

On diffusive badges and VOC sampling in IAQ investigations

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ABSTRACT

This paper presents examples, application and limitations of diffusive badges in sampling VOCs in non-industrial indoor microenvironments. It reviews a number of IAQ field surveys and experimental investigations that have used passive badges in their sampling campaigns. It revisits basic fundamentals of passive diffusion. It reveals preliminary results of an experimental study initiated to examine the practical application of diffusive badges in a novel portable field sampler designed and developed for *in situ* emission sampling of VOCs by interior finishes and furnishings. However, according to our preliminary findings, the uses of diffusive badges have proved to be non-ideal and limiting. Passive diffusive sampling may not even be suitable for non-industrial IAQ sampling campaigns due to: (1) the inherent low indoor air velocities present in non-industrial settings; and (2) unpredictable background impurities that were consistently found in different blanks from batches of passive diffusive badges. Diffusive badges are appropriate for sampling VOCs in industrial environments where concentrations and air velocities are at levels that are relatively high ($>1 \text{ mg/m}^3$ and $>20 \text{ cm/s}$, respectively). These lower end industrial levels are hardly encountered in normal non-industrial indoor microenvironments. Even if indoor air velocities were abnormally increased and maintained to match diffusive badges' uptake rate validation level ($>20 \text{ cm/s}$), the background impurities found in blank, unused and off-the-shelf passive diffusive badges limit their application in sampling low level ($<1000 \text{ } \mu\text{g/m}^3$) VOCs in non-industrial indoor settings.

INDEX TERMS

Passive diffusive sampling; Uptake rate; Indoor VOCs; Air velocity; Blank impurities

DIFFUSIVE SAMPLING: REVISITING SOME IGNORED ISSUES

Each passive diffusive badge is designed with a critical range of face velocities that should not be used outside (especially below) the prescribed range. According to a literature review on passive diffusive badges, changes in air velocities influence the diffusive sampling rate. Decline in sampling rates are more pronounced at the lower air velocity range ($<20 \text{ cm/s}$) than at the higher range ($>20 \text{ cm/s}$) by several folds. Most commonly used diffusive badges require a minimum critical face velocity of 15–20 cm/s (ACGIH, 1995). This critical and 'minimum' face velocity range is prescribed to limit the starvation effect in diffusive transport mechanism. Higher air velocities and turbulences maintain some continuity to the positive concentration gradient between the volume of air outside the badge and the still air within the badge (i.e. the diffusion chamber inside a badge) (Pozzoli and Cottica, 1987). Air velocities that are commonly encountered in offices and homes ($<10 \text{ cm/s}$) provide limited continuity to the transport of VOCs into the diffusion chamber of passive badges. Accordingly, molecules of VOCs near the exterior surface of the badge cannot be steadily renewed once they enter into the diffusive chamber. An external balancing and complimentary driving force is

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required (based on empirical research) so that a constant mass transport mechanism is guaranteed throughout the diffusive sampling process (Tompkins and Goldsmith, 1977). The diffusive transport process can be summarized as: (1) the VOCs in the bulk indoor air enters into the boundary film near the exterior inlet of the badge (known as the anti-convective membrane); (2) permeation into the diffusive membrane; (3) diffusion through the diffusive chamber; (4) molecular diffusion through a thin film into the pore spaces between carbon particles of the sampling medium (i.e. activated carbon felt/granules); and finally (5) resting onto deep surfaces of carbon particles.

