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The Application of SW-846 Method 8261 to New SAM Analytes. Part One: Determination of Relative Volatility Values

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Introduction

Method 8261 provides analysis of problematic matrices, introducing novel quality tools including the determination of method performance by analyte in each analysis. The method uses analyte chemical properties, boiling point, and relative volatilities to measure method performance as functions of these chemical properties. Boiling point values for compounds are readily available in the literature but relative volatility values are unique to Method 8261.

Relative volatility is a chemical engineering variable that compares water-to-air partition coefficients to describe the relative recoveries of compounds in a given distillate. In the SW-846 Method 8261 application of vacuum distillation, relative volatility is an experimentally determined constant that relates to the water-to-air partition coefficient. The reader is encouraged to review the presentation, "An Overview of SW-846 Method 8261 Chemistry" for a background discussion of relative volatility.¹ This process of determining relative volatility constants has been previously reported.² This study is an extension of the earlier work.

This study reports the determination of the relative volatility values for analytes that are listed in SAM that have not been established.³

Study Approach. Series of distillations are performed on a water samples spiked with compounds. The amount of each compound in each distillation is determined as their response detected by a gas chromatograph/mass spectrometer (GC/MS). A recovery of a compound can be determined in a distillate by comparing responses in all distillates in a series. The recovery of a compound in a given distillate is the response of the compound in the distillate divided by the sum of response all distillates.

The amounts of compounds that are contained in the distillates depend on their relative volatilities.^{1,2} In addition to the study analytes, reference standards are added to the water sample before the series of distillations; reference standards with established relative volatilities are also added. The recoveries of reference compounds in the distillates are used to plot a relationship of recovery to relative volatility, and it is used to determine the relative volatility of the study analytes. The recovery of an analyte is then compared with the recoveries of the reference compounds, and an experimental relative volatility for the analyte is interpolated.

The compounds that have low relative volatility values, *e.g.* hexafluorobenzene, are easily distilled from water and will be completely recovered in the early distillates and will not be detected in the last distillate. Compounds that have a strong affinity for water, *e.g.* pyridine, will be far less recovered in the early distillates and will have a greater fraction in the later distillates. Therefore, comparing the fractional recovery of an analyte to the fractional recoveries of the reference standards allows the interpolation of relative volatility. For instance, if the fraction of a compound in a distillate lies between the fractions for hexafluorobenzene and benzene-*d*₆, we would know the compound's relative volatility would be between 0.86 and 4. Repeating the fractional distillation sets allows the determination of a compound's relative volatility value numerous times, therefore generating a confidence interval.

Experimental

Vacuum distiller: A Cincinnati Analytical Instruments (Cincinnati, OH) vacuum distiller (CAI, Model VDC1012) performed the distillations in the study. The operating conditions are presented in Table 1. Vacuum distillation times were varied, and the flush time was extended so that the vacuum distillation cycle time matched the GC/MS cycle time.

Table 1. Vacuum Distillation Parameters	
<i>Stage</i>	Time (min)
Vacuum distillation	7.5
Transfer	2.5
Bake-out	2.5
<i>Temperature</i>	°C
Condenser heat	95
Condenser cool	-10
Cryotrap desorb	120
Cryotrap trapping	-160
Cryotrap bake-out	200
Transfer line	200
Vacuum distiller lines	95
Multiport valve	200
Autosampler lines	95
<i>Decontamination</i>	
Cycles	16
Pressurization time (min)	0.1
Evacuation time (min)	1.4

GC/MS apparatus: The vacuum distiller is interfaced to a GC/MS so that the vacuum distillate is transferred directly to the GC/MS for analysis after distillation. In this study, the GC/MS was

a Thermo DSQ mass spectrometer and Thermo Trace GC. The GC capillary column was a 30-m x 0.25-mm i.d., 1.5- μ m film VOCOL column (Supelco, Bellefonte, PA). The GC operating conditions were 2.5 min at -20°C, 40°C/min ramp to 60°C, 5°C/min ramp to 120°C and held at 120°C for 1 min, 20°C/min ramp to 220°C and held for 12 min, resulting in a GC run time of 34 min. The injection was split 30:1 with a constant flow rate of 1.4 ml/min. The mass spectrometer was scanned between 35 and 300 amu at 1 scan/sec.

