Principles, Practices, and Equipment for Performance Evaluation of Personal Monitoring Badges

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#### Personal Sampling has arisen ...

#### In response to the

#### Occupational Safety and Health Act of 1970 OSHA Rules 29CFR1910.1000 & later

placed limits on time-averaged chemical concentrations within employees personal breathing zones

## Two types of Samplers: Active & Diffusive

## Active Sampling

- Tubes
- Pump Delivers Analyte to Sorbent
- Less work to validate (4 tests)

## Diffusive Sampling

- Badges
- Diffusion Delivers Analyte to Sorbent
- More work to validate (7 tests)

## **Published Protocols**

Described Evaluation Parameters for Diffusive Samplers

- NIOSH Draft Protocol
- CEN EN 838 (Europe)
- ANSI/ISEA 104-2009
- ASTM D6246
- MDHS 27 (UK)

- Analytical Recovery & Blank
- Sampling (uptake) Rate
- Reverse Diffusion
  - Breakthrough
- Velocity/Orientation Effects
- Humidity Effects
- Temperature Effects
- Storage Stability

## Analytical Recovery & Blank (Desorption Efficiency)

- Add Analyte to each Sampler
- Add Analyte to Extraction Fluid

- 5x replicates
- 3 concentrations: low, medium, high
- Blank
- Analyze Samplers & Calculate Recovery
  - % Recovery = DE = (Qty Found, Sampler) (Blank) (Qty Found, Fluid)

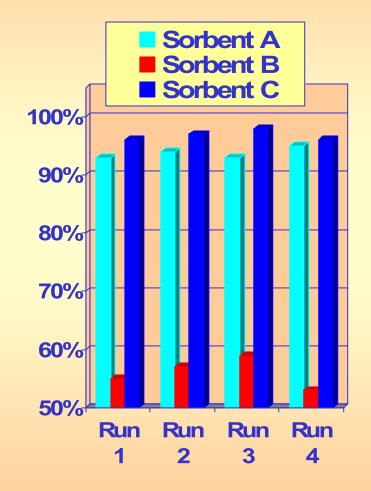
- Analytical Recovery & Blank
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## Analytical Recovery & Blank (Desorption Efficiency)

#### **Possible Causes of Low DE**

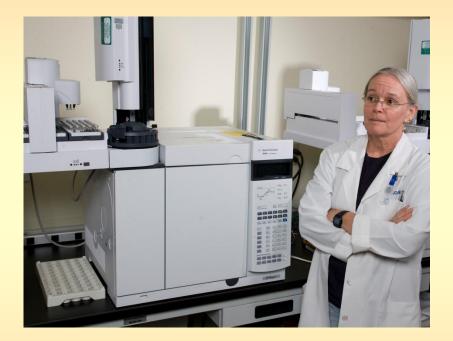
- Weakly attracted to sorbent Re-evaporation
- Strongly Held on Sorbent Incomplete Recovery
- Decomposition

- Analytical Recovery & Blank
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## Analytical Recovery & Blank Equipment Needed





- Analytical Recovery & Blank
- Sampling (uptake) Rate
- Reverse Diffusion
  - Breakthrough
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- Storage Stability

## **Sampling Rate Test**

- In a dynamic (flowing) exposure chamber:
  - Generate Analyte
    - Constant concentration
  - Expose Diffusive & Active Samplers
    - Active sampler is reference method
    - Set period of time
  - Analyze Samplers
    - Qty found on each sampler
  - Sampling Rate =

Qty Found (diffusive) x Sample Volume (active) = mLQty Found (active) x Sampling Timemin

Personal Sampler Evaluation Parameters

- Analytical Recovery & Blank
- Sampling (uptake) Rate
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- Velocity/Orientation Effects
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## **Sampling Rate Test**

