Using Surrogates to Measure Matrix Effects and Correct Analytical Results

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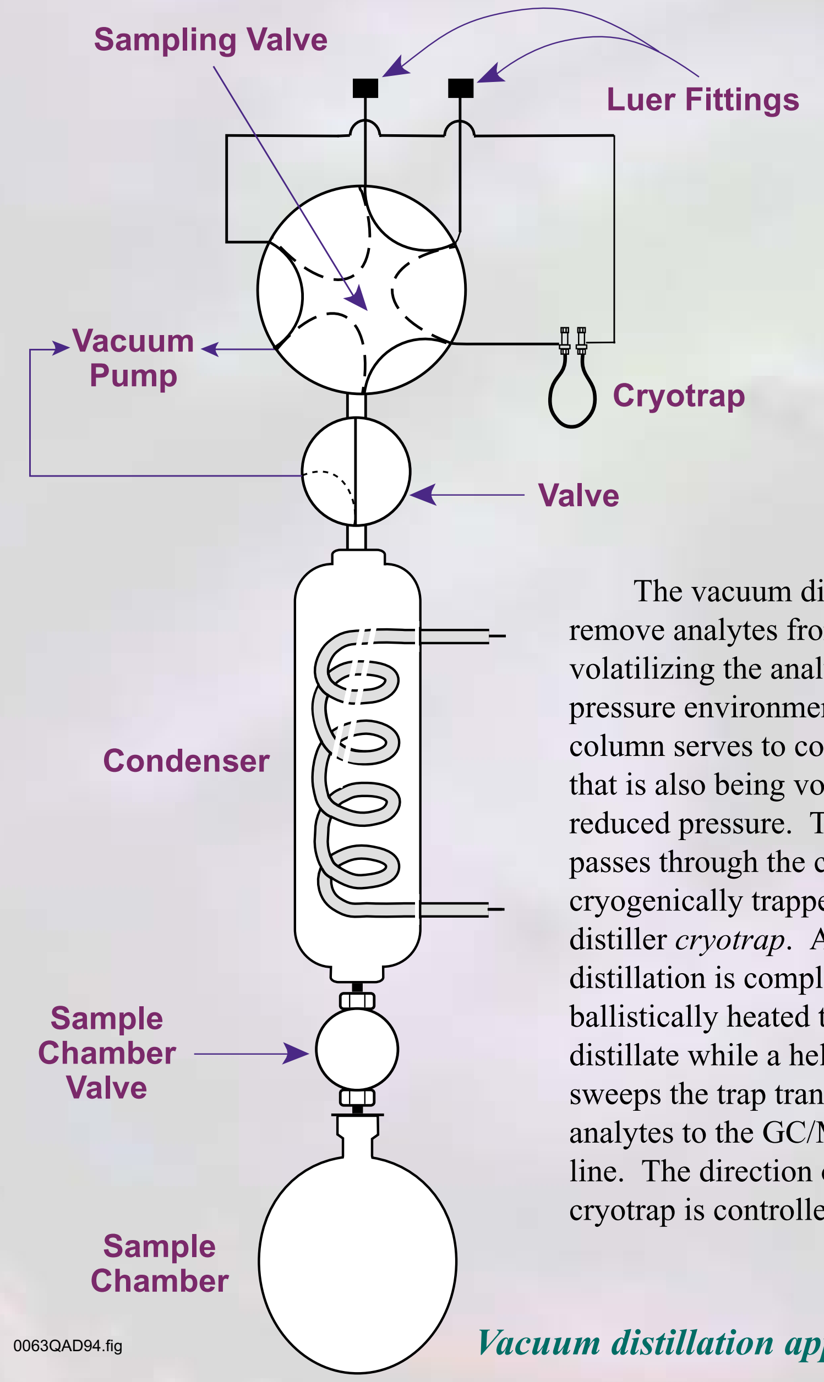
Vacuum Distillation



