Getting the Best Performance from your GC/QQQ for the Analysis of Pesticides in Environmental Matrices

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Types of Matrices Encountered

- Drinking Water
- Waste Water
- Soil
- Fruits/Vegetables Commodities
- Essential Orange Oil
- Grains (Wheat, Rice, Barley)

Top Ten Common Problems and Solutions

- Based on extensive visits to customer sites across the US the following top 10 common Problems and Solutions list has been generated.

- This list will increase your laboratory's productivity via method and instrument robustness for the analysis of pesticides in environmental and other tough matrices.

No. 10

Consistent drop in analyte response throughout the day

Common Problem: Calibrations Curves are not stable from day to day or Morning to Afternoon

Solutions: Use Amber vials (analytes may be photo degrading), place the autosampler rack away from direct sunlight, use adequate ISTDs.

No. 9

Retention times are not reproducible

Common Problem: Analyte Retention Times vary from run to run or injection to injection

Solutions: Check oven Program, ramping too fast? Fast Oven not available, Implement RTL , Implement Backflush, possible leak check your ferrules and gas connections.

No. 8

QC samples are being quantitated below or above accepted levels greater than 20% off from actual levels is seen.

Common Problem: QC should be 50ppb Quantitates to be ~30ppb or lower or ~70ppb or higher

Solutions: Implement Analyte Protectants in standards and/or matrix matching, Implement adequate ISTDs for proper quantitation

No. 7

Low response for late eluting compounds

Common Problem: Late eluting compounds show a relatively low response

Solutions: Increase the source temperature and transfer line temperature to match at least the upper temperature of GC Oven Ramp (Most Customers are running the MS Source at 230°C) ; 280 – 300 °C would be more adequate

No. 6

Peak areas are not reproducible most analytes have high %RSDs

Common Problem: %RSDs greater than 10% injection to injection from the same vial

Solution: Implement adequate ISTDs, Implement Analyte Protectants and/or Matrix Matched Standards. Use amber Vials. Use more sample washes and or check your syringe for clogs and or air bubbles

No. 5

Greater sensitivity is needed to reach required LOQs.

Common Problem: Very difficult to reach required LOQs for all or some analytes.

Solutions: Implement a cold splitless injection with the MMI, increase the MS detector Gain to 10-20, Clean MS source, replace EM if gain factor is less than 200 on tune (Typically replaced every 2yrs) Inject more than 1µL, Consider LVI

No. 4

MS source requires maintenance too frequently

Common Problem: The MS source gets dirty too quickly after running 30-50 samples or less

Solutions: Implement Blackflush ensuring to include bleeder-T, perform additional sample clean-up, Use glass wool UI Liners. Bakeout the MS Source at 350 °C when not in use.

No. 3

Carry-over and "Ghost Peaks" are present in chromatogram

Common Problem: The solvent blank injection shows extraneous "bonus" peaks

Solutions: Increase the solvent washes to the syringe, increase inlet temperature during analysis, inject a lower upper concentration level (not a 10ppm std). Inject less volume. Use 2 different solvents for syringe wash in between injections. Replace your inlet Septum

No. 2a

The MS tune shows a drop in response for PFTBA ions

Common Problem: m/z 69 shows abundance of ~2x 10^5 vs. an abundance of at least ~ 2x10^6 typically seen.

Solutions: Check for Leaks on the MS transfer line or PUU. MS Source may need to be cleaned. Worst case scenario the EM should be replaced.

No. 2b

Calibrations curves all are quadratic vs. a desired linear fit

Common Problem: Calibration curves for most analytes are quadratic fit for a concentration range of 1ppb to 800ppb

Solutions: Set the MS gain to 10 instead of 20 or 100 also if possible include an extra dilution and change your upper limit standard concentration (1-500ppb vs. a 1-1000ppb range)