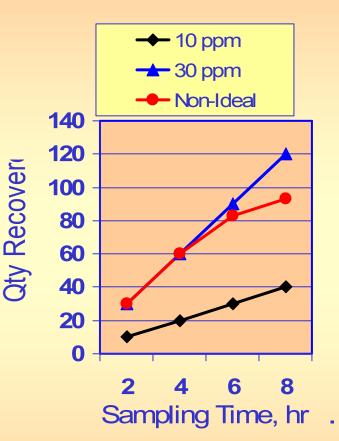
### **Analyte Uptake:**

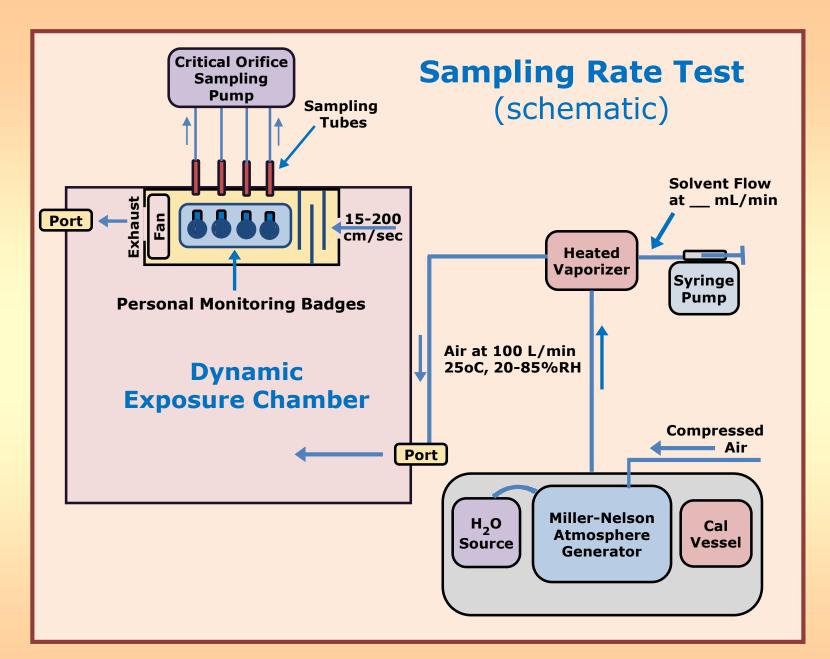
- Linear
  - Time
  - Concentration
- Slope ~ Sampling Rate

Personal Sampler Evaluation Parameters

- Analytical Recovery & Blank
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- Reverse Diffusion

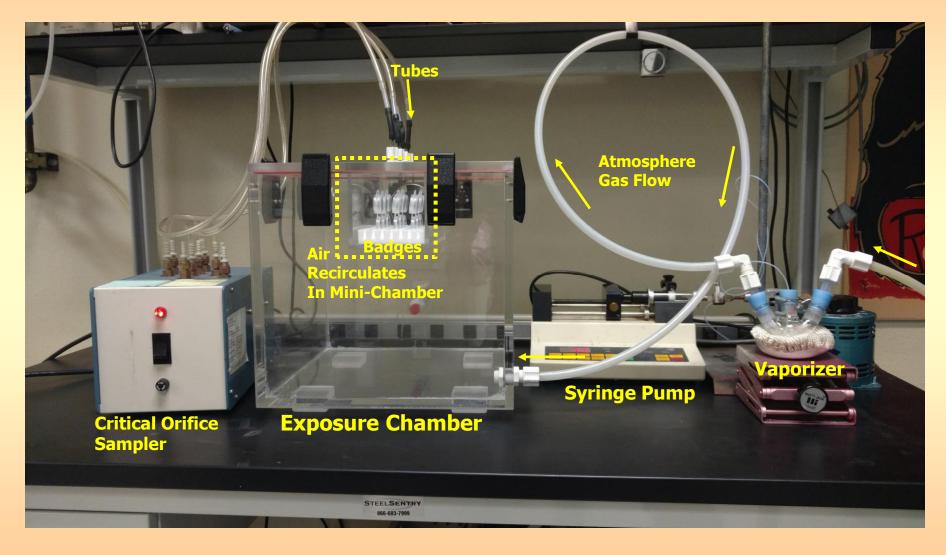
- Velocity/Orientation Effects
- Humidity Effects
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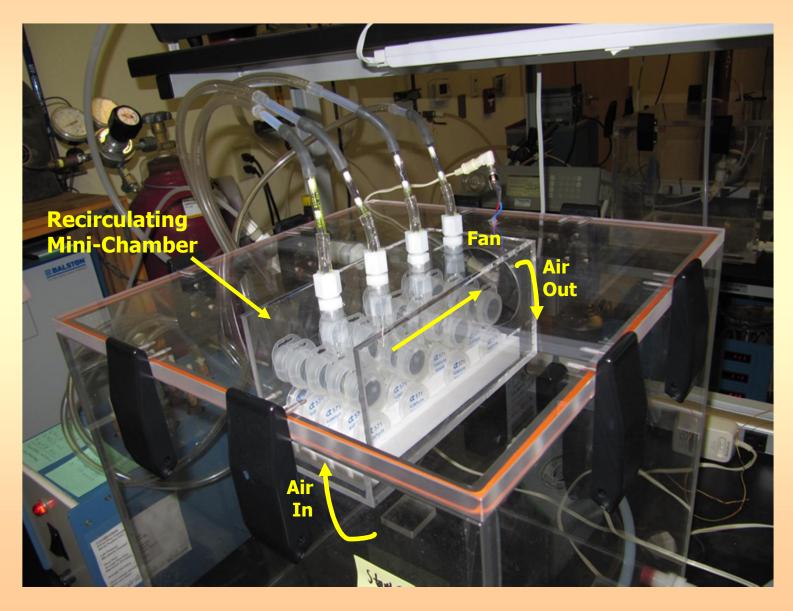
## **Sampling Rate Test Set-Up**

