Analysis of an Expanded List of Volatiles by Gas Chromatography Using EPA Methods 502.2 & 8021.

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ABSTRACT

Traditionally, column development has relied on analyzing a list of compounds using all existing stationary phases, and then choosing the column that produces the best separation. Also, with the recent changes in US EPA methods for the analysis of volatile compounds using GC/PID-ELCD, many laboratories struggle to achieve resolution of a continually expanding compound list. All of the current phases available for these types of analyses suffer from lack of resolution between critical compounds, and many suffer from low thermal stability and long analysis times. With the aid of computer stationary phase modeling, existing polymers, combinations of polymers, and new functionalities can be tailored to the application-to give unsurpassed separation of specific compounds of interest.

Disinfectant by-products of drinking water, known as the trihalomethanes (THM), are the most commonly found contaminants in the public water supply. They must be well resolved from other target analytes to prevent poor compound quantitation of "real-world" samples. All other currently available columns either have unacceptable resolution or coelutions of these ubiquitous compounds with other analytes in the method compound list. This paper will discuss an alternative Volatile GC column that addresses these issues. It is designed using computer modeling and results in a column with unsurpassed resolution and fast analysis for all compounds listed in US EPA Methods 502.2 and 8021. Method-specific chromatograms will be presented, including "added" compounds commonly requested with this analysis.
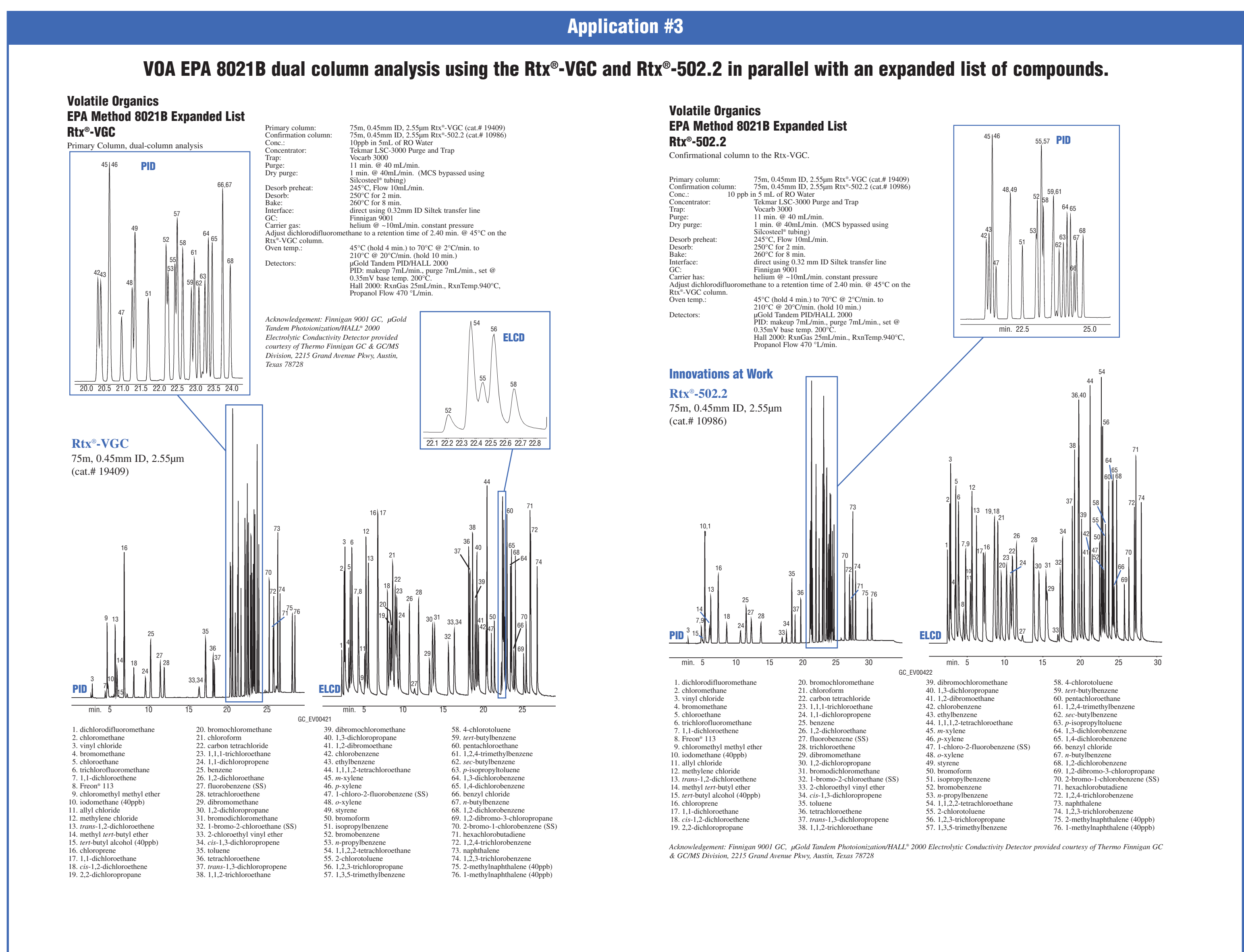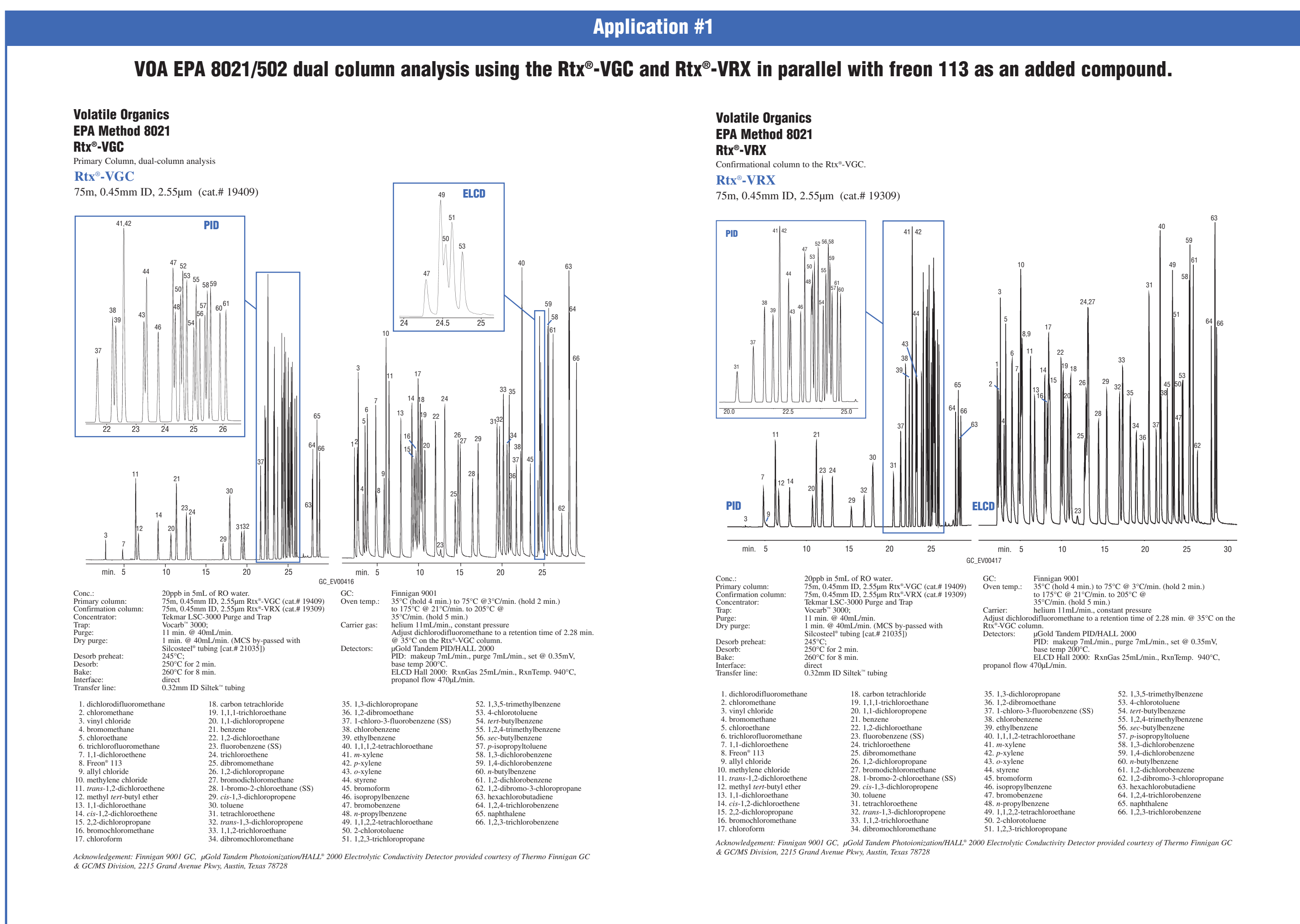
INTRODUCTION

US EPA Methods 502.2 and 8021 employ purge and trap to concentrate volatile contaminants in water, soil and wastewater. While purge and trap significantly increases sensitivity relative to other sample introduction techniques, it has its downside. Early eluting volatile compounds typically exhibit broad peak shapes due to inefficient sample transfer from the trap to the gas chromatograph (GC). This distorted peak shape decreases resolution between closely eluting compounds, placing demands on the analytical system and GC operating conditions.