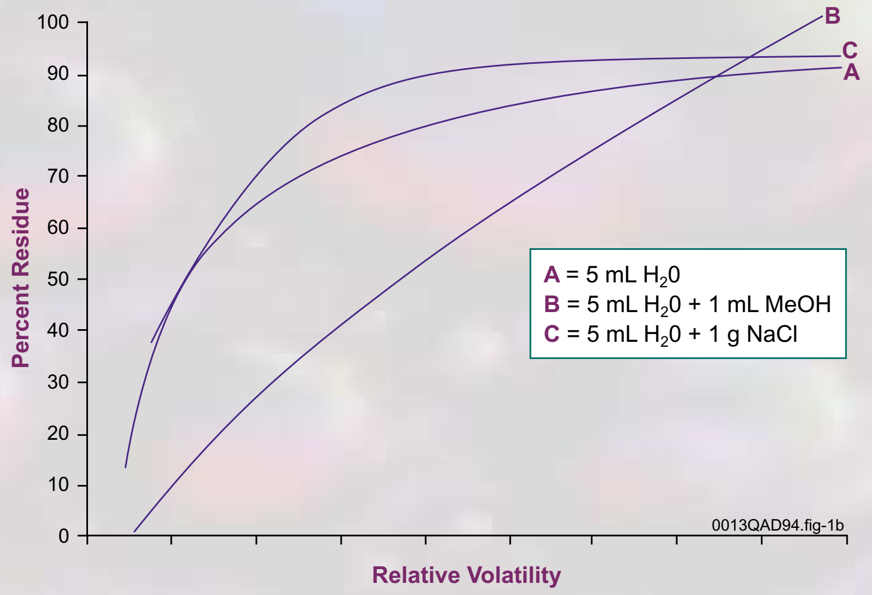
The vacuum distiller serves to remove analytes from a sample by volatilizing the analytes in a reduced pressure environment. A condenser column serves to condense most water that is also being volatilized at the reduced pressure. The material that passes through the condenser is cryogenically trapped in the vacuum distiller *cryotrap*. After the vacuum distillation is complete, the cryotrap is ballistically heated to volatilize the distillate while a helium carrier gas sweeps the trap transferring the analytes to the GC/MS via a transfer line. The direction of flow at the cryotrap is controlled by a 6-port valve.

Vacuum distillation apparatus.

Residue

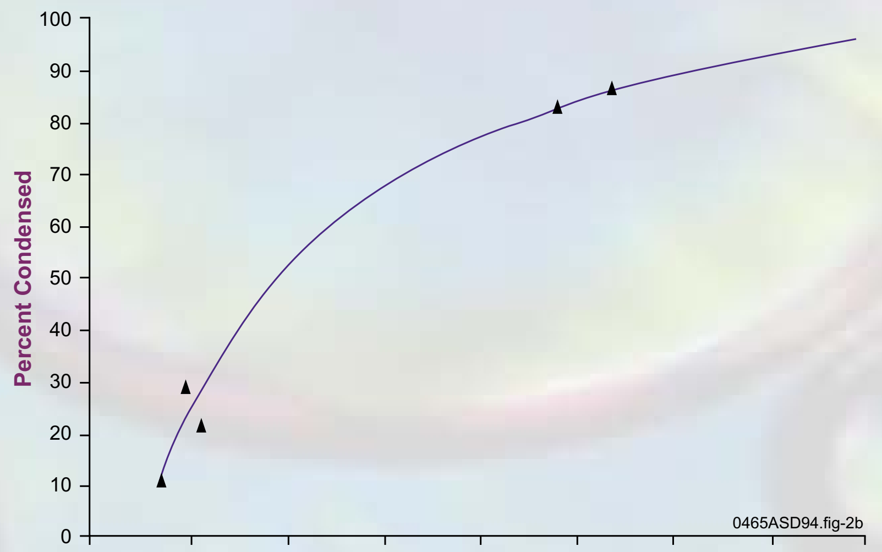
The material that remains in the sample container after a vacuum distillation corresponds to a compound s partition coefficient between air and water (K_{wa}).

