NEW DEVELOPMENTS IN PASSIVE SAMPLERS

PERFORMANCE STANDARDS, TECHNOLOGY, & APPLICATIONS

Presented by

SKC

…BUT FIRST LET'S LOOK BACK IN TIME

THE EMERGENCE OF PASSIVE SAMPLING TECHNOLOGY.

A LOOK BACK IN TIME
THE 1970's

A REVOLUTION IN EXPOSURE EVALUATIONS

Goodbye:

- Heavy pumps
- Calibration
- Worker Complaints

Hello:

- Simplicity
- Convenience

OH HAPPY DAY!

BUILDING ON EARLIER TECHNOLOGY

- **1927**-Gordon and Lowe patented a “passive monitor” for **CO** using palladium chloride salts →color change
- **1960’s**-Plantz developed a “personal dosimeter” for **hydrazine** using a “colorimetric substance” (bindone) → purple color which was compared to color standards to estimate exposures.

HISTORY IN THE MAKING

- **1973**-Palmes and Gunnison first produced a *quantitative* device based on the principle of *diffusion* of gaseous contaminants through a stagnant air layer. A mercuric chloride medium was used for a colorimetric determination of sulfur dioxide.
- **1977**-The GASBADGE was commercially produced for **organic vapors** using adsorption onto charcoal.
- **1980**-3M and DuPont introduced organic vapor monitors.

HISTORY IN THE MAKING

Beginning in the 1990's, passive sampling advancements occurred:

- Passive samplers with a choice of sorbents and with various levels of validation for organic vapors.
- Chemically coated and specialty sorbents for unique target compounds.
- Passive samplers using thermal desorption for ppb level measurements.

In 2011:

The technology continues to evolve!

THE OPERATING PRINCIPLE
FICKS FIRST LAW

$$Q = D\ (A/L)\ C\ T$$

Where:

Q = Amount collected (ng)

D = Diffusion coefficient (cm^2/min)

A = Cross-sectional area of the diffusion path (cm^2)

L = Diffusive path length (cm)

C = Airborne concentration (mg/m^3)

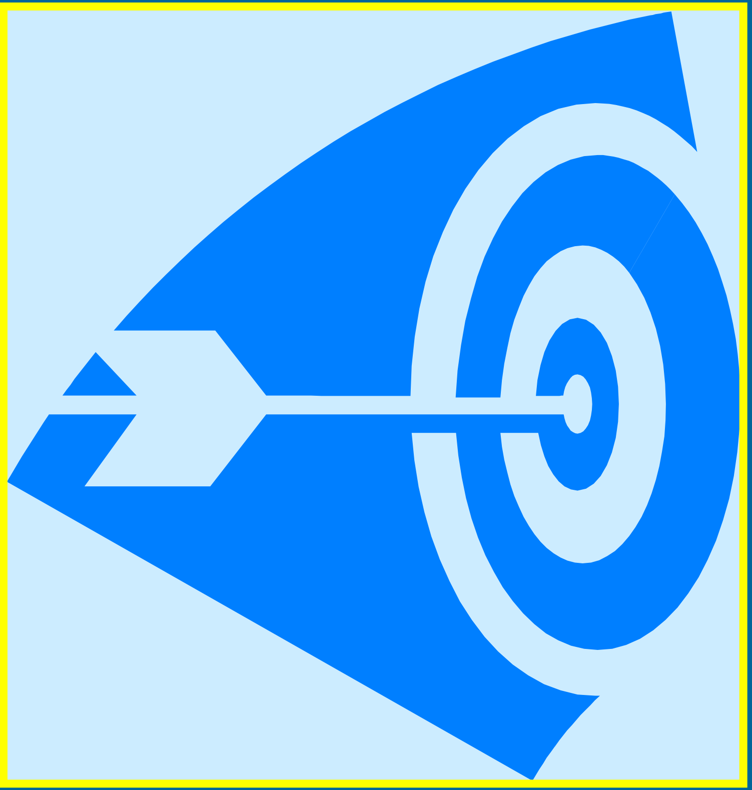
T = Sampling time (min)

Used to determine theoretical uptake rates of diffusive samplers for specific compounds.