US EPA GC methods for the determination of volatiles often recommend the use of photo ionization detector (PID) and an electrolytic conductivity detector (ELCD) installed in series on the GC system. The PID responds to aromatics, alkenes, alkynes and oxygenates. The ELCD detector is sensitive to halogenated compounds. Therefore, it is allowable to have coelutions on an analytical column as long as they can be resolved using separate detectors. The more problematic of these two detectors is the ELCD because of the characteristic peak tailing; sensitivity can be increased on the ELCD, but not without a sacrifice in peak shape. Optimization of this detector results in minimized tailing and maximized sensitivity. Even under these conditions, choosing an analytical column that can give reasonable separation of these halogenated compounds is difficult.
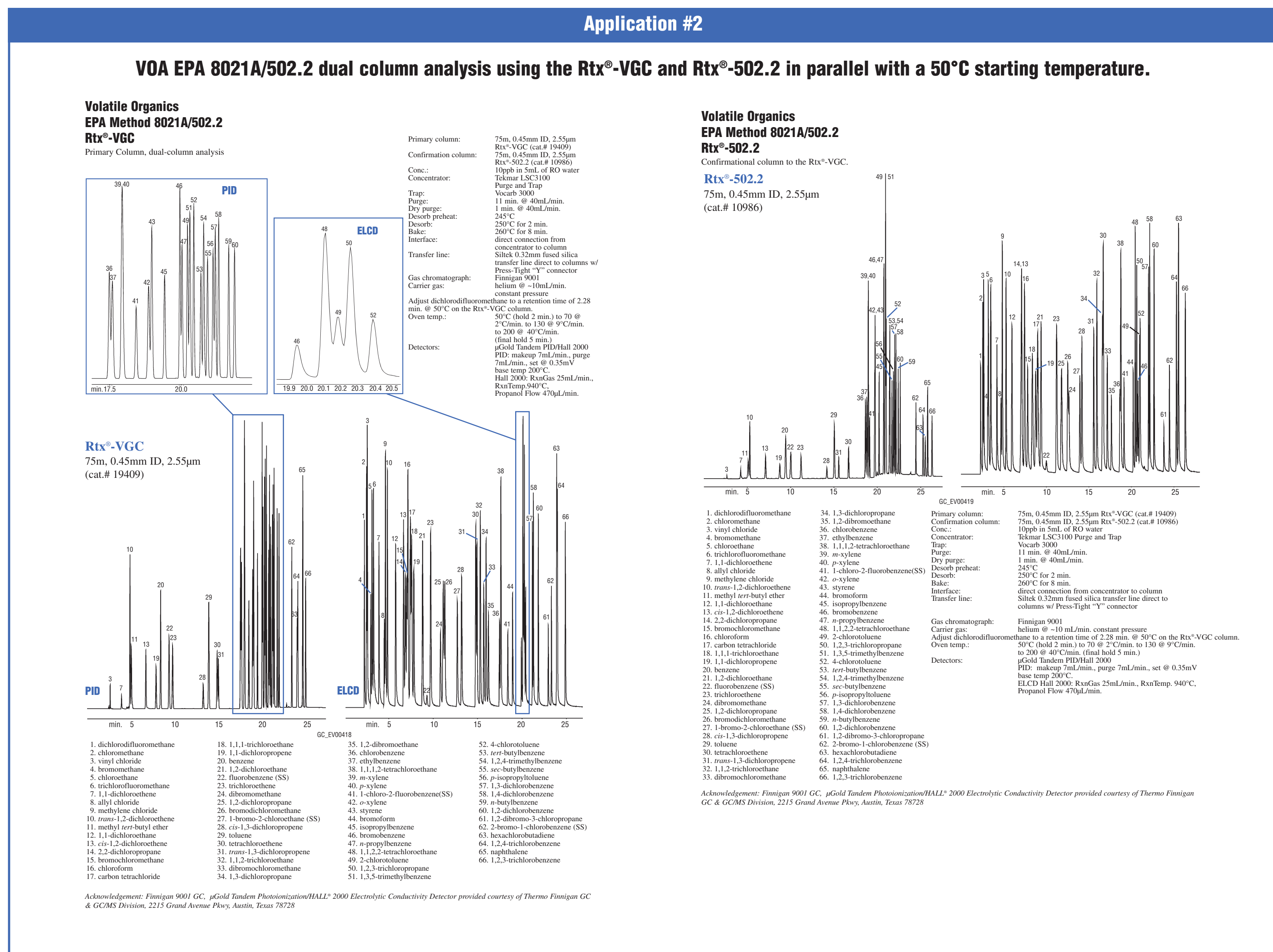
The Rtx®-VGC column is specifically designed to analyze volatiles using GC/PID/ELCD. The phase is optimized to achieve excellent separation of gases and early eluting compounds, specifically the four critical trihalomethanes (chloroform, bromodichloromethane, dibromochloromethane & bromoform). The column also provides unsurpassed separation in the fastest analysis time & cycle time, thereby increasing sample throughput.