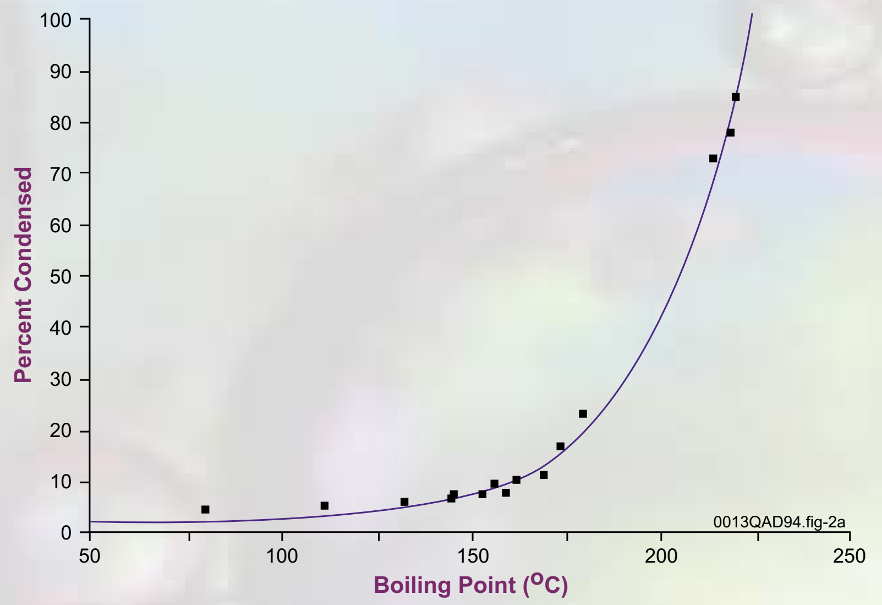
Comparison of the relative volatility of the analytes to the percent of analytes remaining in the sample residue for various matrices.