VERIFYING FICKS FIRST LAW

- **In practice, theoretical uptake rates may not prove valid under various field conditions.**
- In recent years, a variety of validation protocols and performance standards have been published for evaluating (and verifying) the performance characteristics of diffusive samplers.

NEW DEVELOPMENTS:
PERFORMANCE STANDARDS AND VALIDATION PROTOCOLS



UNITED STATES DEPARTMENT OF LABOR

TO ENSURE SAMPLING RELIABILITY WITH PASSIVE SAMPLERS

NIOSH VALIDATION PROTOCOL (1986)

- Analytical recovery
- Sampling rate and capacity
- Reverse Diffusion
- Storage Stability
- Temperature
- Accuracy & Precision
- Shelf-Life
- **Factor Effects** including concentration, exposure time, face velocity, RH, interferences, and monitor orientation.
- **Field Studies** with area and personal sampling.

ASTM D 6246-08
ANSI/ISEA 104-1998 (r2009)

Standard Practice for Evaluating the Performance of Diffusive Samplers

- The aim is to provide a concise set of experiments for classifying samplers according to **ACCURACY.**
- Stated accuracy figures refer to a set of conditions under which the samplers can be used including temperature, atm pressure, RH, wind speed.

HSE MDHS Method 88

AN EXPEDITED APPROACH

- MDHS Method 88 (1997) describes tests that should be done in a ***full validation*** to document an overall uncertainty ≤ 30% for samples in the range of 0.5 to 2 X OEL.
- They also describe a ***partial validation*** option that is done by demonstrating that key members of a homologous series comply with full validation. SKC used this approach in our bi-level validation studies.

EUROPEAN ADOPTED BRITISH STANDARD EN 838:2010

Sampler Requirements

- Uptake rate
- Air velocity and orientation effects
- Leak test (acceptable blank value)
- Indication of shelf life
- Sample ID area
- Labeled for product ID
- Instructions for use

Measuring Requirements

- Sample time
- Reverse diffusion
- Sample storage
- Quantification limit
- Typical blank value
- Method performance
- Analytical requirements

A SIGNIFICANT U.S. PERFORMANCE STANDARD

Acceptance by U.S. OSHA Inspectors!

- In 1998, OSHA released a report on the importance of determining sampling rate variation for specific passive sampler designs. This figure compares to the 5% variation typically used for sample pumps.
- The sampling rate variation along with the analytical error allows the calculation of overall sampling & analytical error (SAE).

SAMPLING RATE VARIATION
OF PASSIVE SAMPLERS

3M 3520:

6.4%

SKC 575-Series:

8.7 %

SKC UME^{X} 100:

8 %

Sampling rate variation is statistically the same and acceptable for these samplers.

VALIDATED OSHA PASSIVE METHODS

- Toluene
- Tetra and Trichloroethylene
- Xylenes and Ethyl Benzene
- MEK and MIBK
- Benzene
- Butyl Acetates
- Styrene
- Formaldehyde
- Inorganic Mercury
- Hydrogen Cyanide

UNITED STATES
DEPARTMENT OF LABOR

QUESTION WORTH CONSIDERING

Do you have a report on file documenting the performance of your passive samplers for your specific target chemicals?

OSHA Methods:

http://www.osha.gov/dts/sltc/methods/toc.html

SKC Research Reports:

http://www.skcinc.com/reports.asp

NEW DEVELOPMENTS:
PASSIVE SAMPLER TECHNOLOGIES

PASSIVE SAMPLER TECHNOLOGIES

- Colorimetric
- Chemically-treated paper
- Generic Solid Sorbents
- Specialty or Chemically-coated Sorbents
- Specialty Sorbents that allow for ultra-low level determinations using thermal desorption.

