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

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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" (http://www.epa.gov/nerlesd1/chemistry/vacuum/training/pdf/theory-rev5.pdf) for a background discussion of relative volatility. This process of determining relative volatility constants has been previously reported[1]. This study is an extension of the earlier work.

Relative volatility values have been experimentally determined for all Superfund volatile analytes from the current statement of work (SOW) with the exception of six volatile analytes identified in SOM01.1. This study reports the determination of the relative volatility values for these six analytes so that they may be covered by Method 8261.

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

Stage	Time (min)
Vacuum distillation	7.5
Transfer	2.5
Bake-out	2.5
Temperature	ºC
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
Decontamination	
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-µm 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. A 5-mL water sample was fractionally distilled to obtain a set of distillates. The water was spiked with approximately 250 ng per compound (see Table 2). Seven water samples were distilled to obtain seven sets of fractional distillates. The first distillate in each set was obtained by distilling for 6 seconds. The second and third distillates in each set were obtained by distilling the water for 2 minutes. The last two distillates in each set were obtained by distilling the samples for 7.5 minutes.

Table 2. Relative Volatility Reference Standards and New CLP Analytes

Compound	Amount (ng)	Relative Volatility
Relative Volatility Reference Standards		
hexafluorobenzene	250	0.86
benzene-d_6	250	4.0
o-xylene-d_{10}	250	6.14
1,2-dichloroethane-d_4	250	20
ethylacetate-^{13}C	2500	150
acetone-^{13}C	3100	600
dioxane-d_8	2400	5800
pyridine-d_5	12500	15000
Study Analytes		
1,1,2-trichloro-1,2,2-trifluoroethane	250	
methyl acetate	250	
carbon disulfide	250	
methyl *tert*-butylether (MTBE)	250	
cyclohexane	250	
methyl cyclohexane	250	

Study Approach. The six study analytes and the reference standards are spiked into 5 mL of water. By performing a series of fractional distillations on the water, we obtain distillates which are then analyzed for the study compounds. Determining what portion of each compound is in each distillate provides the data necessary to determine relative volatility. The compounds that have low relative volatility values, like 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, like 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 a compound of unknown relative volatility 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.

Results and Discussion

The first part of this study was to determine how many times the mixture of reference standards and analytes would be distilled and how long each distillation should take. For instance, if we distilled a sample so long that all of the analytes and reference standards were completely transferred to the distillate, there would be no way to determine the effects of relative volatility. The challenge would be to determine a series of distillations where the relative volatilities of the compounds being studied are easily measured.

Before proceeding a convention must first be addressed. Notice in Table 2 that the most volatile reference standard, hexafluorobenzene, is 0.86. Determination of relative volatility values less than 0.86 would not be bracketed by another reference standard so any value would need to be extrapolated. Therefore we introduce a hypothetical "ideal" reference standard that is close to zero (it has no affinity for water) and no matter what the distillation conditions are, 100% is always recovered in a distillation. Actually we use the value '0.01' instead of zero, as zero can cause problems when evaluating natural logarithms (a useful transform) of relative volatility. Therefore, with this convention, compounds more volatile than hexachlorobenzene are flanked by the internal standard hexafluorobenzene and the ideal reference standard with relative volatility of 0.01.

Figure 1 displays the recoveries of the reference standards in a distillate. The data points in the line from left to right are the reference standards, starting with the ideal standard, then hexafluorobenzene, 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, a line is 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 33% and 100%.