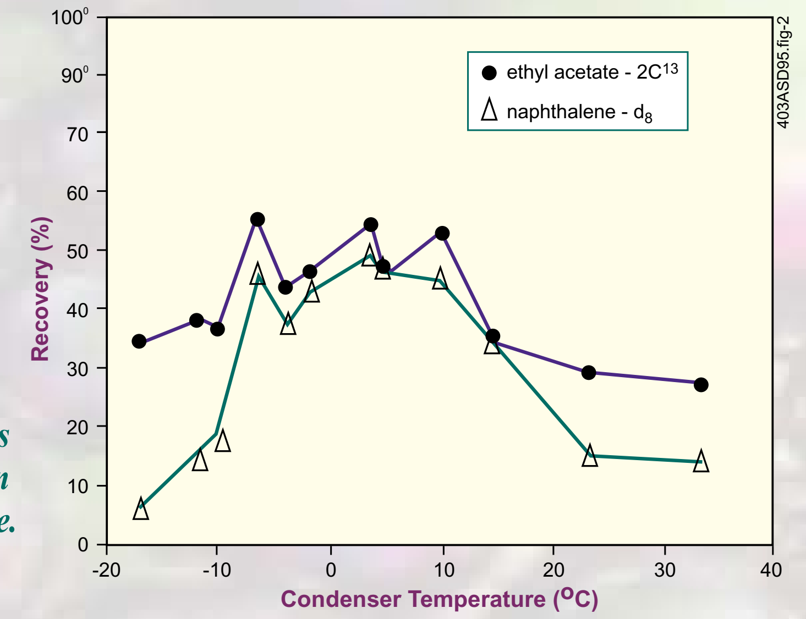
Condenser Effects

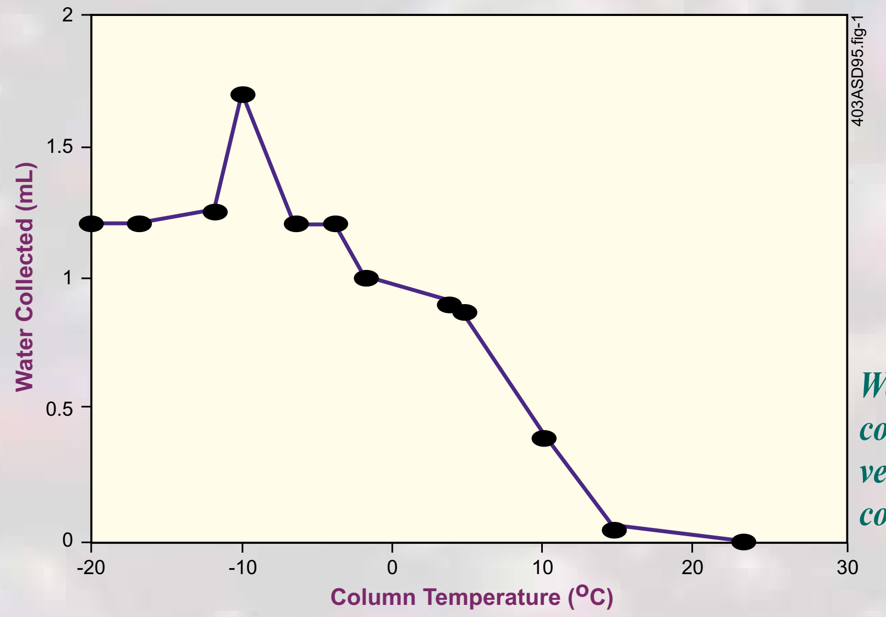
The condenser traps material corresponding a compound's vapor pressure (measured as boiling point, BP) and partition coefficient, K_{wa}. A condenser is calibrated for effects on analyte recoveries by varying its temperature. Too warm and water passes through to the cryotrap which then will interfere with chromatography. Too cold and little of the higher boiling analytes will be collected at the cryotrap.





Analyte recovery versus condenser column temperature.

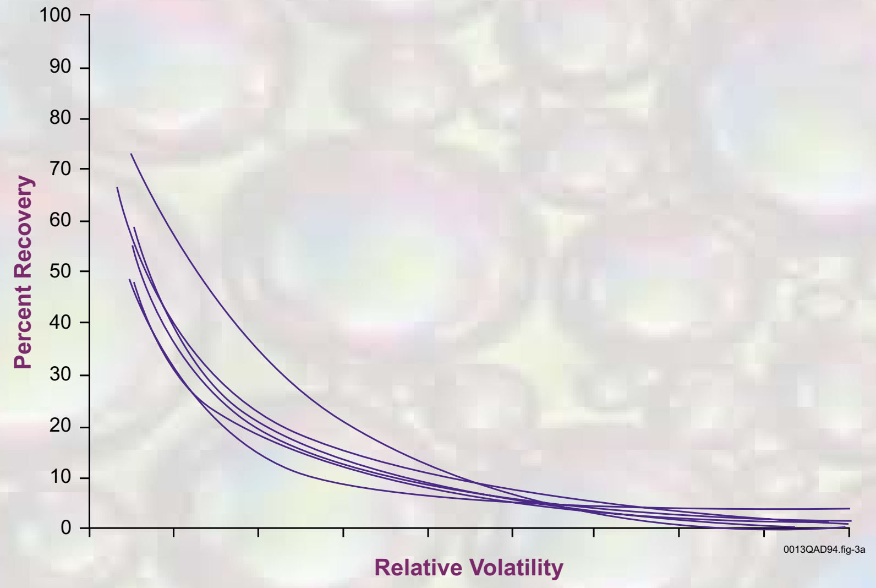




Water collected on condenser column versus condenser column temperature.