#### Photo



## **Sampling Rate Test Set-Up**

#### Close-up showing tubes and badges



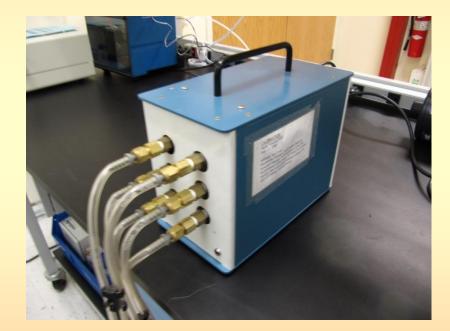
## Miller-Nelson Atmosphere Conditioner



## Syringe Pump

## Critical Orifice Sampler





## **Reverse Diffusion Test**

(evaporative loss during/after sampling)

- Expose 10 Diffusive Samplers
  - Highest Expected Concentration for short time
- Remove & Cap 5 Samplers (A)
  - Store Cold & Analyze Later
- Leave 5 Samplers Open (B)
  - Expose to Zero Air (several hours)
- Analyze All Samplers Together
  - Compare: <u>Analyte Found (B)</u> Analyte Found (A)

#### **Difference (A – B) due to Reverse Diffusion**

Personal Sampler Evaluation Parameters

- Analytical Recovery & Blank
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- Storage Stability

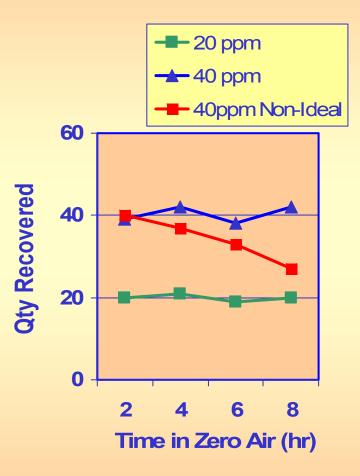
## **Reverse Diffusion Test**

(evaporative loss during/after sampling)

#### **Reverse Diffusion**

- Causes:
  - Exceeding Capacity of Sorbent
  - Weak association
    - between analyte and media
- This test determines the Maximum Sampling Time (MST) for each Analyte

- Analytical Recovery & Blank
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## **Air Velocity Test**

- Expose 5 Samplers @ V = 15 cm/sec (30 ft/min)
  - @ V = 50 cm/sec
  - @ V = 100 cm/sec

Fixed %RH, Time, Concentration

- Compare Analyte recovered on all Samplers for different air velocities
- Sampling Rate should be unaffected by air velocity when V ≥ minimum required air velocity