Sample Preparation and Analyses. Six 5-mL water samples were spiked with compounds listed in Table 2. The amounts of compounds in spikes are also included in the table. Each sample and spike was distilled six times in succession to obtain a set of distillates. Each distillation was for 7.5 min

Table 2. Relative Volatility Reference Standards and Study Analytes		
Compound	Amount (ng)	Relative Volatility ²
<i>Relative Volatility Reference Standards</i>		
hexafluorobenzene	250	0.86
benzene- <i>d</i> ₆	250	4.0
<i>o</i> -xylene- <i>d</i> ₁₀	250	6.14
1,2-dichloroethane- <i>d</i> ₄	250	20
ethylacetate- ¹³ C	2500	150
acetone- ¹³ C	3100	600
dioxane- <i>d</i> ₈	2400	5800
pyridine- <i>d</i> ₅	12500	15000
<i>Study Analytes</i>		
allyl alcohol	20,000	
1,4-dithiane	1800	
ethylene oxide	5000	
2-chloroethanol	50,000	
1,4-thioxane	2500	
propylene oxide	1000	

Results and Discussion

The first part of this study was to determine the experimental conditions necessary to estimate the relative volatility values of the study analytes (e.g., how many times and for how long the mixture of reference standards and analytes would be distilled). For instance, if we distilled a sample so long that all of the analytes and reference standards were completely transferred (100 % recovery) to the initial distillate, there would be no way to gauge differences due to relative volatility. The experiments need be designed so that after a series of distillations there is a breadth of recoveries among the compounds sufficient to define the recovery of compounds as a function of relative volatility.

The analytes in this study were all found to have a strong affinity for water and not quickly distilled and therefore short initial distillation times were not necessary (see Ref 4 for determining the relative volatility of a more volatile compound). The distillation time that is routinely used for analyses is 7.5 minutes and longer distillation times are not typically used. Therefore the distillation sets used to determine the analytes were simply six 7.5-minute successive distillations.

Figure 1 displays the recoveries of the reference standards in a distillate. The graph shows the fractional recoveries of the reference standards compared to the natural logarithm of their relative volatility values. The data points in the line from left to right are the reference standards, starting with hexafluorobenzene then benzene- d_6 , *o*-xylene- d_{10} , 1, 2-dichloroethane- d_4 , ethyl acetate- ^{13}C , acetone- ^{13}C , dioxane- d_8 and pyridine- d_5 . By connecting all of the points (not using the graph line shown in Figure 1), lines are made that describes how compounds are recovered in the distillate as a function of their relative volatility values. Therefore if we can measure the fraction of a compound in the distillate, we can interpolate its relative volatility value as long as the recovery lies between 5% and 85%.