DIRECT-READING PASSIVE SAMPLERS

- Employ colorimetric technologies
- The length of a color band on passive color tubes indicate concentration
- Intensity of a color change correlates to concentration on passive color badges

Photo: Morphix Technologies

PASSIVE COLOR TUBES

- Break open one end and place in designated holder
- Sample from 1-8 hours
- Length of stain indicates air concentration in ppm-hr
- Divide by hours sampled to obtain ppm concentrations in air

TARGET COMPOUNDS
PASSIVE COLOR TUBES

- Acetic Acid
- Ammonia
- Butadiene
- Carbon Dioxide
- Carbon Monoxide
- Ethanol
- Hydrochloric Acid
- Hydrocyanic Acid
- Hydrogen Sulfide
- Nitrogen Dioxide
- Perchloroethylene
- Sulfur Dioxide
- Toluene
- Trichloroethylene

Additional passive color tubes are manufactured by Gastec.

COLOR BADGES

- Badges contain a chemically coated filter paper or *indicator layer*.
- Target chemicals in air react with the chemical coating used in the badge and produce a color change.

APPLICATIONS
COLOR BADGES

- Visual indication to evacuate work area in presence of dangerous chemicals!
- Semi-quantitative exposure level screening
- Leak Detection

TARGET COMPOUNDS
COLOR BADGES

- Ammonia
- Aniline
- Carbon Dioxide
- Carbon Monoxide
- Chlorine
- Dimethyl Amine
- Formaldehyde
- Hydrazine
- Hydrogen Chloride
- Hydrogen Sulfide
- MDI
- Mercury
- Nitrogen Dioxide
- Ozone
- Phosgene
- Sulfur Dioxide

SOURCES OF ERROR
COLOR TUBES/BADGES

- Accuracy is limited
- Interfering compounds cause similar reactions and readings on tube
- Affected by temperature and humidity
- UV light may discolor indicator layer in badges

PASSIVE SAMPLERS
CHEMICALLY TREATED PAPER

- Based on the same chemistry as active sampling methods using chemically coated filters or sorbent tubes.
- After collection, the filter paper is extracted for analysis of the target chemicals.

Aliphatic Amines

SO_2/NO_2

Formaldehyde

PASSIVE SAMPLERS
CHEMICALLY TREATED PAPER

Published Sampling Methods:

- **OSHA Method 1007 for formaldehyde**
  specifies passive samplers using DNPH chemistry including SKC UME^X 100
- **EU ISO 16000-3-4-2004 and EPA IP-6C for formaldehyde**
  specify the same as above.

UMEX 100

PASSIVE SAMPLERS
GENERIC SOLID SORBENTS

- Passive samplers for organic vapors were first introduced by 3M and DuPont in 1980 using charcoal sorbents.

- In the 1990's, SKC introduced passive samplers with *a choice of solid sorbents* to trap unique targeted organic vapors.

SKC 575-SERIES SAMPLERS
SORBENT OPTIONS

- **Coconut Shell Charcoal (575-001)**

  For nonpolar and intermediate polar organic vapors including BTEX
- **Anasorb 747 (575-002)**

  For nonpolar and polar organic vapors including BTEX, MEK, acetone, alcohols
- **Anasorb 727 (Chromosorb 106)** (575-003) - For terpenes, naphthalene, cyclohexanone

NOTE REGARDING U.S. OSHA METHODS

OSHA validated methods specify the use of 575-002 with Anasorb 747.

- This sorbent is very versatile and will allow for collection of more compounds with one sampler. So OSHA prefers this sorbent.
- Anasorb 747 is more expensive than charcoal however. Passive samplers containing charcoal are specified in SKC validation studies where appropriate.

NOTE REGARDING U.S. OSHA METHODS

OSHA validated passive sampling methods specify a maximum sample time of 4 hours.

- This 4-hr sample time is specified *for OSHA field inspectors* so they will have

  (2) separate samples to analyze in a compliance survey.
- Other users do not have to comply with this

  4-hr limitation. SKC provides guidance on maximum sample time in our literature.

BACK-UP LAYERS IN PASSIVE SAMPLERS?

- 3M organic vapor monitors are available offer solid sorbent passive samplers with a backup layer.

3M 3520

- SKC does not offer a back-up layer in passive samplers since there is no active air flow.
- Instead passive samplers are available with more sorbent (350 mg+) in a single layer sampler validated for target compounds
up to 2 X OEL.

