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 revolved around selecting 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/ECD, many laboratories struggle to achieve a continually expanding compound list. All of the current phases available for these types of analytes suffer from lack of resolution between critical compounds, and many suffer from low thermal stability and long analysis times. While the use of computer stationary phase modeling, selecting polymers, and new functionalities can be tailored to the applications give unsatisfactory separation of specific compounds of interest.

Disinfectant by-products of drinking water, known as the trihalomethanes (THMs), are the most commonly found contaminants in the public water supply. The THMs are formed as a result of disinfection with chlorine. They are formed by the reaction of chlorine with natural organic compounds in the water. The THMs have been shown to be carcinogenic and are hazardous to human health. The USEPA has established secondary drinking water regulations for the THMs, which provide maximum allowable concentrations for the THMs.

Several factors contribute to the total analysis time of volatile separation, 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 long-time purge periods, and long trap times. Long oven cool-down times result from slow coolings to 35°C, slow oven temperature rise times, and low column-operating temperatures. Although lowering the oven-temperature improves the separation of early eluting compounds, most environmental laboratories do not use the time to increase oven temperature rise time and cool without a significantly increasing resolution.

INTRODUCTION

US EPA Methods 502.2 and 8021 apply 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 drawbacks. Early eluting volatile compounds typically exhibit broad peak shapes due to inefficient sample transfer from the trap to the gas chromatograph (GC). This broadened 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 volatile compounds often require the use of flame ionization detector (FID) and an electronic conductivity detector (ECD) interfaced in series on the GC systems. The FID provides quantitation, detection limits, and selectivity, but does not have sufficient sensitivity on an analytical column as long as they can be resolved using separate detectors. The mass sensitivity of the ECD is limited by the extremely narrow, peak tailing, sensitivity can be increased on the ECD but not without a sacrifice in selectivity, second detector response, and increased background. Even under these conditions, obtaining an analytical column that can give acceptable separation of such baseline-separated compounds is difficult.

The Rtx® VGC column is specifically designed to analyze volatiles using GC/PID/ECD. The phase is optimized to achieve excellent separations of gases and early eluting compounds, specifically the four critical halogenated methanes: dichlorodifluoromethane, dichlorodichloromethane, dibromodichloromethane, and bromodichloromethane. 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 separation, 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 long-time purge periods, and long trap times. Long oven cool-down times result from slow coolings to 35°C, slow oven temperature rise times, and low column-operating temperatures. Although lowering the oven-temperature improves the separation of early eluting compounds, most environmental laboratories do not use the time to increase oven temperature rise time and cool without a significantly increasing resolution.

Application #1

Application #2

Application #3

Application #4

These chromatograms (Application #4) incorporate a broader range of analytes, many of these compounds are found in US EPA Method 8021B, along with other compounds such as the 4-2 methylphenols. These chromatograms on the Rtx® VGC are resolved on the Rtx®-502.2 column. Even with the addition of the semi-volatile methylphenol classes 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, dibromodichloromethane, and bromoform are found in all treated municipal drinking water. The THMs must be well resolved from other volatile organic contaminants to prevent poor quantitations, inaccurate data, or misidentifications. All other columns exhibit partial or complete coelutions of the THMs with other target analytes even under optimized conditions. The Rtx® VGC column provides better than 95% resolution of the THMs from other volatile compounds (Application #4).

The Rtx® VGC column provides 98% resolution of 1,1,2-trichloroethane and greater than 99% 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.

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