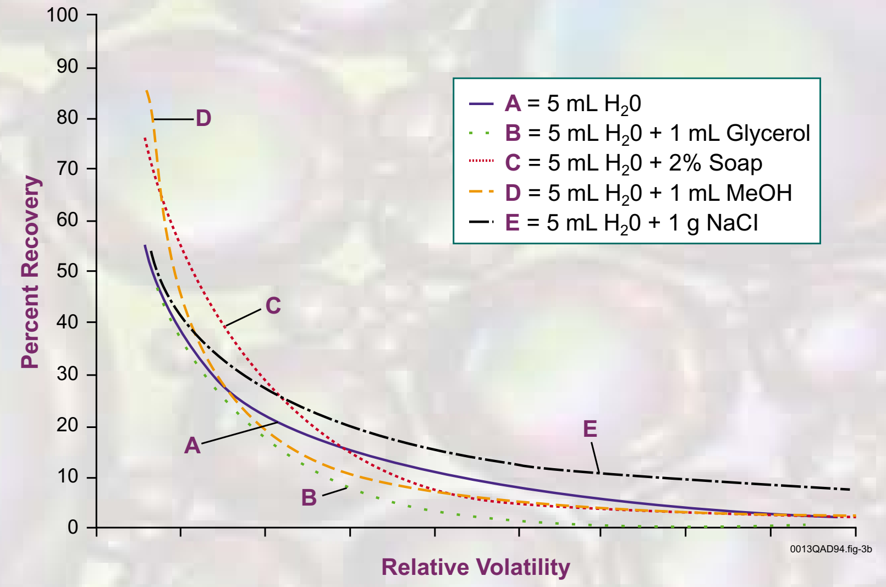
Effects Are Rugged

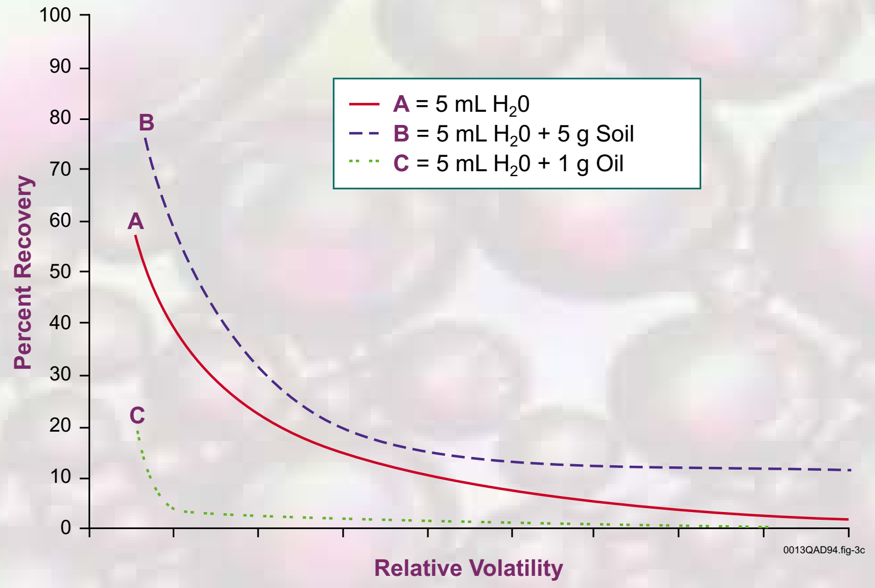
The recovery of analytes at the cryotrap corresponds to their vapor pressure and K_{wa} despite drastic changes in sample matrix. The ruggedness of these relationships allows a description of analyte recoveries from a wide range of matrices using surrogate compounds (with appropriate BP and K_{wa} values).



Comparison of the recovery of the analytes in the cryoloop to the relative volatility of the analytes after the vacuum distillation of 5 mL of water samples.

