

PASSIVE DIFFUSIVE SAMPLERS: A COMPREHENSIVE REVIEW



SKC PRESENTS:

- Basic Concepts
- Frequently Asked Questions
- Advancements in Science and Technology



PASSIVE SAMPLING DEFINED

The collection of airborne gases and vapors at a **rate controlled by diffusion through a static air layer** without the movement of air through an air sampling pump.



PRINCIPLE OF OPERATION IN BASIC TERMS

Chemicals will diffuse from an area of higher concentration in the air to an area of lower concentration on the sampler and the rate of diffusion for individual chemicals can be scientifically determined.



PRINCIPLE OF OPERATION IN MORE SCIENTIFIC TERMS

Diffusive sampling involves the movement of contaminant molecules across a concentration gradient which can be defined by **Fick's First Law of Diffusion.**



FICK'S FIRST LAW OF DIFFUSION

DEFINED

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

Where:

Q = Amount collected (ng)

D = Diffusion coefficient (cm²/min)

A = Cross-sectional area of the diffusion path
(cm²)

L = Diffusive path length (cm)

C = Airborne concentration (mg/m³)

T = Sampling time (min)



EXPLAINING THE PARAMETERS IN FICK'S FIRST LAW

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

Diffusion Coefficient- chemical property unique to the gas or vapor being sampled. (cm²/min)

Area- cross-sectional area of the diffusion path (cm²) based on the geometry of the sampler

Length- diffusive path length i.e. the distance from the diffusive barrier to the sorbent layer (cm)

Note: The units for D (A/L) are ml/min—the same as with active sampling using low flow sampling pumps.



IF YOU ARE NEW TO PASSIVE SAMPLING

- It is important to note that each chemical being sampled has its own unique sampling (uptake) rate. These values are provided to users by the manufacturer (SKC) of the passive sampler.
- The sampling rates are based on the **geometry of the sampler** and the unique **properties of the chemical** as just discussed in previous slides.



A NOTE ON RELIABILITY AND FICK'S FIRST LAW

- Fick's First Law allows for the mathematical calculation of the sampling rate for individual chemicals. This calculated sampling rate may not hold true under all environmental field conditions.
- Alternatively, passive Samplers that have undergone studies to experimentally verify the sampling rate and other critical parameters will provide a higher degree of reliability as needed for compliance and other critical projects.



BE AN INFORMED USER OF PASSIVE SAMPLERS

Manufacturers of passive samplers provide sampling (uptake) rates for designated chemical compounds.

1. Know how the **sampling rate** was determined: mathematical calculation or scientific validation.
2. Ask if there is a **validation report or government agency method** to support the data generated by the sampler for your target compound.



SKC PASSIVE SAMPLING GUIDE

- SKC provides a list of chemicals for which we supply passive samplers along with information on the amount of scientific testing done for each.
- See the Passive Sampling Guide on SKC's website or in our printed catalog for details on passive sampler validations done by SKC chemists or methods produced by government agencies.



FREQUENT QUESTION: SAMPLING RATES

Question: Does the type of sorbent in the passive sampler determine the sampling rate?

Answer: No; the sampling rate is determined by the geometry of the passive sampler and the diffusion coefficient of the contaminant. The sorbent however may affect the possibility of reverse diffusion.



FREQUENT QUESTION: SAMPLING RATES

Question: Are sampling rates the same when sampling inside and outside?

Answer: The major concern is **low** air velocity (face velocity). As long as there is some air movement indoors, the sampling rates will be the same inside and outside. Sampling rates may **decline up to 60%** if doing area sampling indoors with no air movement.



FREQUENT QUESTION: SAMPLING RATES

Question: How do you determine the sampling rate of a mixture such as petroleum distillates?

Answer: With mixtures, sampling rates are estimated by using the *average* sampling rate of the mixture or by selecting a *marker compound* and using the sampling rate for this compound.



