Exploring Lower-Level Analysis with DWRL-TCP Method: Insight into 123-TCP, EDB and DBCP Evaluation

Tuan Nguyen, Eugene Chae, Carolyn Carroll, Lily Sanchez, Prem Parmar

Phillip L. Anthony Water Quality Laboratory, Orange County Water District, Fountain Valley CA 92708

INTRODUCTION

1,2,3-Trichloropropane (1,2,3-TCP), 1,2-Dibromoethane (EDB), and 1,2-Dibromo-3-chloropropane (DBCP) have significant industrial applications that are regulated by environmental agencies due to their potential health effects and environmental impacts. The State Water Resource Control Board (SWRCB) has set a maximum contaminant level (MCL) at 5 ng/L for 1,2,3 TCP that was adopted in 2017.

The DWRL123TCP Method Revision 2021.0 was published by the California Division of Drinking Water (DDW) as a revised method for the determination of 1,2,3-TCP in drinking water at low concentration (2 ng/L). The Orange County Water District (OCWD) adopted this method to meet and exceed the State-specific MCL of 5 ng/L. In the process, the laboratory has expanded the scope of the method by adding two additional compounds, EDB and DBCP for monitoring with a reporting limit of 5 and 10 ng/L respectively.

METHOD

Instrumentation:

EST Centurion Auto Sampler

EST Evolution Purge & Trap Concentrator

Agilent GC 8890

Agilent MS 5977C

Table 1: Analytical Conditions

GCMS Setting	Purge & Trap Setting
Analytical Column: Agilent DB-VRX	Purge Flow Rate: 40 mL/min
Inlet Temperature: 220°C	Purge Time: 11.0 min
Flow: 2.0 mL/min	Desorb Temperature: 250°C
Split Ratio: 40:1	Desorb Time: 2.0 min
MSD Transfer Line: 220°C	Trap Bake Temperature: 260°C
MS Source: 250°C	MoRT Bake Temperature: 210°C
MS Quad: 150°C	Bake Time: 7.0 min
Acquisition Mode: Selected Ion Monitoring (SIM)	Trap: K Trap (Vocarb 3000)