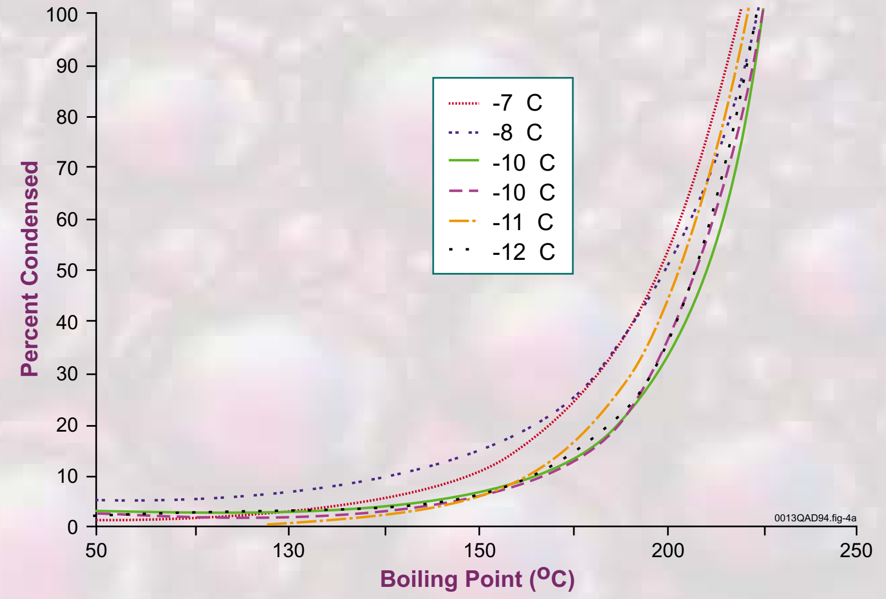
Comparison of the recovery of the analytes in the cryoloop to the relative volatility of the analytes for various water matrices.





Comparison of the recovery of the analytes in the cryoloop to the relative volatility of the analytes for multiphase water samples.

Multiple vacuum distillation comparisons of the boiling points of the analytes to the trapping of the analytes on the condenser column.



Description of Relationships

The relation of recovery of an analyte to its boiling point over a range of boiling points is described by $\text{Recovery}_{(\beta)} = a\,(BP - BP_0) + b)$ and its relationship of recovery to partition coefficient (or relative volatility, αk is described by $\text{Recovery}_{(\alpha)} = e^{(\alpha k + c)}$

The recovery of an analyte at the cryotrap is a function of both boiling point and kα and is described by $\text{Recovery} = \text{Recovery}_{(\alpha)} + \text{Recovery}_{(\beta)}$

Solving these equations constants (a, b, and c) using the recovery of surrogate analytes provides the means to determine the recoveries of other analytes. By adding numerous surrogates to solve these equation constants a precision error can also be determined. Therefore besides having a means to determine analyte recovery, we have a means to provide estimates of analytical precision.

This surrogate information describes the effects of both vacuum distillation and matrix. This information can be presented in a graphical manner that can easily be reviewed.

The graphs pictured at the far right provide examples of such presentation.

Calculation of Recovery Relating to Relative Volatility

	boiling point	rel vol	meas. rec.	linear predict	linear predict
Fluorobenzene	85.0	3.5	0.910	0.9101	
1,2-dichloroethane-d4	84.0	20.0	1.293	1.2927	1.293
tetrahydrofuran-d8	66	355	2.038		2.038
slope			0.246		
intercept			0.585		
error			0.035		

	boiling point	rel vol	meas. rec.	first pass pred	first pass corr			
toluene-d8	111.0	4.3	0.951	0.9543	0.997	0.99		
chlorobenzene-d5	131.0	6.3	0.966	1.0381	0.93	0.943		
bromobenzene-d5	155.0	7.9	0.974	1.0897	0.894	0.888	0.938	
1,2-dichlorobenzene-d4	181.0	8.0	1.050	1.0924	0.961		0.88	
1,2,4-trichlorobenzene-d3	213.0	7.9	0.840	1.0883	0.772		0.809	0.85
naphthalene-d8	217.0	18.0	1.164	1.2696	0.917			0.8282
1-methylnaphthalene-d10	245.0	67.0	1.068	1.606	0.665			0.676
slope				0.001				
intercept				0.866				
error				0.105				