TIMELINE: **THE SCIENCE AND TECHNOLOGY OF PASSIVE SAMPLERS**



EARLY TECHNOLOGY

- **1927**- Gordon and Lowe patented a *passive monitor* for CO based on a color change.
- **1960's**- Plantz developed a *personal dosimeter* for **hydrazine** using a colorimetric substance which was compared to color standards to estimate exposures.



1970-80's: THE PIVOTAL YEARS FOR PASSIVE SAMPLING

- **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.



A REVOLUTION IN EXPOSURE MEASUREMENTS

Goodbye:

- ▶ Old, loud, heavy pumps

Hello:

- ▶ Simplicity
- ▶ Convenience



THE SCIENCE AND TECHNOLOGY OF PASSIVE SAMPLERS CONTINUED TO ADVANCE THROUGH THE YEARS



BEGINNING IN THE LATE 1980's

Advances in passive samplers occurred that in many ways mirrored the advancements in active gas/vapor sampling.

1. Validation protocols/methods were developed to test and document reliability of passive samplers
2. New types of passive samplers were developed with specialty sorbents, chemically coated sorbents, chemically coated filter paper and more.



NIOSH PASSIVE SAMPLER VALIDATION PROTOCOL (1986)

Studies:

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



Summary of NIOSH Validation Protocol¹

Characteristic	Experimental Design	Interpretation of Results														
1. Analytical Recovery	Spike 16 samplers, 4 at each of 4 concentration levels (0.1, 0.5, 1.0 & 2.0 x STD) Equilibrate about 12 h and analyze.	For the higher 3 levels require $\geq 75\%$ recoveries with $S_r \leq 0.1$.														
2. Sampling Rate and Capacity	Expose samplers (4 per time period) for 1/8, 1/4, 1/2, 1, 2, 4, 6, 8, 10 & 12 h to 2 x STD, 80% RH and 20 cm/s face velocity. Plot concentration vs. time exposed. Determine MRST and SRST.	Verify sampling rate. State useful range at 80% RH & 2 x STD. Capacity - sample loading corresponding to the downward break in conc. vs time curve from constant concentration. SRST - time linear uptake rate achieved. MRST-0.67 x capacity (1 analyte) MRST-0.33 x capacity (Multi-analyte)														
3. Reverse Diffusion	Expose 20 samplers to 2 x STD, 80% RH for 0.5 x MRST. Remove and analyze 10 samplers. Expose others to 80% RH and no analyte for remainder of MRST.	Require $\leq 10\%$ difference between means of the two sampler sets at the 95% CL.														
4. Storage Stability	Expose 3 sets of samplers (10 per set) at 80% RH, 1 x STD, and 0.5 x MRST. Analyze first set within 1 day, second set after 2 weeks storage at about 25° C, third set after 2 weeks storage at about 5° C.	Require $\leq 10\%$ difference at the 95% CL between means of stored sampler sets and set analyzed within 1 day.														
5. Factor Effects	Test the following factors at the levels shown. Use a 16 -run fractional factorial design (4 samplers per exposure) to determine significant factors.	Indicate any factor that causes a statistically significant difference in recovery at the 95% CL. Investigate further to characterize its effect.														
	<table border="0"> <thead> <tr> <th><u>Factor</u></th> <th><u>Test Levels</u></th> </tr> </thead> <tbody> <tr> <td>analyte concentration</td> <td>0.1 & 2 x STD</td> </tr> <tr> <td>exposure time</td> <td>SRST & MRST</td> </tr> <tr> <td>face velocity</td> <td>10 & 150 cm/s</td> </tr> <tr> <td>relative humidity</td> <td>10 & 80% RH</td> </tr> <tr> <td>interferant</td> <td>0 & 1 x STD</td> </tr> <tr> <td>sampler orientation</td> <td>parallel & perpendicular (to air flow)</td> </tr> </tbody> </table>	<u>Factor</u>	<u>Test Levels</u>	analyte concentration	0.1 & 2 x STD	exposure time	SRST & MRST	face velocity	10 & 150 cm/s	relative humidity	10 & 80% RH	interferant	0 & 1 x STD	sampler orientation	parallel & perpendicular (to air flow)	
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BASED ON THE NIOSH PROTOCOL

- In the early 1990's, SKC research chemists embarked on a program to validate the performance of SKC 575-series samplers for collection of designated organic vapors.
- SKC's program of passive sampler validation continues today and now includes most passive samplers manufactured by SKC.