Air Velocity Test Looks for Differences at 15 cm/sec vs higher flows

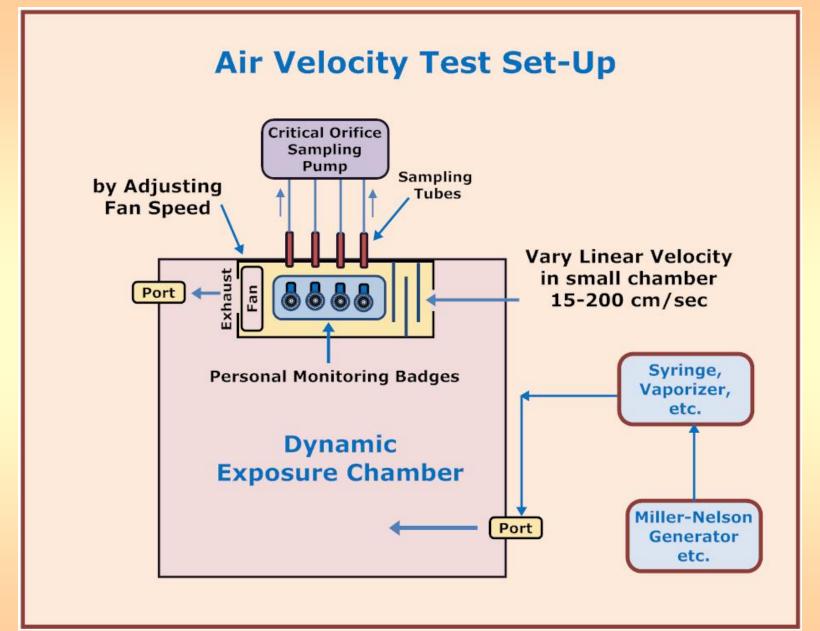
(15 cm/sec = 30 ft/min ... lowest typical air velocity in workplaces)

Personal Sampler Evaluation Parameters

- Analytical Recovery & Blank
- Sampling (uptake) Rate
- Reverse Diffusion

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- Velocity/Orientation Effects
- Humidity Effects
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## **Air Velocity Effects**

#### **Air Velocity Effects**

At some air velocity, Sampling Rate will begin to decrease

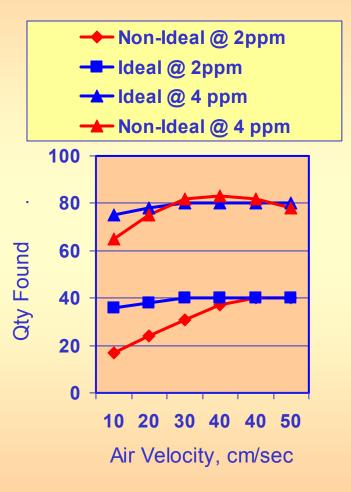
With proper design, Sampler "works" down to 15 cm/sec

**Results for a particular Sampler** will be similar for many analytes

Personal Sampler Evaluation Parameters

- Analytical Recovery & Blank
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# **Humidity Effects**

(typical experiment)

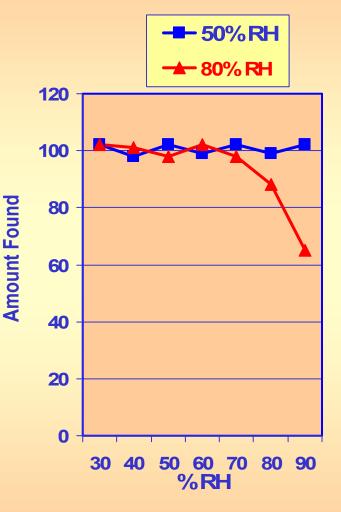
- Expose 15 Samplers at Fixed Concentration, Temp, Time
  - 5 at 20% RH
  - 5 at 50% RH
  - 5 at 80% RH
- Analyze All Samplers
- Compare Amt Found for Different Humidity Exposures