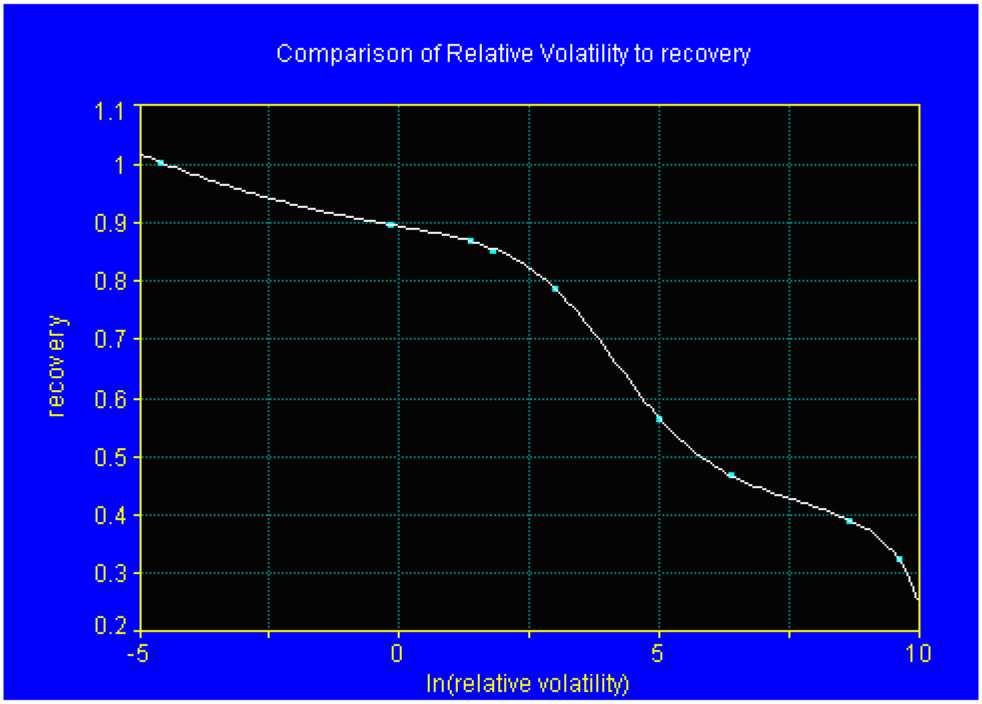


Figure 1. Recovery compared to ln (relative volatility)

But the confidence that we are able to interpolate a relative volatility value varies along the line. Note in Figure 2 that the relative volatility effects between the 5th and 6th reference points (bracketed with parallel yellow lines) are easily observed being that there is more than an absolute 20% difference in their recoveries. The relative volatility effects between the 2nd and 3rd reference standards are not so easily distinguished. If there was a 5% error measuring a recovery in this range (86 to 90%), assigning a relative volatility value would be imprecise.

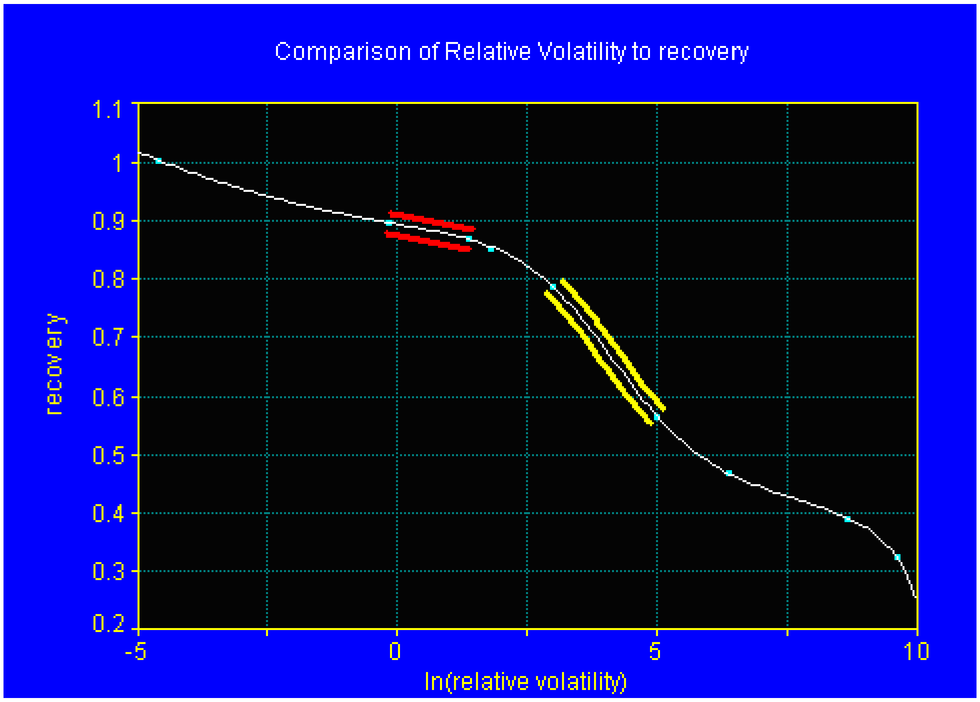


Figure 2. Line segments showing both little (red) and large recovery differences (yellow)

Therefore, setting up the distillation sequence depends on the compounds that are being evaluated for relative volatility values. If the compounds are very volatile (have low relative-volatility values less than hexafluorobenzene), then the initial distillations will be performed for very short periods so that the recovery of hexafluorobenzene will be lower than usual (>95%). By making hexafluorobenzene recovery <90%, it is easier to distinguish relative volatility values lower than that for hexafluorobenzene. One criterion in developing a distillation sequence is that the recovery range between reference standards (bracketing the compounds being investigated) be greater than 10%.

