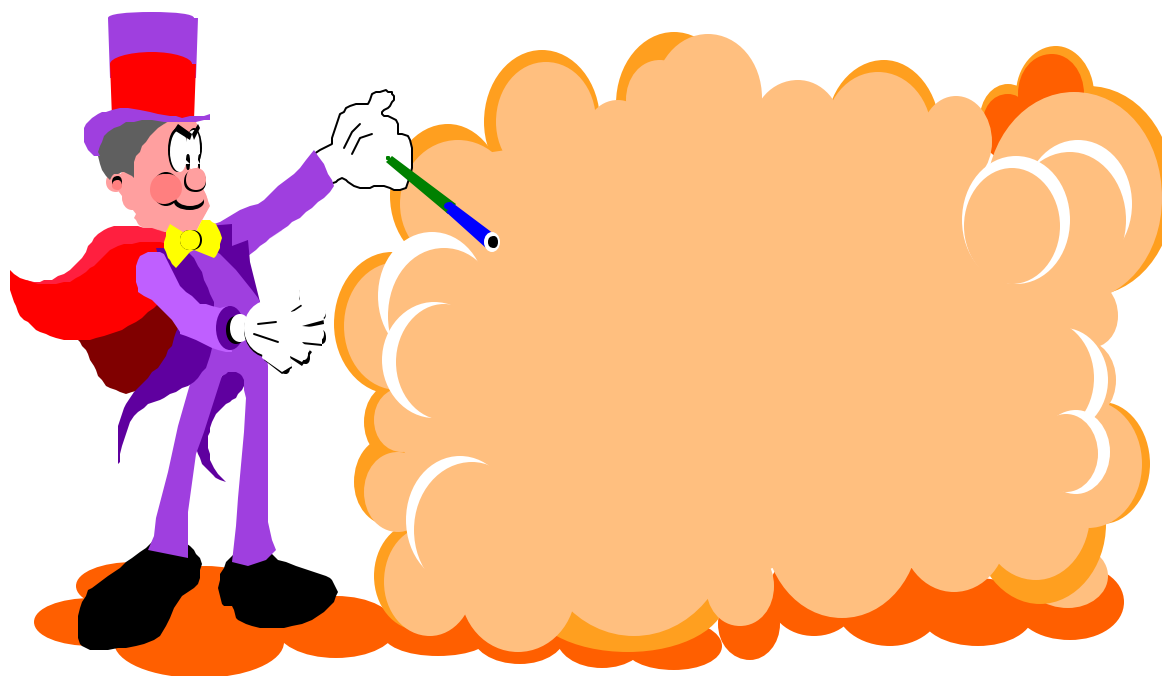




EPA Method 18 Making Spike and Recovery Work





My Resume

- ❖ **BS Chemical Engineering**

- ❖ **Eight Years Stack Testing**

 - Primarily VOC Testing**

 - Designated “Special Projects” guy**

 - Fugitive Emissions**

 - Low Flow**

 - Intermittent Flow**

 - High Vacuum (up to 28” Hg)**

 - Capture Efficiency Testing**





Bit of Wisdom

- ❖ **“If only two people in the country can pass the recovery check, then it’s just a lousy method”
Walt Smith**

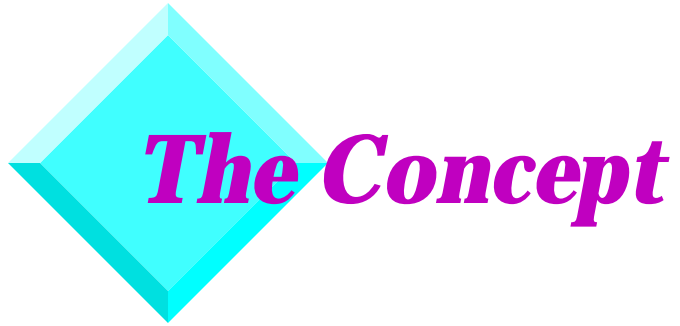




The Rule

- ❖ **Conduct a recovery study of the compounds of interest during the actual field test**
- ❖ **Co-locate two probes in the stack**
- ❖ **Spike all of the compounds of interest onto the adsorbent tube in the spiked train before sampling**
- ❖ **The amount of the spike shall be 40 to 60% of the expected unspiked catch**
- ❖ **Repeat for a total of three runs**
- ❖ **Recovery must be 70-130%**
- ❖ **In-lab procedure for bag samples**





The Concept



+

**Train A
Spike**

Train B



The Math

- ❖ **Mass per volume**

$$Mv = Ms/Vs - Mu/Vu$$

- ❖ **Recovery**

$$R = Mv * Vs / S$$

S = spiked amount (ug)