EXPERIMENTAL

Several factors contribute to the total analysis time of volatile separations, such as purge and trap cycle time, GC runtime, GC oven cool down time (time it takes for the GC to cool down to the initial oven temperature) and column length. Long purge and trap cycles result from lengthened purge times, dry purges, long desorb times, and long trap bakes. Long oven cycle times result from low initial oven temperatures (from sub ambient to 35°C), slow temperature program rates, and low column operating temperatures. Although cryofocusing improves the separation of early eluting compounds, most environmental laboratories do not use it due to increased cost and cycle time. And, while a certain column length is necessary for separation, a column that is too long can increase analysis time and cost without a significantly increasing resolution.

Application #1
VOA EPA 8021/502 dual column analysis using the Rtx®-VGC and Rtx®-VRX in parallel with freon 113 as an added compound.

The Rtx®-VGC provides the best GC separations and fastest analysis time of target compounds found in US EPA Method 8021 & 502.2. Application # 1 shows the Rtx®-VGC as the primary column and the Rtx-VRX as a confirmation column. The target list includes commonly analyzed, but unregulated compounds, such as methyl-tert-butyl ether (MTBE) and Freon® 113. This application shows the separation of the gases and the trihalomethanes -- there are no coelutions using the PID/ELCD detectors in series. The 35°C starting temperature is necessary to resolve the Freon® 113 (1,1,2-trichloro-1,2,2-trifluoroethane) from 1,1-dichloroethane. Without the Freon® 113 added it is possible to start the GC at 50°C as shown in application #2.

Application #2
VOA EPA 8021A/502.2 dual column analysis using the Rtx®-VGC and Rtx®-502.2 in parallel with a 50°C starting temperature.

Application # 2 shows the analysis of the 8021A / 502.2 compound list without the addition of Freon® 113. This allows for a 50°C starting temperature which greatly reduces the total cycle time -- that is the time it takes for the GC to complete the oven cycle and come back down to starting temperature. The time it takes a Hewlett-Packard 5890 GC oven to cool from 205°C down to 35°C is 9 minutes, that time added to the analysis time in Application #1 of 28 minutes results in the fastest possible total cycle time of 37 minutes. Application #2 has a final temperature of 200°C and a starting temperature of 50°C. The time it takes for the oven to cool down is 4 minutes. The application has a total cycle time of less than 30 minutes, significantly faster than any other column available. For instance the VRX stationary phase requires a starting temperature of 40°C this combined with the 28-minute runtime assures that the total cycle time cannot be faster than 35 minutes. This faster sample throughput allows Environmental Laboratories to make at least 4 more runs per day over other volatile columns with better data quality, since the trihalomethanes are better resolved on the VGC stationary phase.

Application #3
VOA EPA 8021B dual column analysis using the Rtx®-VGC and Rtx®-502.2 in parallel with an expanded list of compounds.

These chromatograms (Application #3) incorporated a broader range of analytes, many of those compounds are found in US EPA Method 8021B, along with other requested compounds such as the 1 & 2 methylnaphthalene. There are 72 target compounds in this list, coelutions on the Rtx®-VGC are resolved on the Rtx®-502.2 column. Even with the addition of the semi-volatile methylnaphthalenes the runtime is still under 30 minutes.

CONCLUSION

Disinfectant by-products of drinking water - known as the trihalomethanes (THMs) - are the most commonly found contaminants in the public water supply. These four compounds: chloroform, bromodichloromethane, dibromochloromethane and bromoform are found in all treated municipal drinking water. The THMs must be well resolved from other volatile organic pollutants to prevent poor quantitation, inaccurate data, or mis-identification. All other columns exhibit partial or complete coelutions of the THM's with other target analytes even under optimized conditions. The Rtx®-VGC column provides better than 85% resolution of the THMs from other volatile compounds (application #1).

The Rtx®-VGC column provides 30% resolution of 1,1,2,2-tetrachloroethane/2-chlorotoluene and greater than 60% resolution of all other volatile compounds found in US EPA Methods 502.2 and 8021 (application # 1). This column provides the best resolution in less time than any other column for EPA Method 502.2.