One more distillation phenomenon needs to be addressed. The first seconds of a vacuum distillation carries all of the air contained in the sample vessel. This rush of gas causes the efficiency of the cryotrap to drop drastically (Figure 3). Therefore compounds that are in the headspace in the first seconds are not trapped as efficiently as they are after the initial seconds. This is not a problem normally, but when investigating the performance of the most volatile compounds, the change in efficiency can confound the comparison of the first distillation with later distillation for recovery calculations. For this reason, the first distillation is for only a six-second duration to remove air; the response of compounds in this earliest distillate are not used in determining relative volatility values.

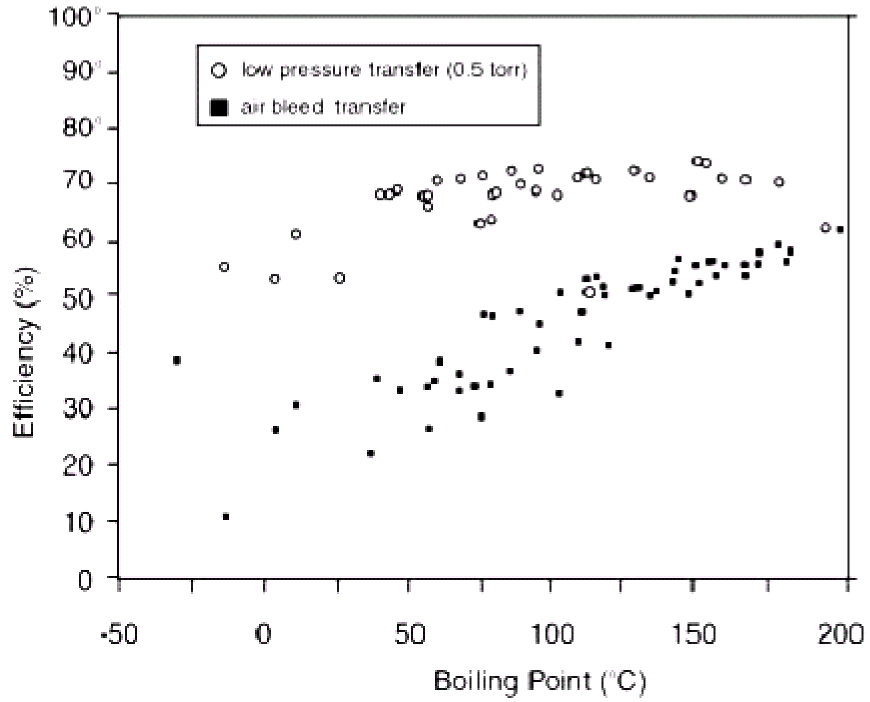


Figure 3. Cryotrap trapping efficiency as a function of boiling point for Method 8261 analytes[1]

Initial experiments found that the CLP analytes being investigated fell into three relative volatility ranges; a value less than 0.86 (hexafluorobenzene), a value between 20 and 150 (1, 2-dichloroethane-d_4 and ethyl acetate-^{13}C), and a value between 150 and 600 (ethyl acetate-^{13}C and acetone-^{13}C). Table 3 presents the groupings. Therefore the next step in this study was to determine a series of distillations that gave at least a 10% recovery difference between the reference standards bracketing the three ranges. The set of distillations that provided acceptable results consisted of 5 distillations with distillation times of 6 sec, 2 min. 2 min, 7.5 min, and 7.5 min distillation times. The response of each compound in the second distillation (first 2 min distillation) was compared with the sum of responses for the second through the last distillation to provide recovery. Figure 1 demonstrates the calculated recovery of the reference standards from the final distillation sequence.