SKC'S COMMITMENT TO SAMPLING RELIABILITY

- Demonstrated in our extensive line of passive samplers with various levels of scientific testing to ensure the data generated is reliable.
- Demonstrated in the scientific data available to our customers including comprehensive research reports on the SKC website and critical sampling parameters listed in the SKC passive sampling guide.



GOVERNMENT AGENCY INITIATIVES: U.S. OSHA

- Beginning in the late 1990's, the U.S. OSHA Technical Center took an important step in both advancing the science of passive samplers and in using the data from these devices for compliance purposes.
- Their research efforts at that time focused on how to determine the overall error of passive samplers.



EVERYBODY LOVES THE CONVENIENCE OF PASSIVE SAMPLERS

But health and safety professionals need to know
if passive samplers generate reliable data.



U.S. OSHA ADVANCED THE SCIENCE WITH VALIDATED METHODS

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

See: <https://www.osha.gov/dts/sltc/methods/toc.html>



PASSIVE SAMPLERS SPECIFIED IN OSHA METHODS



OSHA PASSIVE METHODS FOR ORGANIC VAPORS

- OSHA methods for many organic vapors specify the use of a passive sampler with a carbon based sorbent including the SKC VOC Chek 575-series.





Example: U.S. OSHA Validated Method

Method number:	1005
Target concentration: OSHA PEL:	1 ppm 1 ppm (3.19 mg/m ³)(TWA); 5 ppm (16.0 mg/m ³)(15-min STEL); 50 ppm (160 mg/m ³)(10-min Peak) in General Industry (29 CFR 1910.1028) 10 ppm (31.9 mg/m ³)(TWA); 25 ppm (79.8 mg/m ³)(15-min Ceiling) in sectors excluded from General Industry (29 CFR 1926.1028) 1 ppm (3.19 mg/m ³)(TWA); 5 ppm (16.0 mg/m ³)(15-min STEL); 50 ppm (160 mg/m ³)(10-min Peak) in Shipyard and Construction Industries
ACGIH TLV:	0.5 ppm (1.6 mg/m ³) TWA; 2.5 ppm (8.0 mg/m ³)(15-min STEL) (Skin)
Procedure:	Active samples are collected by drawing workplace air through charcoal tubes with personal sampling pumps. Diffusive samples are collected by exposing either SKC 575-002 Passive Samplers or 3M 3520 Organic Vapor Monitors (OVM) to workplace air. Samples are extracted with carbon disulfide and analyzed by GC using a flame ionization detector (FID).
Recommended sampling time and sampling rate: Charcoal tubes:	240 min at 50 mL/min (12 L)(TWA); 10 min at 50 mL/min (0.5 L)(Peak); 15 min at 50 mL/min (0.75 L)(STEL)
 SKC 575-002 Passive Sampler and 3M 3520 OVM:	240 min (TWA); 10 min (Peak); 15 min (STEL) (Note: SKC 575-002 Passive Samplers and 3M 3520 OVMS must be exposed for at least 10 min)
Reliable quantitation limit (RQL) and standard error of estimate (SEE):	

Media	RQL		SEE*
	(ppb)	(µg/m ³)	(%)
Charcoal tube	3.32	11	5.1
SKC 575-002 Passive Sampler	4.25	14	8.8
3M 3520 OVM	3.55	11	7.4



OSHA METHODS SPECIFY

SKC 575-002 PASSIVE SAMPLERS

- **The SKC 575-002 sampler contains Anasorb 747 sorbent.** This sorbent is very versatile and will allow for collection of polar and non-polar organic vapors in many cases. So OSHA prefers this sorbent.
- Anasorb 747 is more expensive than activated charcoal however. So SKC 575-001 passive samplers containing charcoal are specified in SKC internal validation studies where appropriate as a cost-saving option.



