 09 21 10
 f: +33 (0)1 30 09 21 11
 franceinfo@phenomenex.com

Germany

t: +49 (0)6021-58830-0
 f: +49 (0)6021-58830-11
 anfrage@phenomenex.com

India

t: +91 (0)40-3012 2400
 f: +91 (0)40-3012 2411
 indiainfo@phenomenex.com

Ireland

t: +353 (0)1 247 5405
 f: +44 1625-501796
 eireinfo@phenomenex.com

Italy

t: +39 051 6327511
 f: +39 051 6327555
 italiainfo@phenomenex.com

Luxembourg

t: +31 (0)30-2418700
 f: +31 (0)30-2383749
 nlinfo@phenomenex.com

Mexico

t: 01-800-844-5226
 f: 001-310-328-7768
 tecnicomx@phenomenex.com

The Netherlands

t: +31 (0)30-2418700
 f: +31 (0)30-2383749
 nlinfo@phenomenex.com

New Zealand

t: +64 (0)9-4780951
 f: +64 (0)9-4780952
 nzinfo@phenomenex.com

Norway

t: +47 810 02 005
 f: +45 4810 6265
 nordicinfo@phenomenex.com

Puerto Rico

t: +1 (800) 541-HPLC
 f: +1 (310) 328-7768
 info@phenomenex.com

Spain

t: +34 91-413-8613
 f: +34 91-413-2290
 espinfo@phenomenex.com

Sweden

t: +46 (0)8 611 6950
 f: +45 4810 6265
 nordicinfo@phenomenex.com

Switzerland

t: +41 61 692 20 20
 f: +41 61 692 20 22
 swissinfo@phenomenex.com

United Kingdom

t: +44 (0)1625-501367
 f: +44 (0)1625-501796
 ukinfo@phenomenex.com

USA

t: +1 (310) 212-0555
 f: +1 (310) 328-7768
 info@phenomenex.com

**All other countries
 Corporate Office USA **

t: +1 (310) 212-0555
 f: +1 (310) 328-7768
 info@phenomenex.com

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CAUTION: this patent only applies to the analytical sized guard cartridge holder, and does not apply to SemiPrep, PREP or ULTRA holders, or to any cartridges.

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