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The Effect of Taggant Vapor Adsorption and
Containment on the Predetonation Detection
of Explosives

Gunnar I. Senum, Eugene M. Ferreri, Margaret W. Greene,
Robert P. Gergley and Russell N. Dietz

October 1979

Research sponsored by the
Bureau of Alcohol, Tobacco and Firearms
of the U.S. Department of the Treasury
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INFORMAL REPORT

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Department of Energy and Environment

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ABSTRACT

Predetonation detection of explosives in realistic scenarios may be accomplished by detecting vapors emitted by the explosive. These vapors could be either the vapor emitted from the inherent compounds present in the explosive or the vapor emitted by a specific vapor taggant introduced into the explosive at the time of manufacture. The emitted vapor concentration in various detection scenarios can be diminished either by vapor adsorption onto adsorptive surfaces present in the scenario, e.g., clothing, curtains, rugs etc., or by enclosing the explosive in a relatively airtight enclosure, e.g., box, luggage, etc., which will impede the vapor emission into the detection scenario.

These two effects are modeled to ascertain the magnitude of the vapor concentration reduction in various scenarios. Experiments have been performed to provide a necessary input parameter for the containment model and to confirm the predictions of the model.

Seven potential vapor taggants were experimentally examined for their vapor concentration depletion by adsorption in a typical scenario. Three potential vapor taggants, perfluorodimethylcyclobutane (PDCB), perfluoromethylcyclohexane (PMCH) and perfluorodimethylcyclohexane (PDCH) were determined to have a negligible adsorption loss. Perfluorodecalin (PFD) and L-4412, a 3M Company proprietary compound, were determined to have a slight adsorption loss, i.e., 66 and 40 percent respectively. Three other potential taggants; Decafluorobiphenyl (DFBP), octafluoronaphthalene (OFN), and octafluorotoluene (OFT) have significant adsorption losses, i.e., greater than 80 percent that precluded their use as effective vapor taggants.

Six enclosures were examined experimentally for their ability to contain taggant vapors. Of these, a box filled with styrofoam packing, a suitcase, a heat sealed polyethylene bag, and an attache case provided no significant impediment to the release of the vapor taggant into the detection scenario, i.e., these enclosures had a negligible degree of airtightness. The remaining two examined enclosures, a paint can and a zip lock plastic bag, showed significant vapor containment and thus possibly could hinder the vapor detection of explosives which are placed in these enclosures.

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GLOSSARY OF TERMS

- A--the total area of the cracks in the barrier (cm^2)
- a--attenuation factor due to surface adsorption
- $a_0 \dots n$ --power series expansion coefficient
- c--empirical constant associated with the adsorption phenomena
- $C(t)$ --the taggant concentration inside the scenario at time (t) - (ppt)
- $C(\infty)$ --steady state taggant concentration - (ppt)
- $C_o(t)$ --the concentration of taggant in the scenario with no barrier
- $C_{en}(t)$ --the concentration of taggant inside the barrier at time (t) - (ppt)
- D--the taggant diffusion constant in air (cm^2/min)
- DFBP--decafluorobiphenyl
- 2,4-DNT--2,4-dinitrotoluene
- EGDN--ethylene glycol dinitrate
- f--the volume fraction of the taggant in the air leaving the scenario
- $f(s)$ --the Laplace transform of $V(t)$
- $g(s)$ --the Laplace transform of $V_{en}(t)$
- k--barrier constant (ℓ/min)
- L--the average depth of a crack in the barrier - (cm)
- L-4412--perfluorohexylsulfurpentafluoride
- mil--one thousandth of an inch
- NG--nitroglycerine
- nL--nanoliters
- OFN--octafluoronaphthalene
- OFT--octafluorotoluene
- P--partial pressure of the taggant chemical