PASSIVE SAMPLERS
SPECIALTY SORBENTS

Inorganic Mercury

- Passive samplers containing a specialty sorbent comprised of oxides of manganese/copper are specified in OSHA Method ID 140.
- This sorbent has been sold as Hopcalite, Hydrar, Carulite, and now Anasorb C300.
- The samples are dissolved in acid and analyzed by cold vapor-AAS.

PASSIVE SAMPLERS
SPECIALTY SORBENTS

OSHA HG SAMPLER
SKC 520-SERIES

- Packaged as a two-part system: sorbent capsules and a reusable capsule holder.
- Allows long-term sampling up to 120 hours. See OSHA back-up report.

PASSIVE SAMPLERS
SPECIALTY SORBENTS

Hydrogen Cyanide

- In November 2010, OSHA released Method 1015 using a passive sampler with soda lime sorbent. Since the sorbent tends to clump, it must be field loaded by the user.
- Analyzed by ion chromatography.

NEW

OSHA HCN SAMPLER

SKC 590-400

PASSIVE SAMPLERS

CHEMICALLY COATED SORBENTS

STYRENE

- In November 2009, OSHA released Method 1014 using Anasorb 747 coated with tert-butyl catechol.
- This passive sampler uses the same sorbent specified in the OSHA sorbent tube method for 1,3 butadiene.
- Analysis is by GC/FID.

OSHA STYRENE SAMPLER
SKC 575-006

PASSIVE SAMPLERS

CHEMICALLY COATED SORBENTS

ETHYLENE OXIDE

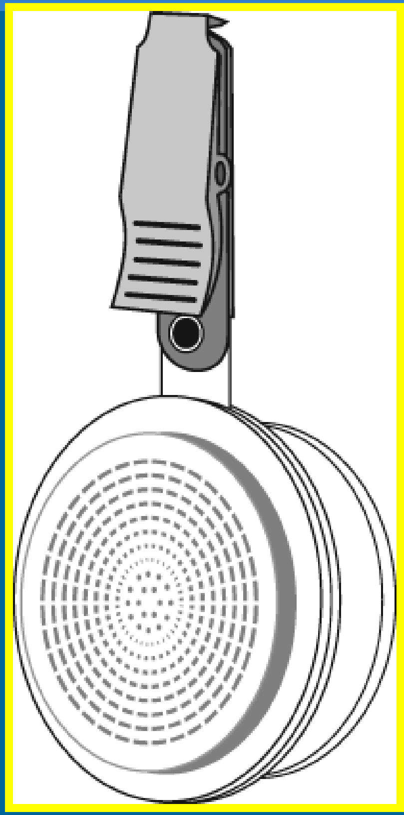
- Anasorb 747 sorbent coated with hydrobromic acid is used in a passive sampler for ethylene oxide.
- This is the same sorbent specified in OSHA's method 1010 for EtO using sorbent tubes. SKC researchers have validated this passive sampler (not OSHA).
- Analyzed by ion chromatography.

Ethylene Oxide Passive Sampler
SKC 575-005

PASSIVE SAMPLERS

DESIGNED FOR THERMAL DESORPTION

- SKC chemists have patented a new passive sampler that allows for **sub-ppb level measurement** of organic vapors through the use of thermal desorption.



Ultra Sampler

590-Series

THE ULTRA DESIGN

- Specialty sorbents used in the sampler allow for thermal desorption including Tenax, Chromosorb 106, Carbopack X, and Anasorb GCB1.
- Sorbent transfer is done by pouring the sorbent from the back of the sampler housing into a standard (empty) thermal desorption tube.

ILLUSTRATION OF SORBENT TRANSFER

Ultra I Design

Ultra II Design

TWO ULTRA CONFIGURATIONS: WHY?

U.S. EPA Method TO-17 recommends that purged sorbent be used within 30 days to ensure sorbent cleanliness.

ULTRA I

- Samplers are shipped **pre-filled** with sorbent that has been thermally purged.

ULTRA II

- Ultra II samplers are shipped empty and are **user-filled** with purged sorbent up to 30 days before use.
- Your analytical lab or SKC can supply purged sorbents in vials for transfer into/out of the badge housing.
- Housing is reusable.

