Optimization of 1,4-Dioxane Analysis By Purge And Trap – GC/MS

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INTRODUCTION

1,4-Dioxane is a byproduct of the hydrolysis of ethylene oxide and can be found in approximately 46% of all personal care products, such as cosmetics, lotions and liquid soaps. The compound can be absorbed through the skin or inhaled while taking a hot bath and is currently classified as a group 2B probable carcinogen by the USEPA and presents other health risks primarily to the liver and kidneys. The compound is highly soluble in water and is resistant to natural degradation. Due to its wide use, the compound is commonly found in drinking water and requests for this analysis have been increasing the past few years.

Testing for 1,4-Dioxane at low levels can be problematic due to its affinity for water, decreasing its volatility and purge efficiency by traditional purge and trap methods. Most systems struggle to maintain system cleanliness due to high a degree of carry over. An optimized method, which dramatically reduces carryover, yet maintains a large dynamic range (1ppb-2000ppb) is presented.

EXPERIMENTAL

Since carryover is one of the biggest concerns while performing this analysis, many analysts choose to purge samples inside the 40 ml vial, basically treating the sample as a traditional soil sample. This eliminates the transfer of the sample from the vial to the front of the purge and trap sparger vessel and should greatly reduce residual carryover. This does require, however, that analysts manually prep these samples and use additional VOA vials for the analysis. Due to the poor purging efficiency of 1,4-Dioxane, most analysts choose to heat samples anywhere from 40-80 °C in order to improve the purging efficiency and maximize the amount of analyte transferred to the analytical trap. Most analysts have this ability on their purge and trap autosamplers if they treat the samples as soil samples. Analysts would require a heater on their purge and trap sample concentrators sparge vessel to heat water samples.

In order to compare carryover and linearity differences while running samples as waters or soils, four calibration curves were set up on an EST Centurion WS autosampler (**Figure 1**). Two calibrations were performed as liquid samples, and two were run as soil samples. Six point calibrations were set up and ranges were established from 1-50 ppb in SIM mode, and 50-2000 in full scan mode. Encon Evolution (**Figure 2**) purge and trap conditions can be seen in **Table 1** with general GC/MS condition in **Table 2**.

Figure 1. Centurion WS Autosampler

Figure 2. Encon Evolution

Table 1. Purge and Trap Concentrator Parameters

Purge and Trap Concentrator	EST Encon Evolution
Purge Flow Rate	40ml/min
Purge Time	11 min
Purge Temperature	80 °C
Dry Purge	Ambient for 1 min
Dry Purge Flow	40ml/ min
Desorb Time/Temp	1 min @ 250 °C
Bake Time/Temp	8 min @ 260 °C
Trap Type	EST Analytical EV1 Trap
Valve oven	120 °C
Sample size	5ml

Table 2. GC/MS Parameters

GC/MS system	Agilent 7890/5975
Temperature Program	40° for 2 min, 12°/min to 150, 25°/min to 220 for 2 min
Inlet	Split/Splitless at 200°
Split rate	30:1
Colum Flow	0.9ml/min
GC Column	Restex RTX-VMS (Cat# 19915) (30m x 0.25 x 1.4um)
Aux Temp	180°
Trap Type	EST Analytical EV1 Trap

Four different calibration curves were performed and average response factors were calculated across the calibration curves. Results for the calibration curves can be seen in **Table 3**. An example of an extracted ion chromatogram in SIM mode is shown in **Figure 3**. An example of a full scan TIC can be seen in **Figure 4**.

Table 3. RF %RSD for SIM and full scan calibration curves. Linearity on all curve resulted in a 0.999 correlation coefficient.

	SIM mode (Primary Ion 88) 1-50ppb	Full scan 50-2000ppb
Centurion WS (Water)	11.5	3.98
Centurion WS (Soil)	12.1	8.3

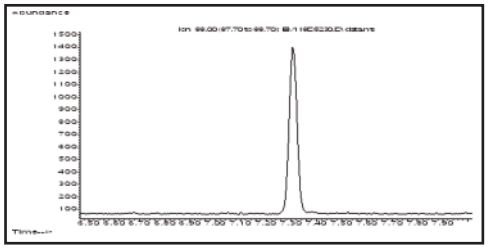

Figure 3. 1ppb 1,4-Dioxane SIM Mode Ion 88

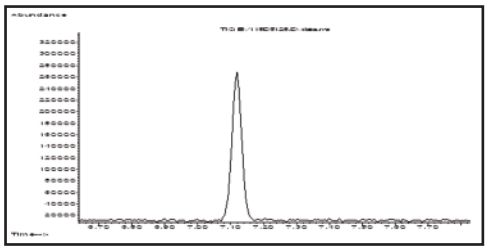

Figure 4. 50ppb Full Scan 1,4-Dioxane

CARRYOVER STUDY

Since most laboratories complain about their current system's carryover, a study was set up to look at % carryover after a 50ppb sample in SIM mode and after 2000ppb run in full scan mode. Many laboratories see anywhere from 2-10% carryover depending upon whether they run samples as a soil sample or a water sample. In general, the laboratories that run 1,4-Dioxane as a water sample see higher percent carryover due to the surface area of the system exposed to sample during the sample transfer to the purge and trap concentrator. In addition, 1,4- Dioxane has a high affinity for water and glass components of the system. Any water left behind in the glassware will hold on to 1,4-Dioxane and create high levels of carryover for the subsequent analysis.

In order to help control carryover of water samples, the Encon Evolution employs a patent-pending mode that allows the user to bake the glassware at up to 130 °C (**Figure 5**) during the bake step of the purge and trap concentrator. This high temperature bake, along with a high flow of helium, ensures sample pathway cleanliness and that any moisture left behind can be completely dried and removed. The results of the carryover study can be seen in **Table 4**. Percent carryover was calculated in SIM mode after a 50ppb run and after a 2000ppb run in full scan mode.

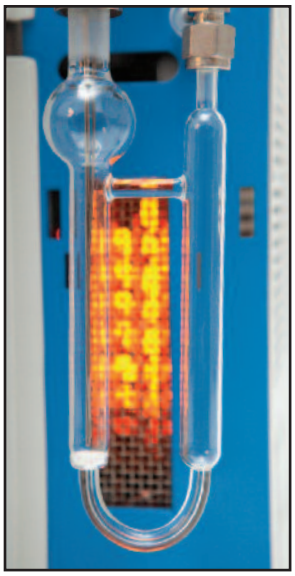

Figure 5.

Table 4. % Carryover calculated after 50ppb in SIM mode and 2000ppb in full scan mode. Data includes carryover from the whole system including the autosampler, concentrator, and GC system.

	SIM mode (Primary Ion 88) % Carryover after a 50ppb run	% Carryover after a 2000ppb run 2000ppb
Centurion WS (Water)	1.28	3.3
Centurion WS (Soil)	2.21	0.25

CONCLUSION

Requests for 1,4-Dioxane analysis will continue to increase as the awareness of the compound and its potential risks continues to rise. Testing on acceptable exposure limits continues, and the long term regulation of this compound is being developed. The FDA does not currently require independent testing of new products and chemicals. However, recall of children's products that contain 1,4-Dioxane has already occurred in countries throughout Europe.

Due to the difficulties in running 1,4-Dloxane analysis, most customers choose to run this compound independently of their 8260 analysis. Further method optimization should allow this compound to be analyzed in the same analytical run as 8260 without sacrificing data quality or method robustness.