To facilitate the above diffusive process, an external balancing, complimentary and synchronizing driving force is needed. This force is provided by the turbulent (in terms of air velocity) and mixed (in terms of spatial distribution of concentration profile) conditions present in most industrial environments. To this end, passive sampling is an acceptable means for sampling contaminants in industrial settings. The range of air velocities (>20 cm/s) that is required in passive sampling can be easily encountered in most industrial indoor environments. However, when it comes to non-industrial indoor environments such as inside offices and homes, the average air velocities are hardly above 10 cm/s. According to ASHRAE, a 20 cm/s air velocity in an indoor non-industrial office workstation significantly contributes towards the range of 20% dissatisfied (ASHRAE, 1997). This indicates that passive diffusive badges—as presently designed and validated—are not suitable for sampling VOCs in non-industrial indoor environments. Studies indicate that among the three major environmental parameters of: (1) air velocity; (2) relative humidity; and (3) temperature, air velocity is the most influential in determining the precision, accuracy and validity of passive diffusive sampling (Pozzoli and Cottica, 1987). In a previous study (Charron *et al.*, 1998), a field validation of three different passive diffusive badges (AT, 3M, and SKC) for VOC exposure in a facility with indoor air velocities ranging from 4 to 14 cm/s was performed. Although the study might have overlooked the influence of low air velocities in sampling and data validation, it concluded that all three types of passive diffusive monitors failed NIOSH's (National Institute for Occupational Health and Safety, USA) accuracy (i.e. overall uncertainty) in its standard recommendation of $<25\%$ at a mean VOC level of <1 ppm. The study, not mentioning the requirement of minimum air velocity for passive sampling, attributed the uncertainty to the presence of 'unique non-homogenous atmospheres' that may have influenced the sampling campaign at the location and during the sampling period.

It may be of interest to note that measuring air velocities at levels below 10 cm/s requires special measuring devices. The standard hot-wire anemometer used in most indoor air velocity measurement studies are designed for air velocities higher than 8 cm/s, which is at the high end of indoor air velocities in most non-industrial indoor environments (Zhang, 1991). Reporting values below 5 cm/s is no doubt erroneous unless specialized and sophisticated velocity measuring instruments are used. Needless to say, most validation studies for passive samplers (those by manufactures and those by regulatory agencies including OSHA—Occupational Health and Safety Administration—USA) are performed in laboratory conditions with air velocities above, and in many cases, twice that of 20 cm/s. OSHA in its own experimental work towards the development of a protocol for laboratory testing of diffusive samplers (OSHA, 1996), has reported that determination of sampling rates at 20 cm/s is inappropriate if sampling rate variations as determined from their protocol are to be used as estimated variations for future work. OSHA stated that a linear velocity of 40 cm/s would be more suitable because average sampling rates for passive diffusive sampling rate versus the linear velocity used in their experiments occurred at approximately 40 cm/s. At 40 cm/s, non-industrial indoor environments are 'non-industrial' no longer!

USE OF PASSIVE SAMPLING IN FIELD STUDIES: FEW EXAMPLES

Table 1 summarizes some studies that utilized passive diffusive badges in sampling indoor VOCs in non-industrial environments. Some studies took into consideration the limitations mentioned above, while others overlooked these limitations and relied heavily on the data generated.

Table 1 VOC concentrations in homes and offices using passive badge sampling

Reference	Number of sites	Location	Species monitored	Mean concentrations of selected VOCs ($\mu\text{g}/\text{m}^3$)
Fellin and Otson (1994)	754 homes	Canada	26 VOCs	Benzene (5.5); <i>d</i> -limonene (20.8); toluene (39.7)
Ilgen <i>et al.</i> (2001a,b)	114 homes	Germany	BTEX ^a	Ethylbenzene (2.8); benzene (2.9); xylene (9.4); toluene (28)
Wolkoff <i>et al.</i> (1991)	Twin apartments	Denmark	21 VOCs	Benzene (3.2); toluene (16)
Schneider <i>et al.</i> (2001)	405 homes	Germany	BTEX ^a	Benzene (2.7); ^b xylene (6.1); toluene (38.5)
Shields <i>et al.</i> (1996)	70 offices	United States	31 VOCs	Ethylbenzene (2.1) ^c ; <i>n</i> -undecane (10.7)
Weschler <i>et al.</i> (1990)	4 office buildings	United States	36 VOCs	Toluene (14.5); <i>d</i> -limonene (39.6)

^aBenzene, toluene, ethylbenzene, xylene. ^bMedian concentrations reported. ^cGeometric means reported.