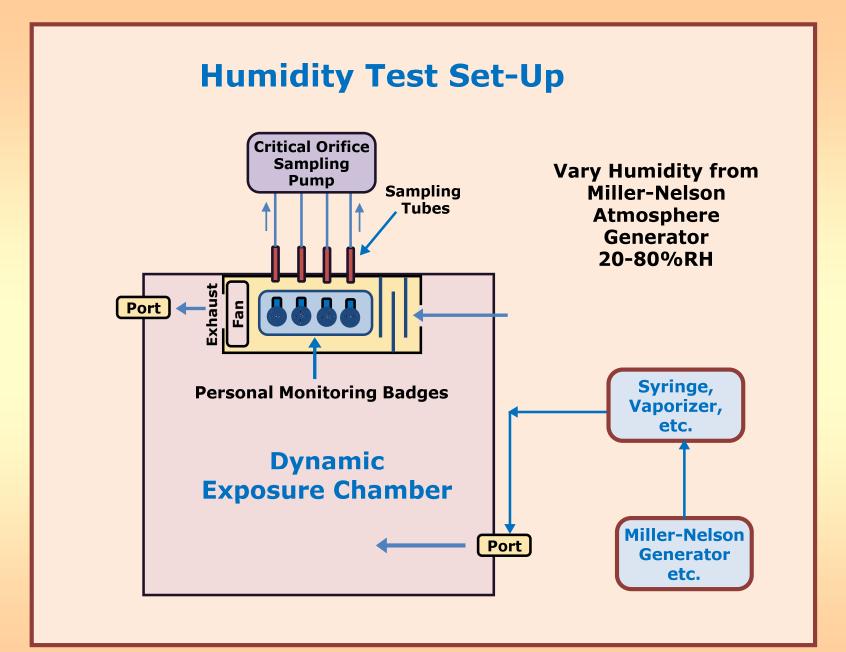
   Difference Due to Evaporative Loss Arising from Moisture

   Personal Sampler Taking Up Sorbent Capacity

Evaluation Parameters

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- Storage Stability





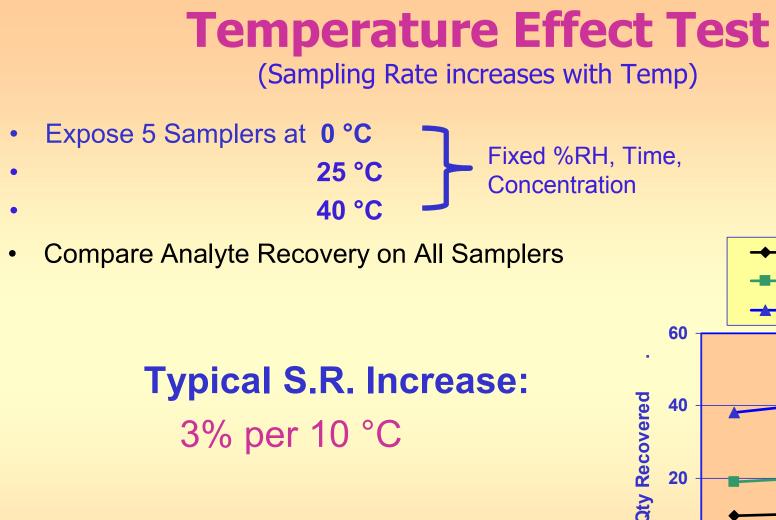
## Miller-Nelson Atmosphere Conditioner Supplies air at controlled flow, temp, and %RH



Personal Sampler Evaluation Parameters

- Analytical Recovery & Blank
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- Reverse Diffusion

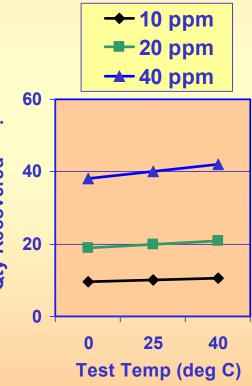
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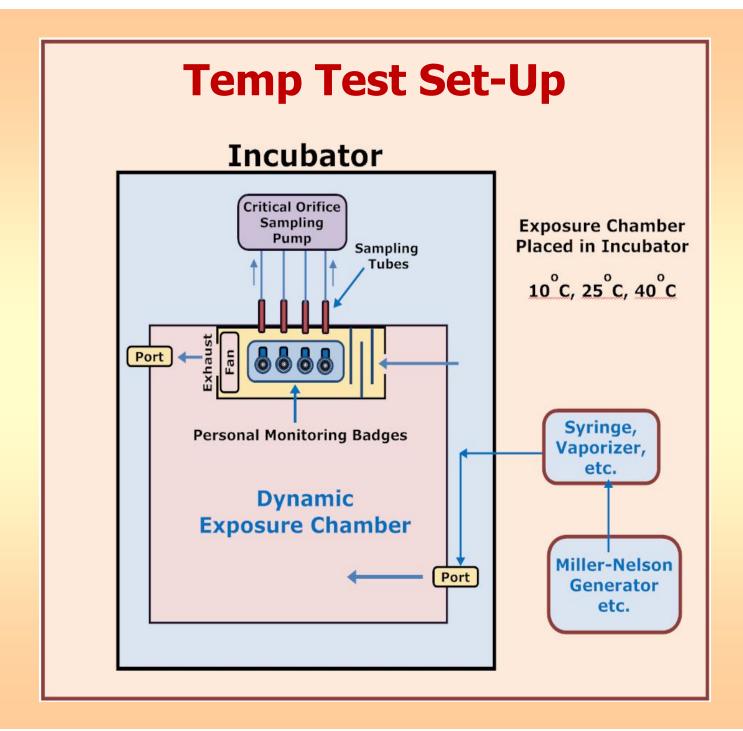