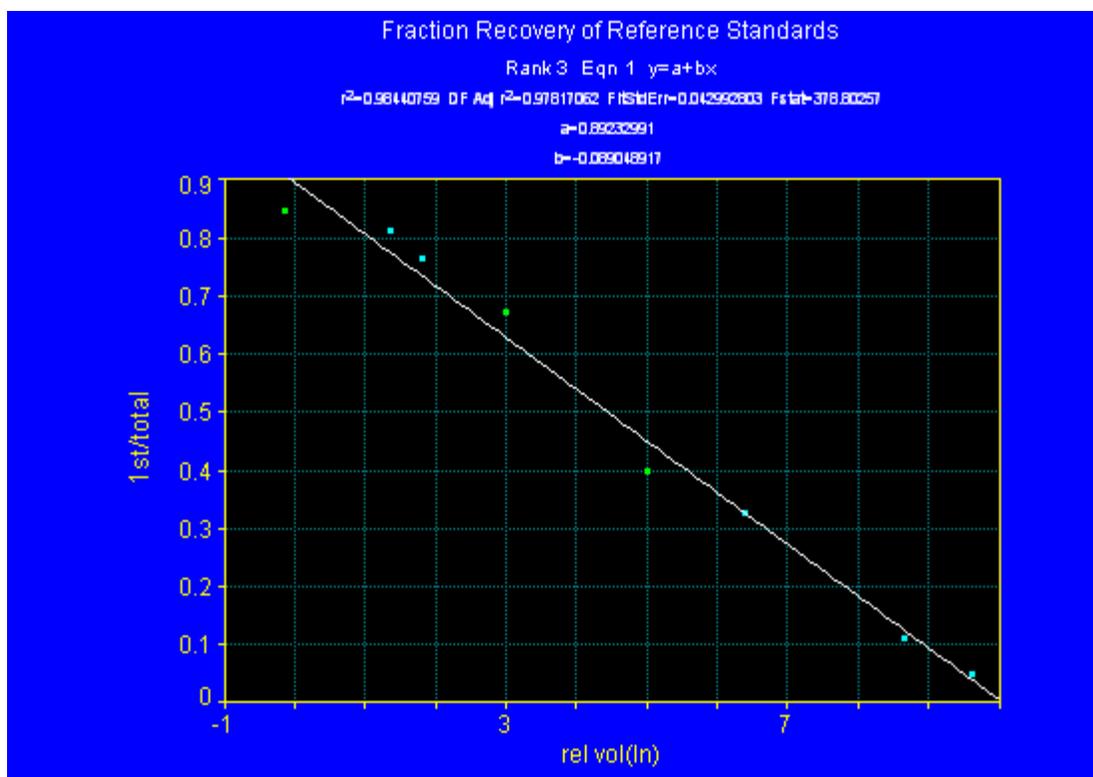


Figure 1 Recovery compared with the natural logarithm of their relative volatility

With the exception of 2-chloroethanol, the recoveries of the analytes were found to consistently fall within the range of the reference standards. The recoveries of the reference standards, 1, 2-dichloroethane- d_4 and ethyl acetate- ^{13}C (fourth and fifth points from the upper right-hand corner in Fig 1) bracketed the recoveries of ethylene oxide and propylene oxide. Therefore a line between these two reference standards was used to interpolate the relative volatility of ethylene oxide and propylene oxide. Similarly, recovery of the 7th and 8th reference standards (ethyl acetate- ^{13}C and acetone- ^{13}C) bracketed the recovery of allyl alcohol, 1, 4-thioxane, and 1, 4-dithiane. The line between the 7th and 8th reference standards was used to interpolate the relative volatility of these analytes.

In general, pyridine- d_5 is an inconsistent reference compound due to its high solubility as well as poor chromatographic behavior. Pyridine can at times behave as a compound with a much lower relative volatility (Fig 2). The determination of 2-chloroethanol's relative volatility therefore was not as straight forward as the other analytes. The reference standard of greatest relative volatility (pyridine- d_5) did not always have a recovery less than that for 2-chloroethanol so 2-chloroethanol's relative volatility value could not always be interpolated. To overcome this inconsistency an extrapolation of the line (Fig 1) described by the 7th and 8th reference standards (omitting pyridine- d_5 was used to determine 2-chloroethanol's relative volatility).