Passive badges have been used to monitor VOC concentrations in a number of indoor non-industrial environments (i.e. homes and offices). Fellin and Otson (1994) used passive badges in sampling indoor VOCs and reported a detection limit range of 1.6–5.9 $\mu\text{g}/\text{m}^3$. Ilgen *et al.* (2001a,b) conducted an extensive instrument validation and calculated a limit of quantitation of 0.15 $\mu\text{g}/\text{m}^3$. The accuracy of the passive samplers was checked against results from integrated samplings on charcoal tubes, and the agreement between the active and passive samplers was reported to be within 10%. Schneider *et al.* (2001) used passive badges placed in the bedroom, living room and outside the home. In 10% of the homes, duplicates and field blanks were taken in the living room to assess precision. The field blanks ranged in concentration from $0.78 \pm 0.20 \mu\text{g}/\text{m}^3$ for benzene to $1.58 \pm 0.92 \mu\text{g}/\text{m}^3$ for toluene, and the detection limits ranged from 0.28 $\mu\text{g}/\text{m}^3$ for xylene to 1.86 $\mu\text{g}/\text{m}^3$ for toluene. Shields *et al.* (1996) monitored VOC concentrations in office buildings using simultaneous indoor and outdoor sampling on passive badges and reported a detection limit of 0.5 $\mu\text{g}/\text{m}^3$. Wolkoff *et al.* (1991) highlighted the importance of choosing a sampling methodology that will accurately and precisely monitor the target species since passive badges may not be the most accurate method for monitoring many volatile organic compounds that are present in indoor environments such as homes and offices.

BASELINE IMPURITIES IN PASSIVE DIFFUSIVE BADGES

Having briefly reviewed some basics of passive diffusive sampling, applications, limitations and field studies, a preliminary evaluation of two commonly used passive badges are performed. The outset intention of this study was to determine sampling rate variations of passive badges in a velocity-starved environment (i.e. inside a static chamber) flowed by a dynamic chamber system using a novel *in situ* material emission sampler. An active sampling experiment using charcoal tubes and comparing the novel dynamic emission sampler with the FLEC and an ASTM-based 50L chamber has been published elsewhere (Rastan *et al.*, 2003). The original intent of this study was to extend the application of the novel emission sampler

to passive badge sampling and introduce a hybrid (passive/active) sampling system that artificially generates a local air velocity gradient at the face of a passive badge in a such a way to maintain the desired sampling air velocity level at 40 cm/s for a steady passive diffusive uptake rate. However, initial results indicated a strange trend in passive badges' baseline blanks before even sampling or mounting them to the new sampler. Not a single passive badge passed our laboratory's lab-blank baseline criterion (i.e. compared with baselines generated by activated coconut charcoal tubes). A clean baseline is a GC-FID generated chromatogram with no discernible peak after Benzene's retention time (because Benzene is present as an intrinsic impurity in the solvent used—CS₂). As a consequence, the initial focus of this investigation was shifted from its original aim to evaluate the extent of baseline impurities in passive diffusive badges. No quantification or identification of baseline impurities was performed in this 'unintended' study. However, differential chromatographic baselines comparing unused passive badges (lab-blanks) with unused charcoal tubes (lab-blanks) were used to assess the extent of impurities.

New 3M, SKC passive badges and standard active sampling charcoal tubes were directly purchased from the manufactures with at least 12 months remaining to expiry date and were directly used as pure lab-blanks. Standard instructions were followed for desorption, and a GC-FID (Varian-30m VOLCOL Col.) was used for sample analysis. Both types of badges indicated the presence of more than 10 distinguishable impurities (i.e. peaks) while the active sampling charcoal tubes had none expect for one single miniscule peak appearing at a retention time representing Toluene (FID response < 000). Figures 1 and 2 present the results of this preliminary experiment. For the sake of this study, an FID response of less than 5000 was considered insignificant. For charcoal tubes, no peaks were reordered above the 5000 FID response limit (except for the solvent that includes benzene) to map on both Figures 1 and 2 for comparison. This is an indication of background purity of charcoal tubes compared with passive badges.