Ms = mass recovered from spiked train

Mu = mass recovered from unspiked train

Vs, Vu sample volume of spiked and unspiked trains

- ❖ **Lab needs Vs and Vu from client to calculate recovery**
- ❖ **Ms, Mu should include knock-outs or silica gel used for moisture control**





Spiking

- ❖ **Spike should be added to the train at the first media that comes in contact with sample**
- ❖ **Often this is the moisture knock-out or silica gel tube**
- ❖ **Spike can be added as liquid by syringe or as a gas. Also as a solution added to knock-out**
- ❖ **Some hydrophobic compounds may need to be added directly to the tube even if a knock-out is used. Otherwise, a layer is formed on top of the water that leads to spike loss**
- ❖ **Put spikes on the train just before sampling**

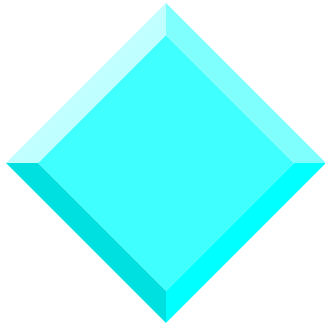




SURE DEATH

- ❖ **Underspiking**
- ❖ **Warm Tubes**
- ❖ **Headspace in VOAs**
- ❖ **Not Co-located**
- ❖ **Wrong Media**
- ❖ **Wrong Solvent**
- ❖ **No Presurvey**
- ❖ **Taking Client's Word on Concentration and Species**
- ❖ **Leaks in sample train (spiked or unspiked)**





Underspiking Example

- ❖ **Expected Concentration - 50 ppmv benzene**
Sample rate - 100 mL per minute
- ❖ **Expected catch 974 ug**
- ❖ **Calculated spike ~ 450 ug**
- ❖ **Actual concentration 250 ppmv**
Actual catch 4871 unspiked train
5321 spiked train.
Assume equal sample volumes.
- ❖ **$5321 - 4871 = 450$ Expected error of method 250-
500 ug**
- ❖ **$450 \pm 500 =$ poor percentage proposition**





Things that Help Recovery

- ❖ **Dispargers for hydrophobic compounds**
- ❖ **Clean -up non-polar compounds with something other than water.**
- ❖ **Desorb double bonded compounds and silica gel immediately**
- ❖ **Zero head-space VOAs**
- ❖ **Use co-solvent when desorbing**
- ❖ **Try new adsorbents - charcoal is not always the right choice.**
- ❖ **Keep catch between 30 and 150,000 ug**
- ❖ **Presurvey, Presurvey, Presurvey**





Shipping and Storage

- ❖ **Keep tubes cold. Ship bags warm.**
- ❖ **Pack VOA's in bubble wrap or foam.**
- ❖ **Usually do not need to send as hazardous goods**
- ❖ **Bag samples need to be sent Priority 1
Saturday Delivery if necessary**
- ❖ **Chain of Custody**
- ❖ **Double bonded compounds and silica gel
should be expedited**



Bag Spike and Recovery

- ❖ **Analyze sample twice - $\pm 5\%$ - use as result**
- ❖ **Analyze sample again 3 times. Use as background for recovery test. (u)**
- ❖ **Spike bag with gas or liquid standard. Target 40-60% of bag concentration or 5X MDL.**
- ❖ **Analyze bag twice more (t)**
- ❖ **Determine the expected concentration that the spike should generate in the bag. (S)**
- ❖ **$R = (t-u)/S$**
- ❖ **Determine volume in bag . See if your guess for S was correct**





Adsorbents

- ❖ **Anasorb 747 - high load, versatile, polar VOCs**
- ❖ **Anasorb 747 CMS - light weight VOCs**
- ❖ **Carboxen - good for polar VOCs**
- ❖ **Orbo - many varieties, specific, light load**
- ❖ **Tenax - same as VOST media**
- ❖ **XAD - same as M0010, M23 media**





Trends

- ❖ **Initial test programs-**
Recoveries: -1000% to +3000%
~ 60% between 70 and 130%.
- ❖ **After a few failures and some training-**
Range 3% to 200%
~ 90% between 70 and 130%.





Wrap-up

- ❖ **Presurvey**
- ❖ **Care and Attention**
- ❖ **Spike high and low**
- ❖ **Use dispargers and knock-outs as appropriate**
- ❖ **Evaluate best media**
- ❖ **Determine Desorption Efficiency beforehand**





Wrap-up

- ❖ **Desorb some types of samples quickly**
- ❖ **Carefully select sample flow rate to collect catches in workable range**
- ❖ **Avoid reactive or very volatile compounds**
- ❖ **Don't force the method. Direct interface and other methods should be examined.**
- ❖ **Historical data available after the presentation!**