METHOD DEVELOPMENT CHALLENGES

I. Moisture from the purge and trap caused a decrease in internal standard (IS), 1,2,3-TCP-d5, response.

II. GC oven parameters were observed to influence peak shape quality and response levels for DBCP qualifier ion.

III. Active sites in the transfer line caused low IS response and recovery decreased overtime.

RESULTS & DISCUSSION I

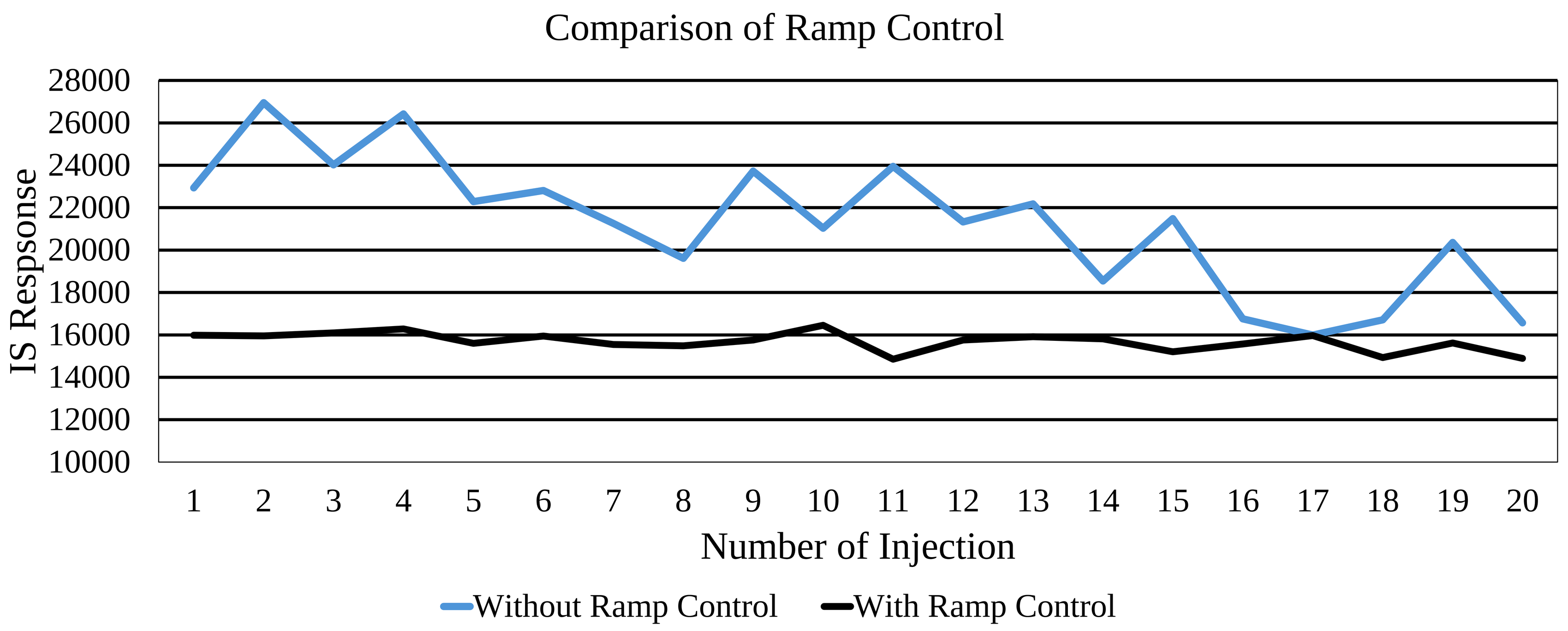
Table 2a:.

Purge & Trap: Sample Heater With Ramp Control	
Initial Temperature	110°C
Initial Hold Temperature	5.0 min
Ramp Rate	100 (°C/min)
Final Temperature	25°C

Table 2b:

Purge & Trap: Sample Heater Without Ramp Control	
Initial Temperature	40°C
Initial Hold Temperature	Constant
Ramp Rate	N/A
Final Temperature	N/A

Graph 1: Comparison of IS response without sample heater ramp control versus with ramp control.



The sample heater simultaneously initiates with the trap baking step during purging, this occurs after desorption is complete. Enabling the sample heater, with the ramp control settings from **Table 2a**, resulted in a continual stable IS recovery after multiple sample injections **(Graph 1).**

Without the sample heater enabled from **Table 2b**, a decrease of IS response was observed over time **(Graph 1**). Having the sample heater enabled allows for better moisture control, thus a stable IS recovery.

RESULTS & DISCUSSION II

Figure 2a. DBCP peak chromatogram with below settings. Left is Quantitation ion; right is Qualifier ion.

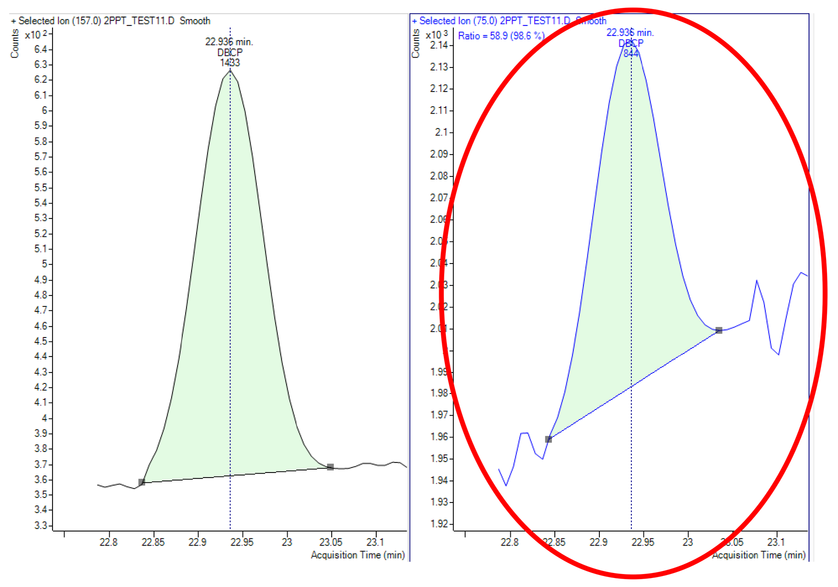


Figure 2b. GC oven ramp without 170°C hold time.