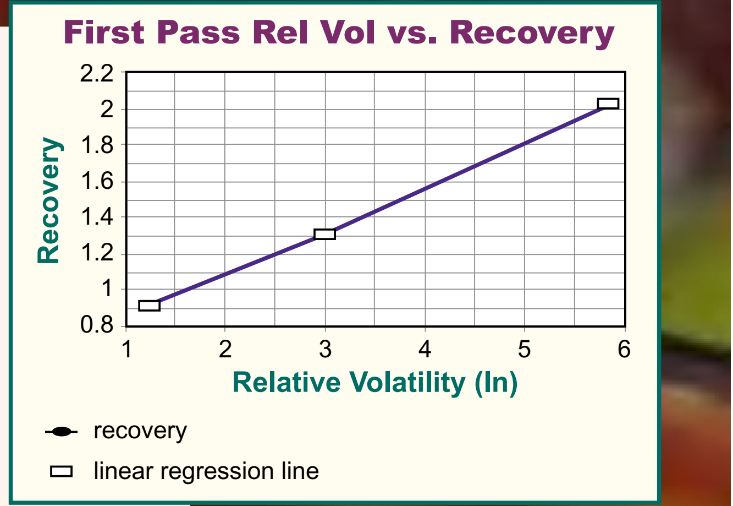
Recovery (bp corrected) vs. Relative Volatility

compounds	bp	rel vol	meas. rec.	bp pred	corr rec						errors
hexafluorobenzene	81.5	0.9	0.992	1.00	0.99	1.029					0.0545
pentafluorobenzene	85.0	1.5	1.054	1.00	1.05	0.993					
Fluorobenzene	85.0	3.5	0.910	1.00	0.91	0.94	0.916				0.0066
1,4-difluorobenzene	88.5	3.8	0.939	1.00	0.94	0.934	0.933				
o-xylene-d10	143.0	6.1	0.939	0.92	1.03		1.023	0.9972			0.1397
chlorobenzene-d5	131.0	6.3	0.966	0.94	1.02		1.027	1.0053			
1,2-dichloroethane-d4	84.0	20.0	1.293	1.00	1.29			1.4517	1.4383		0.212
diethyl ether-d10	35.0	32.5	1.751	1.00	1.75			1.6385	1.5548		
tetrahydrofuran-d8	66.0	355.0	1.983	1.00	1.98				2.1286	2.221	0.2901
acetone-C13	57.0	600.0	2.350	1.00	2.35				2.2545	2.039	
1,4-dioxane-d4	101.0	5800.0	1.137	1.00	1.14					1.252	
pyridine-d5	115.0	15000.0	0.946	0.98	0.97					0.923	