PDCB--perfluorodimethylcyclobutane (mixture of 1,2- and 1,3-isomers)
PDCH--perfluorodimethylcyclohexane (mixture of 1,3- and 1,4-isomers)
PETN--pentaerythritol tetranitrate
Pext--ambient pressure - (torr)
PFD--perfluorodecalin
PMCH--perfluoromethylcyclohexane
ppb--parts per billion (volume per volume)
ppt--parts per trillion - (volume/volume)
Q--the permeability coefficient - (cc (stp) cm/sec-cm² Δ torr)
r₁--coefficient of the Laplace transform
r₂--coefficient of the Laplace transform
R_{ad}--rate of taggant chemical loss due to adsorption (d V_{ad}/dt) - (ℓ/min)
R_{cap}--taggant emission rate - (ℓ/min)
RDX--1,3,5-trinitro-1,3,5-triazacyclohexane
Ren(t)--the taggant effission rate from the barrier into the scenario - (ℓ/min)
R_{ex}--chamber ventilation rate - (ℓ/min)
t--time (min)
2,4,6-TNT--2,4,6-trinitrotoluene
t_v--turnover or ventilation time of the scenario - (min)
V--the taggant volume inside the barrier at time t = 0 - (ℓ)
V_{ad}--volume of taggant contained in the Langmuir adsorption isotherm - (ℓ)
V_{ch}--volume of the scenario (ℓ)
*V_{en}--the initial non-zero taggant volume inside the barrier
V_{en}--the volume of the barrier (ℓ)
Ven(t)--the taggant volume inside the barrier at time (t) - (min)
v_m--gas volume necessary to cover the absorbing surface with a monolayer -
(ℓ)

$V_o(t)$ --volume of taggant present in scenario at time $(t) - (\ell)$

$V(t)$ --the taggant volume inside the scenario at time $(t) - (\ell)$

β --the ratio of the barrier air exchange rate to the scenario ventilation rate, i.e., k/R_{ex} - (dimensionless)

γ --the ratio of the barrier volume to the scenario volume, i.e., V_{en}/V_{ch} - (dimensionless)

τ --turn over time factor, t/t_v - (dimensionless)

INTRODUCTION

The purpose of this report is to derive an accurate estimate of the magnitude of vapor surface adsorption and barrier effectiveness to contain and impede vapor transport from explosives in several realistic scenarios. Explosives predetonation detection based on detection of a specific vapor has progressed along two major lines; first, the detection of a volatile material unique to the explosive, and second, the detection of a unique vapor taggant that has been incorporated into the explosive at the time of manufacture. Presently the second method appears to be more feasible in terms of its simplicity, i.e., detection of a unique vapor taggant as opposed to the detection of one of many explosive vapors (EGDN, NG, 2,4-TNT, 2,4,6-TNT, RDX, PETN, etc.) and of its flexibility, i.e., the vapor taggant can be chosen so as to optimize its detectability as opposed to the apparent insensitivity of vapor detection methods for most of the inherent explosive vapors due to a combination of low room temperature vapor pressures and significant surface adsorption ability.

Common to both detection techniques, however, are two effects which can hinder the detection of these vapors regardless of the ability to either incorporate vapor taggants into explosives or successfully detect the inherent explosive vapors. The effects are first, loss of the vapors by physical adsorption and second, containment of the vapors within an airtight enclosure surrounding the explosives. The two effects are most important when an attempt is made to detect explosives in a realistic scenario, e.g., when explosives are hidden in luggage, boxes, etc. which have been placed in rooms, buildings, aircrafts, etc. Within these scenarios, the vapor, especially the inherent explosive

vapors, can be physically adsorbed onto the various adsorptive surfaces present, e.g., clothing, rugs, curtains, packing material etc., thus reducing the vapor concentration available to detection. The vapor concentration is also reduced by placing the explosives in a relatively airtight enclosure, e.g., boxes, luggage etc, that retains the vapor and thus impedes its release and subsequent detection in the scenario. Both of these effects can effectively diminish the detectability of explosives via vapor detection.

The mechanisms of these two effects, adsorption and containment, are modeled separately. Each effect because they are independent of each other will be considered separately. The mechanism for the containment effect is nearly independent of the specific vapor compound being contained and the modeling results are applicable to the detection of any explosive derived vapor, whether an inherent explosive vapor or a vapor taggant; however, the mechanism for adsorption loss is compound dependent and consequently the modeling results are used to select a vapor taggant that minimizes adsorption losses.

In order to select a vapor taggant, the degree of adsorption loss for various compounds proposed for use as vapor taggants in explosives was determined experimentally. No inherent explosive vapor was examined experimentally because it was known from other studies¹ that most of these have a severe adsorption loss. The duration for the modeling for the adsorptive effect is given in Appendix A with only general predictive results because the modeling involves a large number of undetermined parameters.