	Rate °C/min	Value °C	Hold Time min	Run Time min
(Initial)		35	4	4
Ramp 1	10	100	0.5	11
Ramp 2	20	150	0.5	14
Ramp 3	3	200	2	32.667

Figure 3a. DBCP peak chromatogram with below settings. Left is Quantitation ion; right is Qualifier ion.

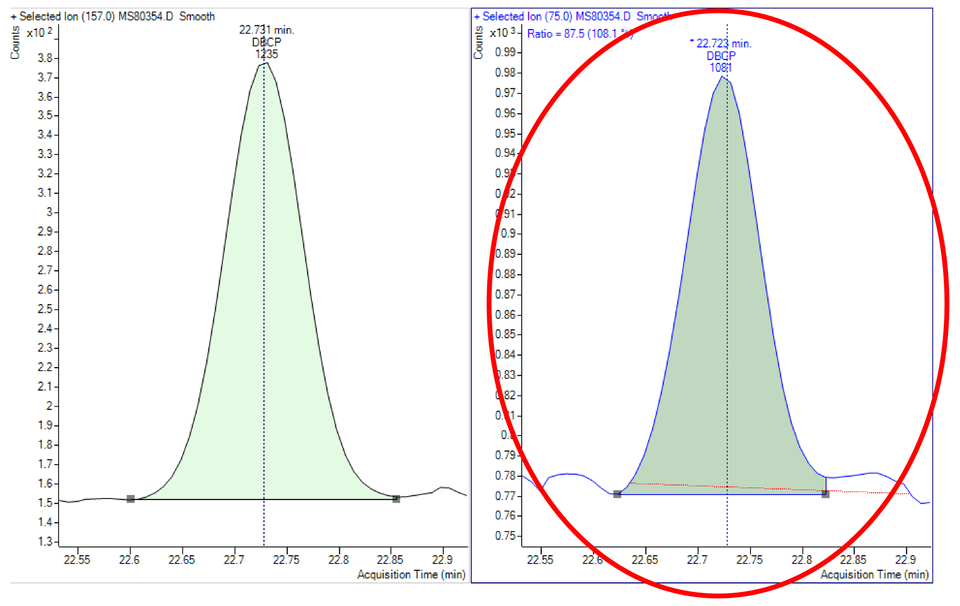


Figure 3b. Modified GC oven ramp with 170°C hold time.

	Rate °C/min	Value °C	Hold Time min	Run Time min
(Initial)		35	4	4
Ramp 1	10	100	0.5	11
Ramp 2	20	150	0.5	14
Ramp 3	10	170	8	24
Ramp 4	50	200	0.4	25

Initial method development resulted with a poor DBCP qualifier ion peak shape and rising baseline **(Figure 2a).** DBCP concentration is at 4 ng/L, our lowest calibration point.