Table 3. Relative volatility reference standards and related analytes

Internal Standard Pairs	Relative Volatility Range	Study Analytes
hexafluorobenzene and “ideal”	0.01 to 0.86	1,1,2-trichloro-1,2,2-trifluoroethane
		carbon disulfide
		cyclohexane
		methyl cyclohexane
1,2-dichloroethane-d_4 and ethyl acetate-^{13}C	20 to 150	MTBE
ethyl acetate-^{13}C and acetone-^{13}C	150 to 600	Methyl acetate

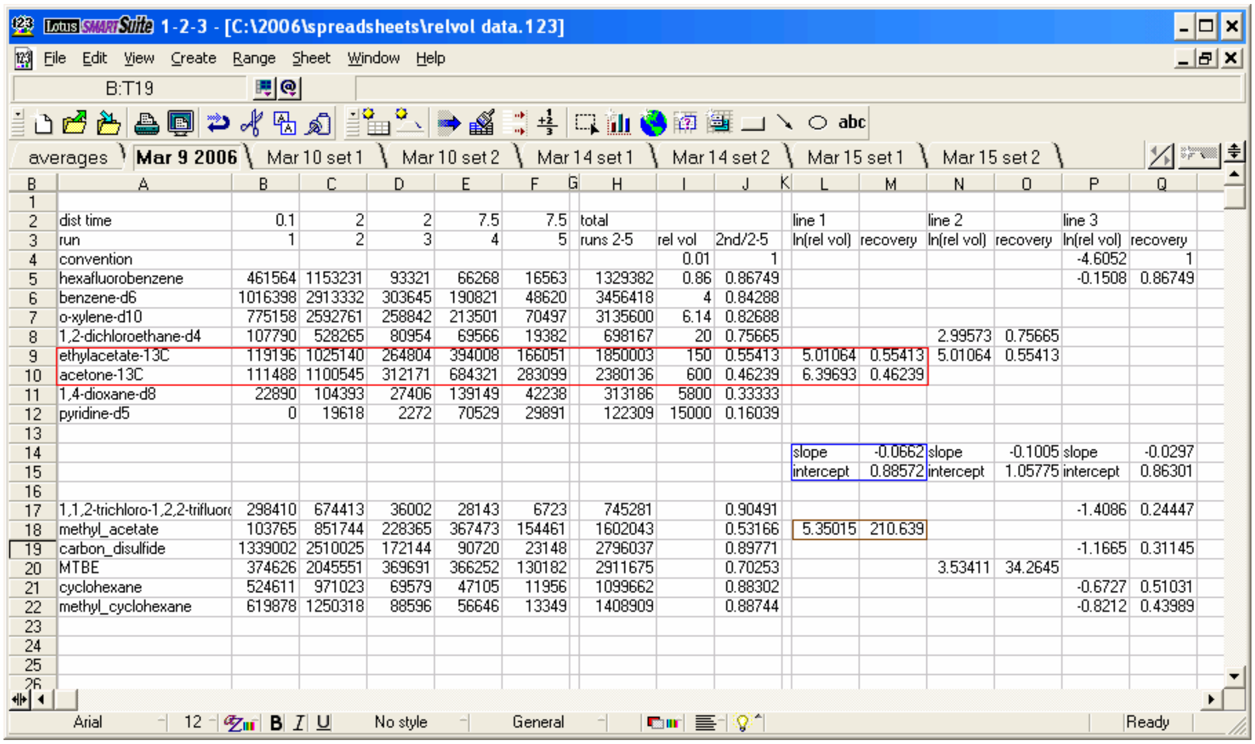
Calculation of Relative Volatilities

There were seven replications of the distillation sets performed on four days. For each set, the response of the analytes in the second distillation was compared with the sum of their responses for the second distillation through to the last distillation (the fifth). As reported previously, the relationship of recovery to the natural logarithm of relative volatility is ideally a straight line[1]. 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.

Figure 4 illustrates the calculations that were performed in a spreadsheet reducing GC/MS analyte responses to relative volatility values. The recoveries were determined as the sum of responses across a row (columns C through F) and are presented in column J. The red rectangle in Figure 5 identifies the relative volatility reference standard responses that were used to determine line 1 (blue rectangle, Figure 4). Note that the first distillation (0.1 min) was not used in the calculations.

In Figure 4, the line described in the blue box (slope in cell M14 and intercept in cell M15) was then used to determine the relative volatility for methyl acetate as its recovery fell between the recoveries of the reference standards making line 1. The brown rectangle displays the ln (relative volatility) value in column L and relative volatility in column M.

Line 2 (slope in cell O14 and intercept in cell O15) was solved using the 1, 2-dichloroethane-d_4 and ethyl acetate-^{13}C reference standards. This line was used to determine the relative volatility value for MTBE. Line 3 (slope in cell Q14 and intercept in cell Q15) was using the “ideal” and hexafluorobenzene reference standards. This line was used to calculate the values for the remaining analytes. This process was repeated for each compound in each of the seven distillation sets.