DISCUSSION

This study attempted to pinpoint sources of few specific peaks (i.e. impurities in passive badge blanks). Sources of impurities could be attributed to the batch, manufacturing, handling and production processes as well as our own laboratory procedure in sample preparation and analysis. The latter has been confirmed to be irrelevant since similar and in parallel procedures for both the active tubes and the passive badge were used. However, after several try-and-error attempts, two major impurities (i.e. peaks) produced by the SKC blank badges were found to be from a component of the SKC sampler itself (i.e. the black O-ring supplied by the manufacturer with each SKC passive badge kit) These O-rings are used to seal-off the mouth of the badges during extraction. It is observed that the extraction solvent (CS₂), have somehow reacted with the O-ring polymer during preparation and extraction. Due to the present design of the SKC badge and its extraction methodology, any liquid solvent, once added to the badge assembly from sample extraction, comes in contact with parts of the O-ring's brim and dissolves some constituents of its polymer. Upon closer investigation and communication with polymer experts and several O-ring manufacturers, it became evident that the type of the polymer used for the O-ring supplied by the SKC in its passive sampling kit was not suitable for solvents such as CS₂. Once the SKC O-ring has been replaced by a more suitable O-ring that is solvent resistant (specially ordered from a Teflon O-ring supplier), the two respective impurities (i.e. peaks) disappeared. To confirm this finding, both types of O-rings (i.e. SKC's original O-ring and the new Teflon-based one) were immersed into liquid CS₂ and the solutions injected into the GC-FID. Chromatographic results clearly mapped the source of the two impurities to the original SKC O-ring. Figure 3 maps the results of the SKC's passive badge blank impurities with th at of the original O-ring immersed into

the solvent. The alternative Teflon-based O-ring sample produced no single peak; hence no response can be shown in the figure.

CONCLUSION AND IMPLICATIONS

Passive badges have apparent limitations, uncertainties, and impurities. Their use and application as sampling mediums for low-level non-industrial indoor VOCs should be carefully re-examined. Chromatographic peaks of SKC blank are less significant (in terms of response magnitude/peak area) than the 3M blanks. The O-ring supplied with each SKC badge sampling kit is a source of two main impurities and should be changed to a more suitable and appropriate O-ring that is solvent resistant (an in-kind contribution to our R&D colleagues at SKC). Regardless of these intrinsic impurities in passive badges (cf. charcoal tubes), air velocity considerations, validity of uptake rates and starvation effects should all be carefully and critically considered before relying on data generated by the application of passive badges in sampling indoor VOCs in non-industrial microenvironments.

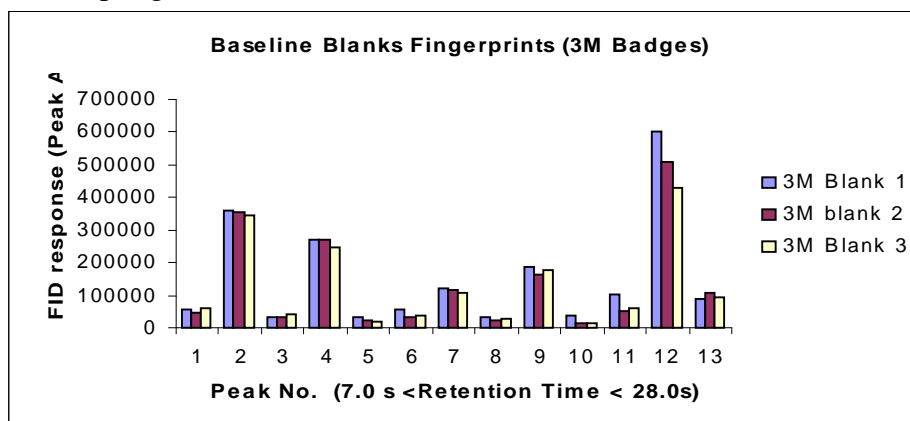


Figure 1 3M OVM 3500 blank impurities (FID response >5000 is significant).

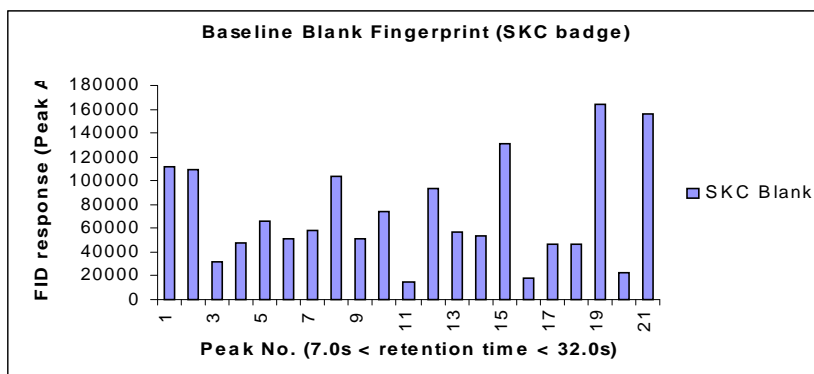


Figure 2 SKC blank impurities (FID response >5000 is significant).