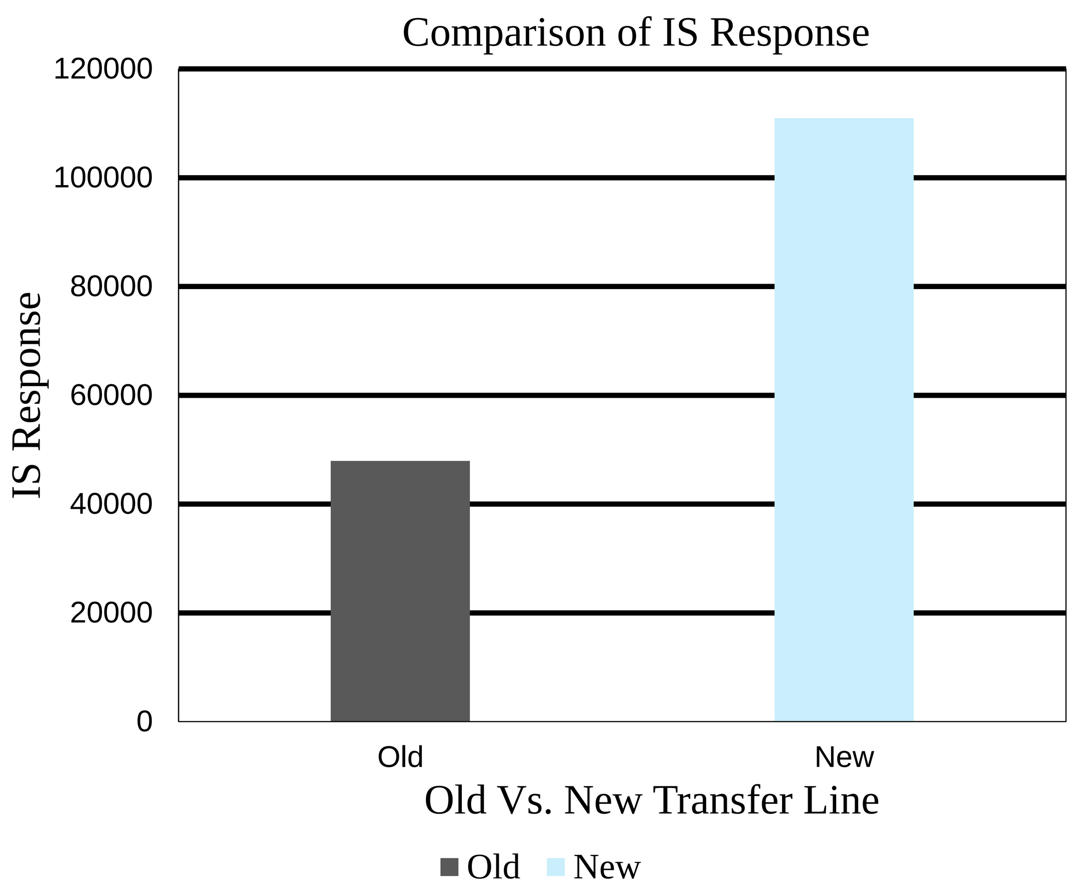
While troubleshooting to improve peak shape, it was observed that 170°C was the optimal temperature for DBCP qualifier ion elution. Improvement of the baseline was also seen for the quantitation ion.

The oven temperature program was updated to ramp to 170°C and held for 8 minutes, to allow for a sufficient time for DBCP to properly elute, achieving an improved peak shape and improved baseline **(Figure 3a).** Also**,** DBCP at our lowest calibration point.