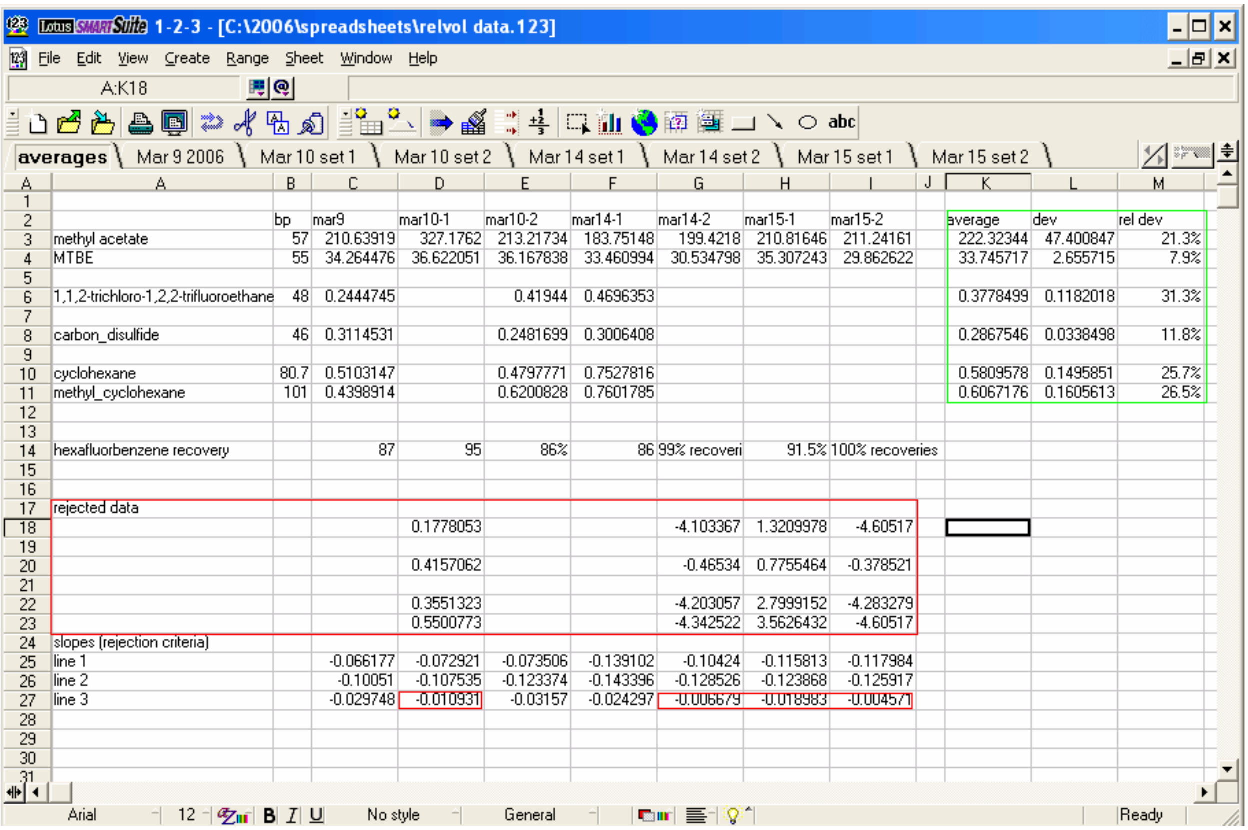


B	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q
1																	
2	dist time	0.1	2	2	7.5	7.5		total				line 1		line 2		line 3	
3	run	1	2	3	4	5		runs 2-5	rel vol	2nd/2-5		ln(rel vol)	recovery	ln(rel vol)	recovery	ln(rel vol)	recovery
4	convention								0.01	1						-4.6052	1
5	hexafluorobenzene	461564	1153231	93321	66268	16563		1329382	0.86	0.86749						-0.1508	0.86749
6	benzene-d6	1016398	2913332	303645	190821	48620		3456418	4	0.84288							
7	o-xylene-d10	775158	2592761	258842	213501	70497		3135600	6.14	0.82688							
8	1,2-dichloroethane-d4	107790	528265	80954	69566	19382		698167	20	0.75665				2.99573	0.75665		
9	ethylacetate-13C	119196	1025140	264804	394008	166051		1850003	150	0.55413		5.01064	0.55413	5.01064	0.55413		
10	acetone-13C	111488	1100545	312171	684321	283099		2380136	600	0.46239		6.39693	0.46239				
11	1,4-dioxane-d8	22890	104393	27406	139149	42238		313186	5800	0.33333							
12	pyridine-d5	0	19618	2272	70529	29891		122309	15000	0.16039							
13																	
14												slope	-0.0662	slope	-0.1005	slope	-0.0297
15												intercept	0.88572	intercept	1.05775	intercept	0.86301
16																	
17	1,1,2-trichloro-1,2,2-trifluor	298410	674413	36002	28143	6723		745281		0.90491						-1.4086	0.24447
18	methyl_acetate	103765	851744	228365	367473	154461		1602043		0.53166		5.35015	210.639				
19	carbon_disulfide	1339002	2510025	172144	90720	23148		2796037		0.89771						-1.1665	0.31145
20	MTBE	374626	2045551	369691	366252	130182		2911675		0.70253				3.53411	34.2645		
21	cyclohexane	524611	971023	69579	47105	11956		1099662		0.88302						-0.6727	0.51031
22	methyl_cyclohexane	619878	1250318	88596	56646	13349		1408909		0.88744						-0.8212	0.43989
23																	
24																	
25																	

Figure 4. Spreadsheet determination of relative volatility

One observation was that the pair of reference relative volatility values describing the most volatile compounds was not always used. This was due to the fact that the recovery of hexafluorobenzene approached 100% for a given distillation and not 90% as was desired. When this occurred, the slope of the line connecting the points for the ideal reference standard (relative volatility 0.01 and recovery 100%) and hexafluorobenzene (relative volatility of 0.86 and recovery near 100%) became negligible and interpolation along the resulting line became unreliable. For this reason, whenever the recovery of hexafluorobenzene for the second distillation of a set was greater than 90%, that set was not used in the determination of relative volatilities less than hexafluorobenzene.