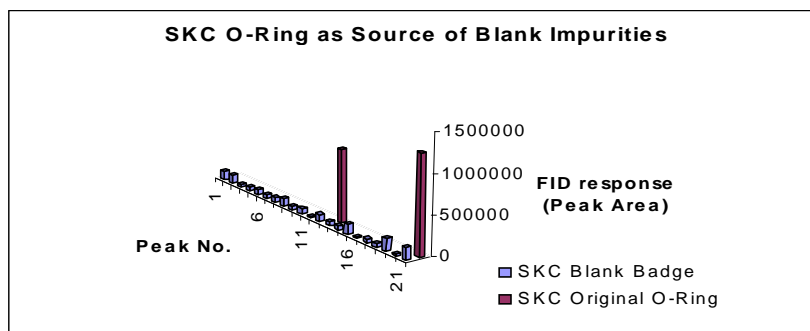


Figure 3 SKC blank impurities mapped on its own O-ring (peak # 13 and 21, cf. Figure 2).

REFERENCES

- ACGIH (1995). *The White Book*, p. 379.
- ASHRAE (1997). *Fundamentals*, p. 8.13. Atlanta: American Society of heating and Air Conditioning Engineers Inc.
- Charron, K.A. *et al.* (1998). Field validation for passive monitors for the determination of employee exposure to methylene chloride in pharmaceutical production facilities. *American Industrial Hygiene Journal* **59**, 353–358.
- OSHA (1996). Development of a Protocol for Laboratory Testing of Diffusive Samplers. OSHA Salt Lake Technical Center Report.
- Pozzoli, L. and Cottica, D. (1987). An overview of the effects of temperature, pressure, humidity storage and face velocity. In: Berlin, A., Brown, R.H. and Saunders, K.J. (eds), *Diffusive Sampling: An Alternative to Workplace Air Monitoring*, pp. 119–130. London: Royal Society of Chemistry.
- Rastan, S. *et al.* (2003). KAPPA—a novel dynamic in-situ material emission sampler. *Cold Climate-HVAC 2003*, Norway.
- Tompkins, F.C. and Goldsmith, R.L. (1977). A new personal dosimeter for the monitoring of industrial pollutants. *American Industrial Hygiene Association Journal* **38**, 371–377.
- Zhang, J.S. (1991). A fundamental study of two dimensional room ventilation flows under isothermal and non-isothermal conditions. PhD thesis, University of Illinois at Urbana-Champaign, USA.

FIELD STUDIES REVIEWED

- Fellin, P. and Otson, R. (1994). Assessment of the influence of climatic factors on concentration levels of volatile organic compounds (VOCs) in Canadian homes. *Atmospheric Environment* **28** (22), 3581–3586.
- Ilgen, E., Karfich, N., Levsen, K., Angerer, J., Schneider, P., Heinrich, J., Wichmann, H.-E., Dunemann, L. and Begerow, J. (2001a). Aromatic hydrocarbons in the atmospheric environment. Part 1: Indoor versus outdoor sources, the influence of traffic. *Atmospheric Environment* **35** (7), 1235–1252.
- Ilgen, E., Levsen, K., Angerer, J., Schneider, P., Heinrich, J. and Wichmann, H.-E. (2001b). Aromatic hydrocarbons in the atmospheric environment. Part 2: Univariate and multivariate analysis and case studies of indoor concentrations. *Atmospheric Environment* **35** (7), 1253–1264.
- Schneider, P., Gebefugi, I., Richter, K., Wolke, G., Schnelle, J., Wichmann, H.-E., Heinrich, J. and Group, I.S. (2001). Indoor and outdoor BTX levels in German cities. *The Science of the Total Environment* **267** (1–3), 41–51.
- Shields, H., Fleischer, D. and Weschler, C. (1996). Comparisons among VOCs measured in three types of U.S. commercial buildings with different occupant densities. *Indoor Air* **62** (17).
- Weschler, C., Shields, H. and Rainer, D. (1990). Concentrations of volatile organic compounds at a building with health and comfort complaints. *American Industrial Hygiene Association Journal* **51** (5), 261–268.
- Wolkoff, P., Clausen, P., Nielsen, P. and Molhave, L. (1991). The Danish twin apartment study; Part 1: Formaldehyde and long-term VOC measurements. *Indoor Air*, 4478–4490.