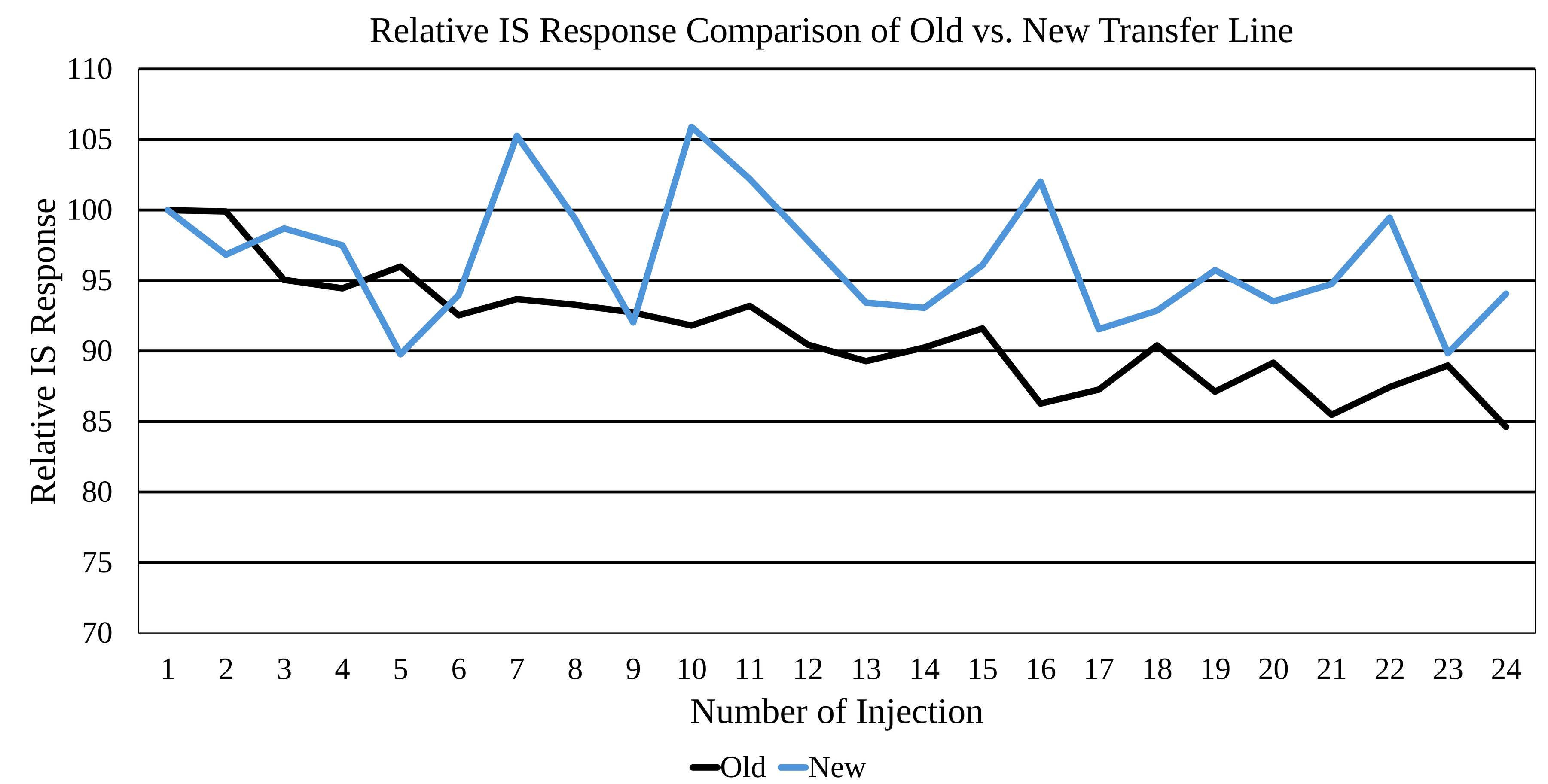
The initial oven temperature program and the modified oven temperature program are shown in **Figure 2b and 3b**, respectively.

RESULTS & DISCUSSION III

Graph 2. Average IS response comparison of an old and new transfer line



Graph 3: Relative IS response from first injection comparison of old and new transfer line



Active sites in the transfer line caused a decrease in IS response. A new transfer line was installed, and the IS response increased **(Graph 2).**

Additionally, active sites continue to decrease the IS response over time. The method requires a 20% of the calibration average IS response, however, the old transfer line is trending towards being outside of the limit **(Graph 3)**.

Installation of the new transfer line showed a more stable IS response after multiple injections, when compared to the old transfer line with active sites **(Graph 3).**

CONCLUSION

Through the expansion of the DWRL123TCP Method Revision 2021.0 published by the DDW, we discovered when enabled sample heater allowed user to set the purge and trap sample heater optimal ramp control setting for moisture control, which make the IS response more stable.

During the process of expanding the method, our simple modifications to the GC oven ramp, we are able to achieve better peak resolution and higher response for DBCP qualifier ion, while achieve low reporting limit for 1,2,3TCP. Temperature must be held at 170°C to allow for DBCP to elute well, while an additional ramp to 170°C produced better results.

Furthermore, we discovered active sites in the transfer line caused IS to have low response and relative IS response to decrease over time. Regular maintenance is recommended.

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Questions? Contact:

Tuan Nguyen (tanguyen@ocwd.com)

Eugene Chae (echae@ocwd.com)