The summary of the calculated relative volatility data is presented in Figure 5. The green rectangle contains the average of the accepted relative volatility values that were determined over the seven distillation sets. The data that was rejected because the recovery difference between the "ideal" and hexafluorobenzene was less than 10% is displayed in the red rectangle in Figure 5.



A	A	B	C	D	E	F	G	H	I	J	K	L	M
1													
2		bp	mar9	mar10-1	mar10-2	mar14-1	mar14-2	mar15-1	mar15-2		average	dev	rel dev
3	methyl acetate	57	210.63919	327.1762	213.21734	183.75148	199.4218	210.81646	211.24161		222.32344	47.400847	21.3%
4	MTBE	55	34.264476	36.622051	36.167838	33.460994	30.534798	35.307243	29.862622		33.745717	2.655715	7.9%
5													
6	1,1,2-trichloro-1,2,2-trifluoroethane	48	0.2444745		0.41944	0.4696353					0.3778499	0.1182018	31.3%
7													
8	carbon_disulfide	46	0.3114531		0.2481699	0.3006408					0.2867546	0.0338498	11.8%
9													
10	cyclohexane	80.7	0.5103147		0.4797771	0.7527816					0.5809578	0.1495851	25.7%
11	methyl_cyclohexane	101	0.4398914		0.6200828	0.7601785					0.6067176	0.1605613	26.5%
12													
13													
14	hexafluorbenzene recovery		87	95	86%	86	99% recoveri	91.5%	100% recoveries				
15													
16													
17	rejected data												
18				0.1778053			-4.103367	1.3209978	-4.60517				
19													
20				0.4157062			-0.46534	0.7755464	-0.378521				
21													
22				0.3551323			-4.203057	2.7999152	-4.283279				
23				0.5500773			-4.342522	3.5626432	-4.60517				
24	slopes (rejection criteria)												
25	line 1		-0.066177	-0.072921	-0.073506	-0.139102	-0.10424	-0.115813	-0.117984				
26	line 2		-0.10051	-0.107535	-0.123374	-0.143396	-0.128526	-0.123868	-0.125917				
27	line 3		-0.029748	-0.010931	-0.03157	-0.024297	-0.006679	-0.018983	-0.004571				
28													
29													
30													

Figure 5. Summary of results for the seven distillation sets

Conclusion

The compounds that had not been evaluated for Method 8261, but contained in Superfund's analyte list, are found to be quite volatile and easily vacuum distilled.

References

[1] Hiatt, M. H. Anal Chem. 1995, 67, 4044-4052. EPA version is posted
http://www.epa.gov/nerlesd1/chemistry/vacuum/reference/analysis/anal.htm