Personal Sampler Evaluation Parameters

- Analytical Recovery & Blank
- Sampling (uptake) Rate
- Reverse Diffusion

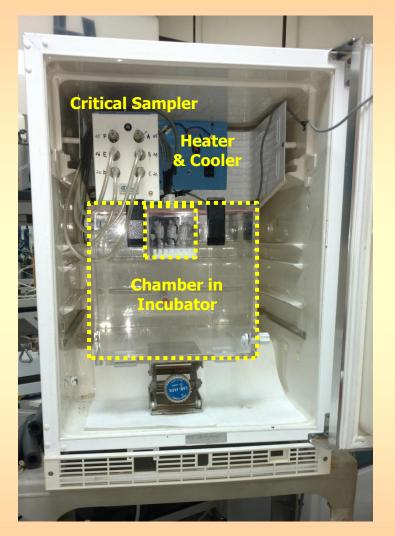
- Velocity/Orientation Effects
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## **Temperature Test**



Personal Sampler Evaluation Parameters

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- Reverse Diffusion

- Velocity/Orientation Effects
- Humidity Effects
- Temp Effects
- Storage Stability

## **Storage Stability Test**

#### (analyte loss on storage)

- Expose 30 Diffusive Samplers
  - At Fixed Concentration, Temp, Time
- Remove & Cap 10 Samplers
  - Store at Room Temp (25°C)
- Remove & Cap 10 Samplers
  - Store In Freezer (-20°C)
- Remove & Cap 10 Samplers
  - Store in Refrigerator (2-8°C)

#### **Analyze Stored Samplers:**

- 15 after 1 week storage
- 15 after 2 week storage

- Analytical Recovery & Blank
- Sampling (uptake) Rate
- Reverse Diffusion
  - Breakthrough
- Velocity/Orientation Effects
- Humidity Effects
- Temp Effects
- Storage Stability

## **Storage Stability Test**

(analyte loss on storage)

Recovered

%

## Causes for decreased storage stability

- Analyte Loss
  - Evaporation
  - Migrates into packaging
- by Decomposition

# Refrig RoomTemp 90% 70% 50% 5 10 15 20

- Freezer

Holding Time, days

#### Personal Sampler Evaluation Parameters

- Analytical Recovery & Blank
- Sampling (uptake) Rate
- Reverse Diffusion

- Velocity/Orientation Effects
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## **Evaluation Criteria**

- Several OSHA Rules & most NIOSH criteria suggest an overall uncertainty of <u>+</u> 25% is acceptable for personal monitoring tests.
- Taking a 25% accuracy criterion, you would accept evaluation results as validation of a sampler provided test variation stay within <u>+</u> 25% overall system variation.
- In some cases in conformance with accuracy requirements, you may place procedural limits on (for example):
  - (a) Allowed %RH or Temperature Range in which Sampler is used
  - (b) Allowed Holding Time or Storage Conditions after sampling
  - (c) Allowed Sampling Time (< 8 hr)

## Summary

- Diffusive Samplers are easy to use, but difficult to evaluate.
- 7 types of tests are needed to evaluate a Personal Monitoring Badge (Diffusive Sampler).
- Complex Sampling Rate evaluations for Badges replace use of the Sampling Pump. (Sampling Rates can be predicated with some accuracy.)
- Desorption efficiency (DE) tests, humidity effects, and sample stability tests are similar for both Diffusive or Active samplers.
- Diffusive Samplers can suffer evaporative losses (Reverse Diffusion) if maximum sampling time is exceeded, but MST is large for most analytes.
- Temperature & Air Velocity affects are simple and similar for many analytes, so they need be performed only 1 time per each type of Sampler.