NOTE ON BACK-UP LAYERS IN PASSIVE SAMPLERS

- Note that the 3M 3520 organic vapor monitor, listed as an option in OSHA methods, has a primary and a secondary layer of sorbent.
- SKC 575- VOC Chek samplers do NOT have two sorbent layers.
- Instead they have more sorbent in a single layer validated up to 2 times the exposure limit.
- **The SKC design reduces cost of analysis since the lab only has to analyze one sorbent layer.**



OSHA METHOD FOR STYRENE

- OSHA Method 1014 for styrene specifies a passive sampler containing Anasorb 747 sorbent that has been chemically coated with tert-butyl catechol.
- The sorbent is prepared by SKC and is shipped preloaded into the passive sampler ready for use.
- Analysis is by GC/FID.



SKC 575-006



OSHA METHOD FOR 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 SKC Anasorb C300.
- The sorbent is dissolved in acid and analyzed by cold vapor-AAS.



MERCURY PASSIVE SAMPLER

OSHA METHOD ID-140



SKC 520-SERIES

- Packaged as a two-part system: sorbent capsules and a reusable capsule holder.
- Suitable for 8-hr TWA or long-term sampling up to 120 hours. See OSHA method and separate back-up report available on-line at <http://www.osha.gov/dts/sltc/methods/toc.html>



OSHA PASSIVE SAMPLING METHOD FOR FORMALDEHYDE

OSHA Method 1007 for formaldehyde specifies passive samplers such as the SKC UMEX 100 that use paper tape media chemically coated with DNPH.



SKC 500-100



TECHNICAL NOTE FROM OSHA: FORMALDEHYDE SAMPLERS

- U.S. OSHA Method 1007 states that NO passive sampler should be used when the source of formaldehyde is formalin.
- Erroneously low results will occur.
- This is because formaldehyde and methanol react to form other compounds and their diffusive rates are different than formaldehyde itself.
- Sorbent tubes should be used to sample formaldehyde from formalin solutions.



TECHNICAL NOTE:

FORMALDEHYDE SAMPLERS

- **Freezer storage** is required for formaldehyde samplers using DNPH chemistry or the DNPH will decompose. The decomposition product, 2,4-dinitroaniline, may be seen as formaldehyde by some labs erroneously elevating your results.
- Expedite shipment to the lab after sampling.



OSHA PASSIVE SAMPLING METHOD FOR HYDROGEN CYANIDE

- OSHA Method 1015 specifies a passive sampler with soda lime sorbent. Since the sorbent tends to clump together, it must be field loaded by the user upon sampling.
- Analyzed by ion chromatography.



SKC 590-400



MORE ON OSHA RESEARCH INITIATIVES

- ▶ OSHA also advanced the science of passive samplers for short-term sampling.
- ▶ Historically, passive samplers have been used in occupational hygiene only for 8-hr TWA measurements.
- ▶ Some of the new validated methods from U.S. OSHA specify a minimum sample time of 10-min for STEL or peak exposure monitoring.



GOVERNMENT AGENCY INITIATIVES:

U.S. EPA

In 2015, EPA released a new regulation that requires fence line monitoring of benzene at petroleum refineries using diffusive thermal desorption tubes for sample periods of 14 days.



WHY PASSIVE SAMPLERS?

- Stainless steel canisters been the sampler of choice for environmental sampling of VOCs.
- But canisters are not typically used for sample times longer than 24-hrs.
- The new EPA regulation specifies sample times of 14 days for fence line monitoring of benzene.
- So for this application, they specify the use of passive thermal desorption tubes.