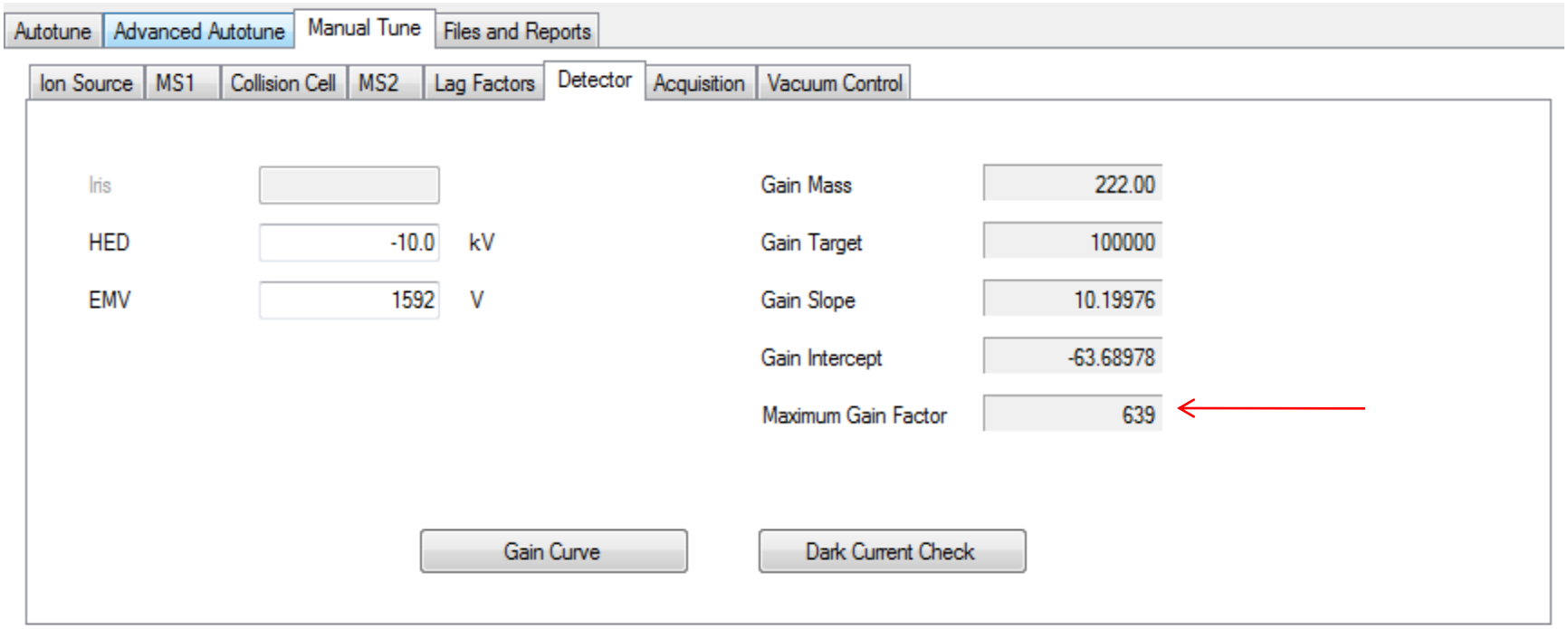
No. 1

Analytes disappear all of a sudden "Houdini Effect"

Common Problem: a handful of analytes are not present at low concentrations or present at all even at 500ppb.

Solutions: The analytes may have photo-degraded and the degradation products should be monitored. These analytes may be better amenable to LC/MS. Amber vials should be implemented to minimize this effect.

1 FAQ: When should I replace my EM?



When the Maximum Gain Factor is below 100
Clean the MS source, run AUTOTUNE, Check Max Gain Factor
If still below 100 then EM needs to be replaced.

Sandwich Injections of Analyte Protectants:

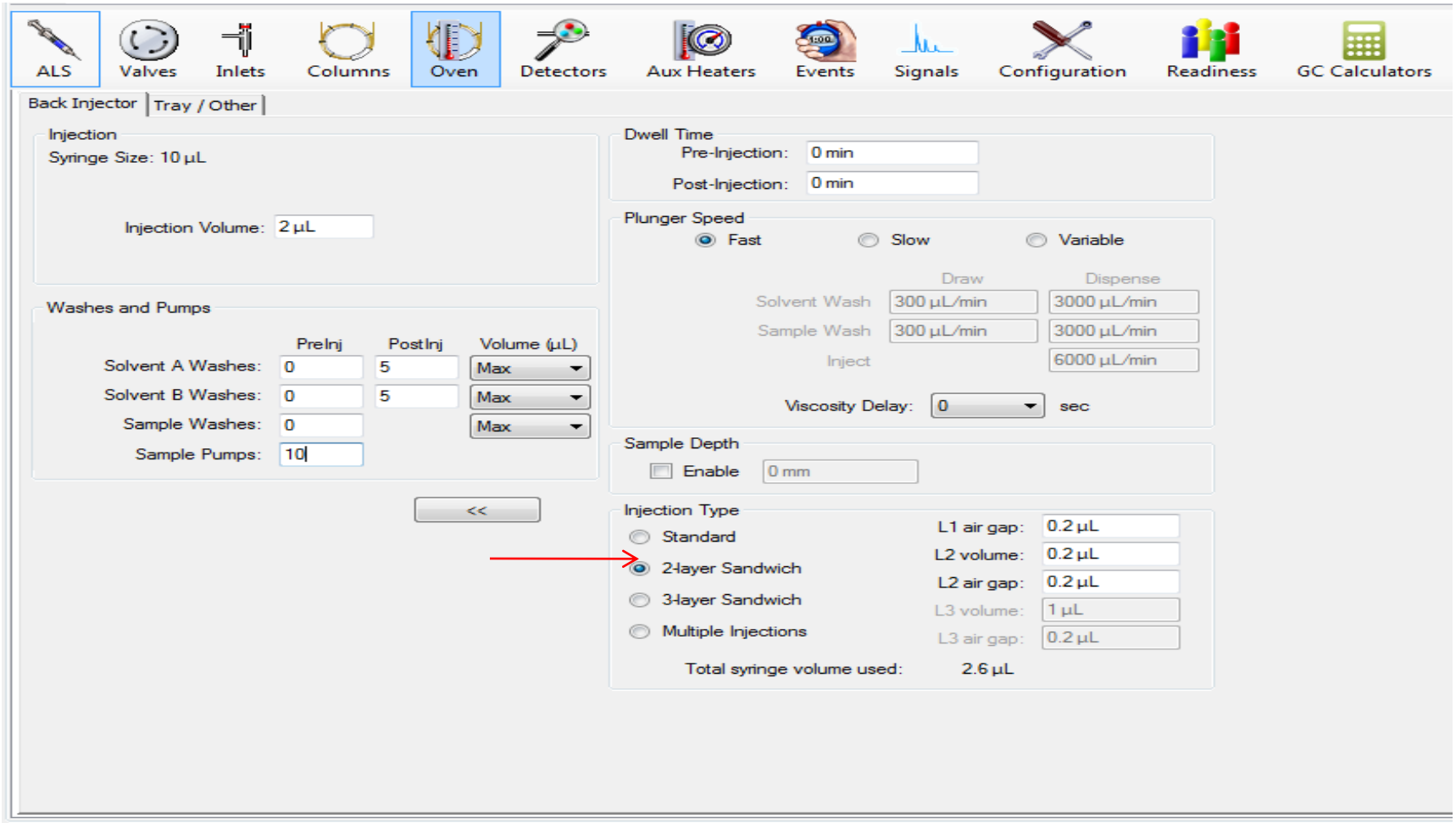
Setting up a sandwich injection:

Place Vial containing Analyte Protectants in position L2 in the autosampler (2mL in the vial) at the desired concentration. Make a 2uL injection of Sample and 0.2uL injection of Analyte Protectants. This will act as your matrix matched standards. Use this technique to inject your standards and samples as well.

Alternatively, you can spike each vial with the analyte protectants however this increases sample prep. (I would personally recommend letting the autosampler do the work for you)

- http://www.chem.agilent.com/en-US/Newsletters/accessagilent/2013/feb/pages/pestgcmsms.aspx?CID=7631

Sandwich Injections for Addition of Analyte Protectants:



Analyte Protectants Resources and Procedure

Analyte Protectant Preparation:

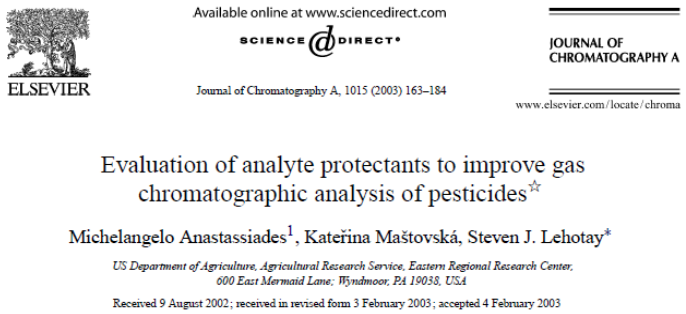
L-Gulonic acid γ-lactone (L-gulonolactone), CAS # 1128-23-0: > 95% purity.

(g) ***D-Sorbitol***, CAS # 50-70-4: > 95% purity.

L-Gulonolactone stock solution: Weigh approximately 500 mg of L-gulonolactone in a 10-mL volumetric flask. Add 4 mL of water and then bring to volume with acetonitrile. Sonicate to dissolve if needed.