The modeling for the containment effect is also given along with some predictive results for various scenarios, e.g., an explosive enclosed in a briefcase with various degrees of airtightness that is being sampled in either a

moderately sized room or an aircraft. Experiments have also been performed to provide a necessary parameter for the modeling and to confirm the results for six enclosures, e.g., a suitcase, a box, an attache case, a heat sealed plastic bag, a ziplock plastic bag and a paint can.

This work is a partial result of the research program "Evaluation of Vapor Taggants and Substrates for the Tagging of Blasting Caps," as sponsored by the Bureau of Alcohol, Tobacco and Firearms of the U.S. Department of The Treasury under the direction of The Aerospace Corporation. This report has been prepared from the final report² of this program because of the wider application of these particular results. The chapters in this report are also included in the program final report along with other chapters related to the detection of specific vapor taggants, the preparation of vapor tagged blasting caps and the characterization of microencapsulated vapor taggants used as taggants for bulk explosives.

2.0 Experimental Determination of Adsorption Losses for the Potential Vapor Taggants

The mechanism for taggant depletion from a detection scenario via adsorption has been mathematically modeled in Appendix A. A major conclusion is that the initial rate of taggant release in the scenario is reduced by an adsorption attenuation factor, i.e.,

$$(1 + av_m) = (1 + v_m c P_{\text{ext}} / V_{\text{ch}} P_0) \quad (2.1)$$

In equation (2.1), v_m is the gas volume necessary to cover the adsorbing surface with a complete monolayer, c an empirical constant of the order of ten, P_{ext} the ambient pressure, P_0 the equilibrium vapor pressure of the taggant, and V_{ch} the volume of the scenario. The conclusion of this modeling is that adsorption losses are greatest when

- (a) v_m is large, i.e., a large surface area is available for adsorption
- (b) P_0 is small, i.e., the adsorbate, the vapor taggant, is non-volatile.

This attenuation, i.e., equation (2.1), can be quantified if v_m , c , and P_0 are known for a particular vapor taggant and known surface. However, in the majority of realistic situations, these parameters are unknown and thus it is more appropriate to select vapor taggants that will have a negligible adsorption loss in the majority of scenarios, i.e., very volatile taggants. The question then becomes, how volatile must a taggant be to have a negligible taggant adsorption loss. This has been determined experimentally for a series of proposed vapor taggants in a test scenario consisting of a towel enclosing a vapor taggant source which is placed in a cloth suitcase. This arrangement was chosen as the test scenario because it is representative of a number of expected detection scenarios and the test arrangement is reasonably reproducible. If the proposed vapor taggants have a negligible adsorption loss in this test scenario, then it is expected that it will have a negligible or at most a small loss in most other scenarios.

The experimental procedure was to place the entire cloth suitcase in a 422 liter sampling chamber having a ventilation rate of 200 mL/min. In-house compressed air was used throughout these experiments. Due to the variability in supply pressure over a 2 to 3 day time period of these experiments, the flow rate would decrease. This resulted in higher measured concentrations of taggant (see Figure 2.1). This phenomena was observed throughout sections 2.0 and 4.0. The taggant source was a vapor tagged blasting cap with a predetermined taggant emission rate. The taggant concentrations in the sampling chamber were determined chromatographically every half-hour after the test suitcase had been placed in the chamber. The adsorption experiment for each potential vapor taggant was performed in two parts. First the tagged source was placed in the chamber without the suitcase and measurements were performed. Then the experiment was repeated with the source in the test suitcase. The difference in

Figure 2.1

results was related to adsorption losses. In the experiment without the above test suitcase, only the vapor tagged sources were suspended in a wire cage in the sampling chamber in order to provide the identical source of vapor taggant for both parts of the adsorption experiments.

To provide a direct comparison between the results for each of the potential vapor taggants (see Table 2.1), the resulting vapor taggant concentrations inside the chamber were normalized by dividing the measured taggant concentration, $C(t)$, by the calculated steady-state taggant concentration, $C(\infty)$ i.e.,

$$\text{Normalized concentration} = C(t)/C(\infty) \quad (2.2)$$

where

$$C(\infty) = R_{\text{cap}}/R_{\text{ex}} \quad (2.3)$$

R_{cap} is the taggant emission rate of the source and R_{ex} is the chamber ventilation rate. The elapsed time was normalized in terms of turnover times, i.e., the elapsed time was divided by the chamber turnover time, the length of time required to entirely ventilate the chamber volume. This turnover time is obtained from the quotient of the chamber volume and the chamber ventilation rate. In realistic scenarios, turnover times generally range from 20 to 60 minutes for ventilated areas in modern buildings.