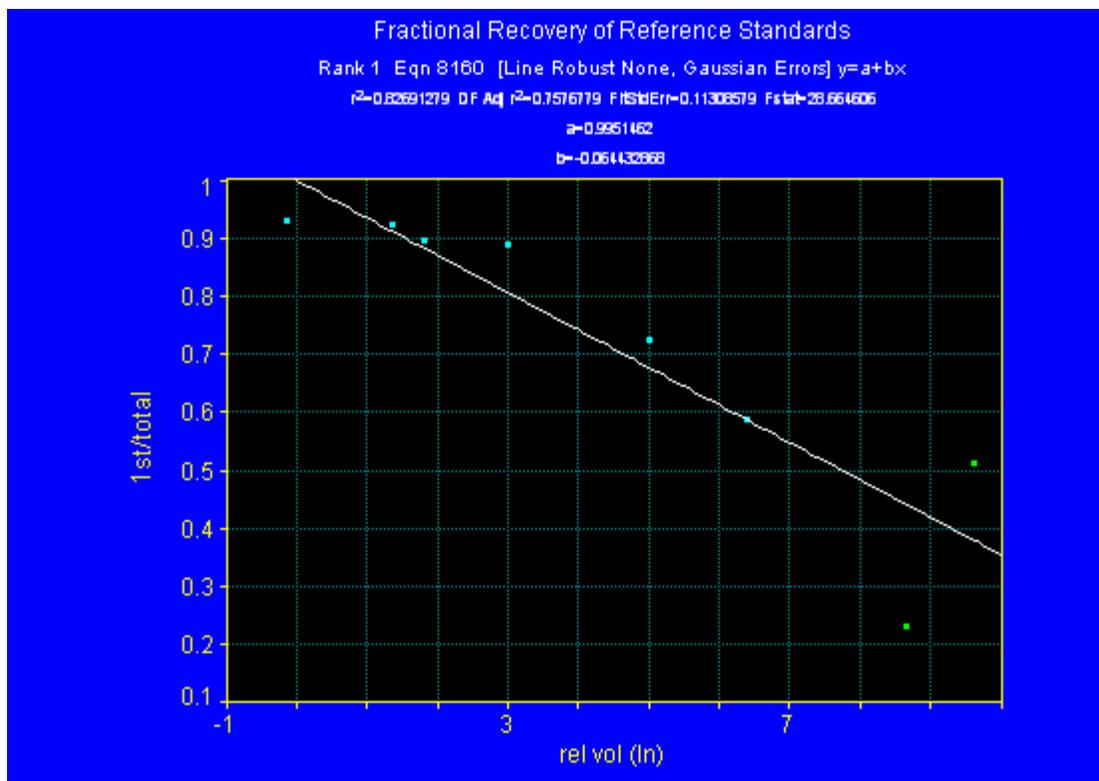


Figure 2 Recovery compared with the natural logarithm of relative volatility (6th set)

Table 3 lists the reference standards, their relative volatility range and the matching of analytes to the reference standards.

Table 3. Relative volatility reference standards and related analytes		
Internal Standard Pairs	Relative Volatility Range	Study Analytes
hexafluorobenzene and benzene- d_6	0.86 to 4	none
benzene- d_6 and <i>o</i> -xylene- d_{10}	4 to 6.14	none
<i>o</i> -xylene- d_{10} and 1,2-dichloroethane- d_4	6.14 to 20	none
1,2-dichloroethane- d_4 and ethyl acetate- ^{13}C	20 to 150	ethylene oxide and propylene oxide
ethyl acetate- ^{13}C and acetone- ^{13}C	150 to 600	none
acetone- ^{13}C and 1,4-dioxane- d_8	600 to 5800	allyl alcohol, 2-chloroethanol, 1,4-thioxane, and 1,4-dithiane

Calculation of Relative Volatilities

There were six replications of the distillation sets performed on four different days. For each set, the response of the analytes in the first 7.5-minute distillation was compared with the sum of their responses for the second distillation through to the last distillation. As reported previously, the relationship of recovery to the natural logarithm of relative volatility is ideally a straight line.² Therefore the pairs of relative-volatility reference standards that bracket the individual analytes were used to define a straight line (y-axis recovery and x-axis the natural logarithm of relative volatility) that would then be used to determine the relative volatility of analytes. The average of the six experimentally determined relative volatilities and their standard deviation are listed by analyte in Table 4.

As noted the 2-chloroethanol values were determined by extrapolation of the acetone-¹³C and 1,4-dioxane-*d*₈ relative volatility-fractional recovery line. The precision of the extrapolation was surprisingly precise and comparable to interpolated values of the other compounds (Table 4). The behavior of 2-chloroethanol was quite consistent, and a labeled analog of 2-chloroethanol would be superior to pyridine-*d*₅ as an internal standard.

analyte	relative volatility	
	average	standard deviation
allyl alcohol	6080	195
1,4-dithiane	604	218
ethylene oxide	75	12
2-chloroethanol	13800	930
1,4-thioxane	2560	173
propylene oxide	106	14

Conclusion

The compounds can be distilled from water and detected through the VD/GC/MS instrumentation. The relative volatility values for the study analytes were determined. Additional studies are necessary to determine the performance of method 8261 for the analytes.

References

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4. Hiatt, M.H. USEPA web presentation, *The Application of SW-846 Method 8261 to Analytes Required in Superfund's Current Statement of Work, SOM01.1. Part One; Determination of Relative Volatility Values*, June 19, 2006, <http://www.epa.gov/nerlesd1/chemistry/vacuum/technotes/pdf/new%20superfund%20analytes3.pdf>