OTHER PASSIVE SAMPLERS

USING THERMAL DESORPTION

NITROUS OXIDE

- A passive sampler containing molecular sieve 5A sorbent is now available for 15-min or 8-hr sampling.
- Saturation is a problem with this compound so a secondary diffusion cap must be used to slow down sample uptake.
- Samples are desorbed thermally and analyzed by GC-ECD.

NEW DEVELOPMENTS:
PASSIVE SAMPLER APPLICATIONS

NEW APPLICATIONS IN OCCUPATIONAL SAMPLING

SHORT-TERM SAMPLING

- OSHA methods for organic vapors such as benzene specify a minimum sample time of **10 minutes**.
- Can be used for peak or STEL sampling in designated methods.
- See the index of OSHA methods at http://www.osha.gov/dts/sltc/methods/toc.html

NEW APPLICATIONS IN INDOOR AIR

VAPOR INTRUSION STUDIES

Vapor intrusion is the migration of volatile chemicals from the subsurface into overlying buildings.

Volatile chemicals in buried wastes and/or contaminated groundwater emit vapors that migrate through subsurface soils and into indoor air spaces of overlying buildings in ways similar to that of radon gas.

VAPOR INTRUSION:
PASSIVE SAMPLER APPLICATIONS

- The April 2010 AIHA *Synergist* reported that the predominant vapors found in indoor air at vapor intrusion sites are chlorinated hydrocarbons and petroleum hydrocarbons.
- For more information, see the EPA Indoor Air Vapor Intrusion Database at http://iavi.rti.org/

VAPOR INTRUSION:
PASSIVE SAMPLER APPLICATIONS

VOCs

- The U.S. EPA Vapor Intrusion Guidance Document specifies a detection limit of 0.5 ppb for organic vapors.
- Passive samplers designed for thermal desorption meet this requirement.
- See the EPA Vapor Intrusion website at http://www.epa.gov/oswer/vaporintrusion to view the guidance document.

NEW APPLICATIONS FOR INDOOR AIR SAMPLING

GREEN BUILDING CERTIFICATION

- The U.S. Green Building Council's LEED program requires air testing for designated compounds in new buildings/major renovation projects.
- For more information, see www.usgbc.org.

GREEN BUILDINGS:

PASSIVE SAMPLER APPLICATIONS

FORMALDEHYDE

- LEED specifies an indoor air limit of 27 ppb.
- SKC UMEX 100 passive sampler has a detection limit of 2 ppb.

TOTAL VOC's

- LEED specifies an indoor air limit of 500 µg/m^3.
- Ultra samplers using thermal desorption can be used to measure VOCs at or below these levels.

SAMPLING (UPTAKE) RATES

STAGNANT AIR APPLICATIONS

- Indoor air sampling situations may have near zero air velocity particularly in unoccupied buildings.
- In this case, standard uptake rates for passive samplers will not be valid.
- SKC now has low face velocity (<5 cm/sec) uptake rates available on our website for organic vapor badges. **See http://www.skcinc.com/prod/590-100.asp#zero**

NEW APPLICATIONS FOR AMBIENT AIR SAMPLING

Photo: Restek Corporation

- Stainless steel canisters have been the primary sampling device for measuring VOC's in ambient air following EPA Method TO-15.

DISADVANTAGES OF CANISTERS

- Must be cleaned, evacuated, and certified before each use
- Bulky to transport
- Expensive to ship
- Cannot be used for collection of semi-volatile compounds
- Sampling time limited to 24-hr

PASSIVE SAMPLERS: A SIMPLER OPTION

AMBIENT AIR STUDIES:
PASSIVE SAMPLER APPLICATIONS

- Passive samplers from Ogawa USA are being used by US EPA for aldehydes, ketones, ozone, nitrogen dioxide, and sulfur dioxide.

- In a European publication, the SKC Ultra was found to be a reliable sampler for the collection of benzene and butadiene in ambient air using Carbopack X sorbent and thermal desorption.

THANK YOU FOR YOUR ATTENTION

ON-LINE TECH SUPPORT:

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