EPA METHOD 325

FOR THE NEW REGULATION

- EPA Method 325 specifies the use of passive stainless steel tubes packed with specialty sorbents such as Carbopack X or Anasorb GCB1.
- Tubes are placed inside of shelter and are deployed for **sample times of 14 days** at locations outlined in the method.
- After sampling, the tubes are **thermally desorbed** for analysis using GC-FID or GC-MS.



SKC PASSIVE SAMPLERS FOR EPA METHOD 325



SKC 226-520;
226-521

- 3.5 inch stainless steel tube deactivated with SilcoNert[®] 2000
- Brass Swagelok[®] screw caps with PTFE ferrules
- Unique identification number and bar code
- Sampling arrow indicator
- REUSABLE for a number of times after thermal purging

TUBE-STYLE PASSIVE SAMPLERS



Tube sealed with Swagelok



Tube with diffusion cap in place for sampling

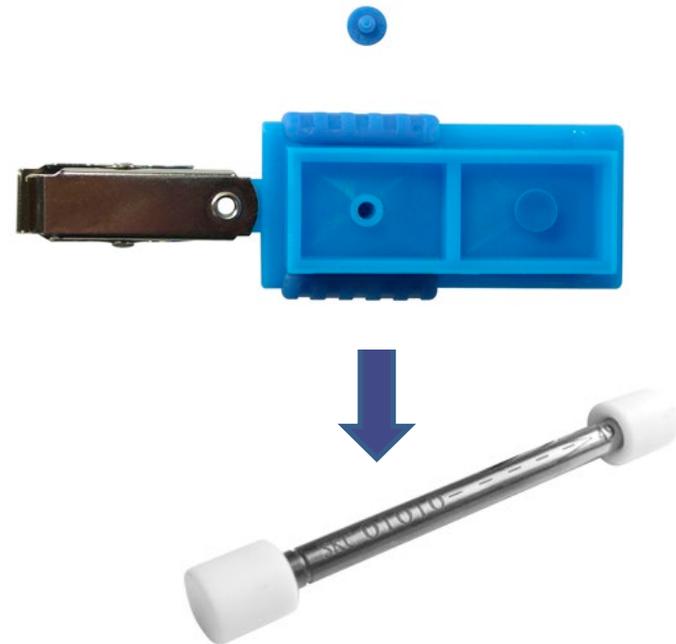
PASSIVE TUBES: FOR MORE THAN JUST BENZENE

Compound	Sampling Rate (ml/min)
Benzene	0.67
Carbon tetrachloride	0.51
Chlorobenzene	0.51
3-Chloropropene	0.51
p-Dichlorobenzene	0.45
1,1-Dichloroethane	0.57
1,2-Dichloroethane	0.57
1,1-Dichloroethene	0.57
1,2-Dichloropropane	0.52
Ethylbenzene	0.46
Styrene	0.5
Tetrachloroethene	0.48
Toluene	0.52
1,1,1-Trichloroethane	0.51
1,1,2-Trichloroethane	0.49
Trichloroethene	0.5
m,p-Xylene	0.46
o-Xylene	0.46



A NOTE ON THE SKC ULTRA PASSIVE SAMPLER

- SKC has been offering a badge style passive sampler designed as an alternative to canisters for ppb level determinations of VOCs.
- Sorbent inside the Ultra sampler is transferred to a thermal desorption tube for analysis.



DIFFERENT SAMPLERS FOR DIFFERENT APPLICATIONS



- ▶ The ULTRA passive sampler has a sampling rate of 16.0 ml/min for ppb level sampling of benzene for 8-24 hours.
- ▶ The Passive diffusive tube for thermal desorption has a benzene sampling rate of 0.67 ml/min for ppb level sampling for up to 14 days.

MORE GOVERNMENT AGENCY INITIATIVES: U.K. HSE

- In June 2016, the Health and Safety Executive released the method **MDHS 104 for VOCs** which comprises three sub-parts.
- Method 1-Active sampling using thermal desorption tubes.
- Method 2-Diffusive sampling using thermal desorption tubes like those just discussed.
- Method 3-Active pumped sampling using solvent desorption.