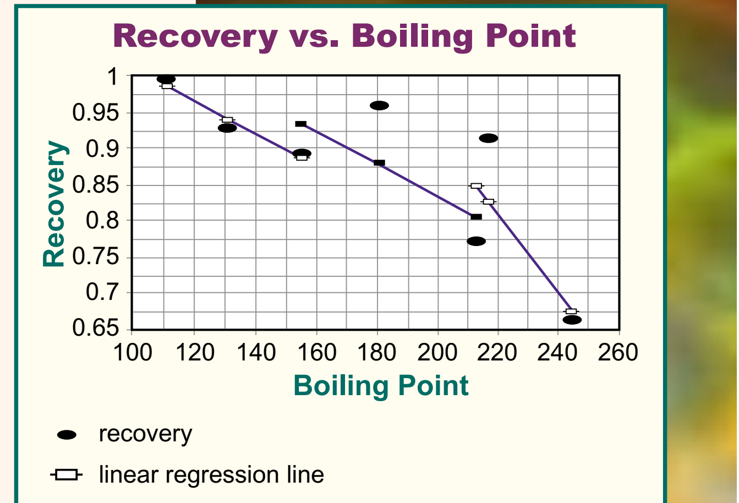
Accuracy of Check Surrogates

compounds	bp	rel vol	meas. recovery	recover bp	recover err	recover rel vol	recover err	pred rec	pred err	report recover	sd
Purgeable VOAs											
benzene-d6	79.0	3.9	0.920	1.000	0.000	0.937	0.007	0.937	0.007	98.2%	0.7%
methylene chloride-d6	40.0	11.1	1.205	1.000	0.000	1.225	0.140	1.225	0.140	98.3%	11.2%
1,2-dichloropropane-d6	95.0	11.0	1.049	1.000	0.000	1.222	0.140	1.222	0.140	85.9%	9.8%
1,1,2-trichloroethane-d3	112.0	26.6	1.379	0.988	0.016	1.561	0.140	1.542	0.140	89.4%	8.1%
4-bromofluorobenzene	152.0	8.1	0.996	0.895	0.016	1.101	0.140	0.985	0.126	101.0%	12.9%
SemiVOAs											
decafluorobiphenyl	206.0	3.0	0.788	0.824	0.099	0.949	0.054	0.782	0.104	100.8%	13.4%
nitrobenzene-d5	210.0	87.5	1.575	0.866	0.118	1.793	0.212	1.553	0.281	101.5%	18.3%
acetophenone-d5	202.0	161.0	1.690	1.285	0.099	1.939	0.212	2.491	0.333	67.9%	9.1%
naphthalene-d8	217.0	18.0	1.164	0.828	0.118	1.411	0.140	1.169	0.203	99.6%	17.3%
non-purgeables											
ethyl acetate-C13	77.0	150.0	2.038	1.000	0.000	1.922	0.212	1.922	0.212	106.1%	11.7%
nitromethane-C13	101.0	510.0	2.151	1.000	0.000	2.216	0.212	2.216	0.212	97.1%	9.3%
aniline-C13	184.0	13700.0	0.488	0.873	0.099	0.954	0.290	0.833	0.270	58.5%	19.0%
pyridine-d5	115.0	15000.0	0.946	0.981	0.016	0.923	0.290	0.905	0.285	104.6%	32.9%

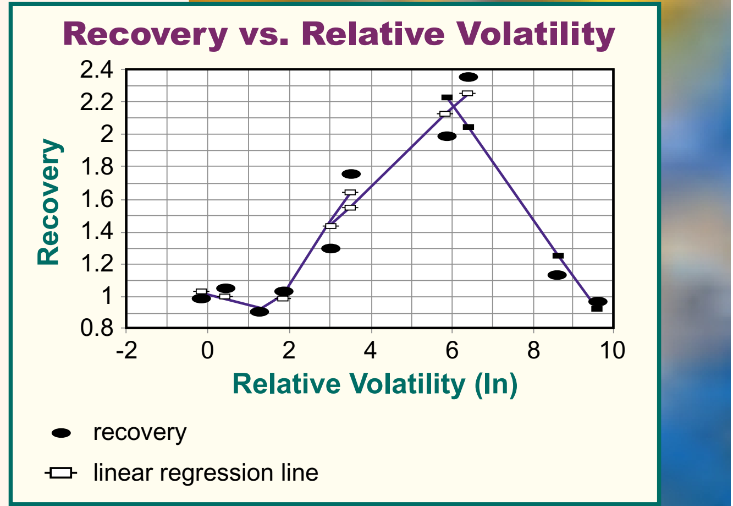
First Pass Rel Vol vs. Recovery



Recovery vs. Boiling Point



Recovery vs. Relative Volatility



Results

Method 8261 is a unique method that provides a means to accurately determine matrix effects. This method also is applicable to a wide range of analytes. This new method has the following advantages:

- *no matrix spike/matrix spike duplicates required*
- *a single calibration curve for all matrices*
- *no dilutions due to unknown matrix effects*
- *visual review of performance data*
- *expanded analyte list/analyses every 40 minutes*
- *log records of each vacuum distillation (time, temperatures, and pressure)*

References

Method 8261 (**http://www.epa.gov/epaoswer/hazwaste/test/txnews.htm**)

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