(k) ***D-Sorbitol stock solution***: Weigh approximately 500 mg of D-sorbitol in a 10-mL volumetric flask. Add 5 mL of water and then bring to volume with acetonitrile. Sonicate to dissolve if needed.

(l) ***Analyte protectant (AP) solution*** *(20 mg/mL L-gulonolactone and 10 mg/mL D-sorbitol composite solution):* Add 4 mL of the L-gulonolactone stock solution and 2 mL of the D-sorbitol stock solution into a 10-mL volumetric flask and bring to volume with acetonitrile.



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Evaluation of analyte protectants to improve gas chromatographic analysis of pesticides☆

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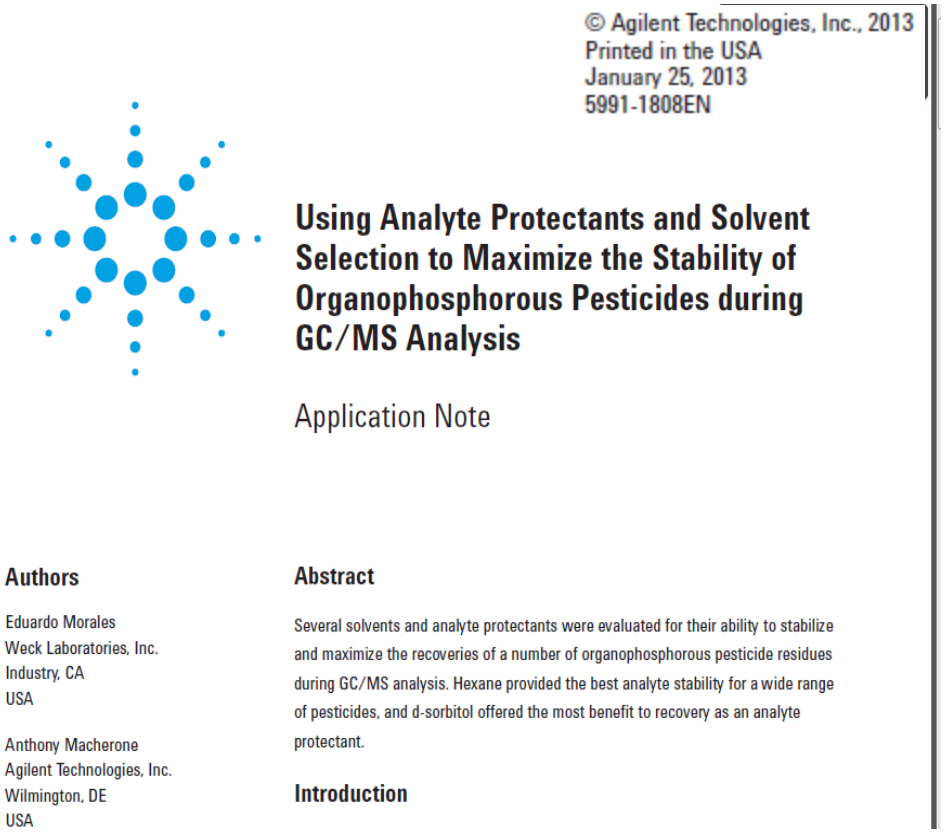
Agilent Application Notes:



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Using Analyte Protectants and Solvent Selection to Maximize the Stability of Organophosphorous Pesticides during GC/MS Analysis

Application Note

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Abstract

Several solvents and analyte protectants were evaluated for their ability to stabilize and maximize the recoveries of a number of organophosphorous pesticide residues during GC/MS analysis. Hexane provided the best analyte stability for a wide range of pesticides, and d-sorbitol offered the most benefit to recovery as an analyte protectant.

Introduction

Search the Agilent website for additional Application Notes on related topics

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Summary

- Implement Cold Pulsed Splitless Injection (Helps Late Eluting Analytes)
- Utilize Backflush capabilities (Keeps the MS Source Clean)
- Use of Amber Vials (Minimizes Photo-degradation)
- Use of Adequate internal standards (Increases Reliability)
- Utilize Retention Time Locking (Increases Method Robustness)
- Analyte Protectants (For Matrix Matching)
- Increase the MS Source Temperature
- (Increase Sensitivity, Minimize Source Cleaning)
- Use the Lowest Possible Gain to get desired LOD (Extend EM Lifetime)

Thank You For Your Time !

Questions?