See: <http://www.hse.gov.uk/pubns/mdhs/pdfs/mdhs104.pdf>



RESEARCH INITIATIVES IN PASSIVE SAMPLING BY SKC CHEMISTS

SKC Validations using 575-
Series VOC Chek
Samplers Include:

- ▶ Methanol (SKC 575-007)
- ▶ Anesthetic Waste Gases (575-002)
- ▶ Ethylene Oxide (575-005)
- ▶ Siloxanes (575-001)
- ▶ Styrene (575-006)



SKC CONTINUES TO ADVANCE THE SCIENCE OF PASSIVE SAMPLERS

With Validations
using UMEX Series
Samplers

- ▶ Various aldehydes
- ▶ Sulfur dioxide
- ▶ Nitrogen dioxide
- ▶ Ammonia



FOCUS ON ALDEHYDES

UMEX 100 VALIDATIONS

- ▶ U.S. OSHA has validated the use of SKC UMEX 100 for formaldehyde in Method 1007.
- ▶ SKC chemists have validated several other aldehydes using the UMEX 100 passive sampler.

Compounds include:

- ▶ Acetaldehyde
- ▶ Benzaldehyde
- ▶ Butyraldehyde
- ▶ Crotonaldehyde
- ▶ Glutaraldehyde
- ▶ Hexanaldehyde
- ▶ Propionaldehyde



FOCUS ON NITROGEN DIOXIDE

UMEX 200 VALIDATIONS

SKC VALIDATION

SKC chemists have fully validated the UMEX 200 sampler for nitrogen dioxide from 15-min to 24-hrs.

See:

<https://www.skcinc.com/catalog/pdf/1789.pdf>

- **OCCUPATIONAL-**
Can measure workplace exposures at the current TLV 0.2 ppm as an 8-hr TWA.
- **ENVIRONMENTAL-**
Can detect down to 2 ppb for 24-hour samples of ambient air.



FOCUS ON SULFUR DIOXIDE

UMEX 200 VALIDATIONS

SKC VALIDATION

SKC chemists have also validated the UMEX 200 sampler for sulfur dioxide from 15-min to 24-hrs.

See:

<http://www.skcinc.com/catalog/pdf/instructions/1781.pdf>

- **OCCUPATIONAL-**
Can measure workplace exposures at OSHA and NIOSH TWA levels. **Not suitable** for the TLV of 0.25 ppm as a STEL.
- **ENVIRONMENTAL-**
Can detect down to 17.4 ppb for 24-hour sampling of ambient air.



FOCUS ON AMMONIA

UMEX 300 VALIDATIONS

SKC VALIDATION

SKC chemists have validated the UMEX 300 sampler for ammonia from 15-min to 24-hrs.

See:

<https://www.skcinc.com/catalog/pdf/1885.pdf>

- **OCCUPATIONAL-**
Can measure **TWA** levels for the ACGIH TLV of 25 ppm and **STEL** levels for the ACGIH TLV of 35 ppm.
- **ENVIRONMENTAL-**
Can detect down to 25 ppb for 24-hour sampling of ambient air.



SKC RESEARCH CONTINUES: NEW SAMPLER DESIGN

- SKC Research Chemists are actively working on new concept in passive samplers.
- The new sampler call Multi-Chek has 3 separate compartments to contain the sorbent.
- If you put the same sorbent in all 3 compartments, the sampler has a very high uptake rate for low level detection.
- If you put different sorbents in the 3 compartments, you can collect multiple compounds that require different collection media.



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.



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



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



COLOR BADGES



www.morphixtechnologies.com

- 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.

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



THANK YOU

- Please visit the SKC webpage at www.skcinc.com to see the passive samplers and research reports documenting critical sampling parameters.
- Email SKCTech@skcinc.com with technical questions or contact your local SKC representative.