The potential vapor taggants which were tested are listed in Table 2.1

Table 2.1 Potential Vapor Taggants		
Chemical Name	Abbreviation	Equilibrium Vapor Pressures (25°C) in atm
Perfluorodimethylcyclobutane	PDCB	0.50
Perfluoromethylcyclohexane	PMCH	0.14
Perfluorodimethylcyclohexane	PDCH	0.046
Octafluoronaphthalene	OFN	.0001
Octafluorotoluene	OFT	---
Decafluorobiphenyl	DFBP	---
SF ₅ C ₆ F ₁₃	L-4412	.024
Perfluorodecalin	PFD	.0087

The results for each taggant are discussed in the following sections.

2.1 PDCB Taggant

A PDCB tagged blasting cap vapor source with an emission rate of 0.55 nanoliters per minute was used in both parts of the experiment. The results are displayed in Figure 2.1 with the measured normalized PDCB concentration $C(t)/C(\infty)$ plotted on the vertical axis and the normalized elapsed time, expressed as the number of turnover times, is plotted on the horizontal axis. As is seen in Figure 2.1 there is negligible PDCB adsorption loss in the test towel/suitcase adsorption scenario, i.e., the normalized concentrations from both parts of the experiment are nearly coincident. In fact it appears that the taggant concentrations for the adsorbent part of the experiment are slightly higher than for the no adsorbent part. The most likely cause of this result was due to a decrease in the in-house compressed air supply used to ventilate the chamber, which increased the measured taggant concentration. Ideally, the chamber ventilation rate was to be a constant throughout the entire series of adsorbent experiments; however, due to length of time required for each experiment (1-3 days), the chamber ventilation rate would often vary after the experiment had begun and consequently would effect the chamber taggant concentrations (see Equation 2.3). Nevertheless, these PDCB results in Figure 2.1 do indicate that within the precision of the experiment there is a negligible PDCB adsorption loss in the test scenario. This result is further validated in the barrier experiments in which the PDCB concentration for the no barrier and barrier experiments are

coincident when the barrier contained significant adsorption surfaces, i.e., polystyrene packing material as discussed in Section 4.1.

2.2 PMCH Taggant

For the PMCH taggant, a tagged blasting cap source with an emission rate of 0.17 nL/min was used. The results are displayed in Figure 2.2 and they indicate negligible PMCH adsorption loss in the test scenario as is evidenced by the near coincidence of the normalized PMCH concentrations for both parts of the experiment.

2.3 PDCH Taggant

Figure 2.3 gives the results for the PDCH taggant. The data indicates the lack of PDCH adsorption loss in the test scenario. As with the PDCB taggant, the adsorbent part of the experiment yielded higher PDCH concentrations than the no adsorbent part. This is again ascribed to a decrease (by approximately 20 percent) in the chamber ventilation rate which increased the PDCH taggant concentration for the adsorbent part of the experiment.

2.4 PFD Taggant

A perfluorodecalin tagged blasting cap was used as a source of the PFD vapor. The results displayed in Figure 2.4 indicate, that within the precision of this experiment, a slight degree of PFD adsorption loss in the test towel/suitcase scenario. This slight degree of adsorption loss can be quantified by comparing the initial slopes of both parts of the experiment in order to determine the adsorption attenuation factor $(1 + v_m c P_{ext} / V_{ch} P_o)$. This comparison gives the factor 1.50 ± 0.21 . It is not possible to determine the individual terms in this factor; therefore, only the total adsorption attenuation term is given.

Figure 2.2

Figure 2.3

PERFLUORODECALIN ADSORPTION EXPERIMENT SUITCASE/TOWEL ADSORBENT

ADSORPTION ATTENUATION = 1.50 ± 0.21

Figure 2.4

This degree of adsorption loss for PFD is slight and does not preclude its use as a vapor taggant; however, the scenario taggant concentrations will be reduced slightly due to adsorption. Specifically in this test towel/suitcase scenario, it was initially reduced to 66% of its expected concentration. However, as is seen in the mathematical modeling in Appendix A, adsorption losses only affect the initial taggant concentration. Given sufficient lapsed time, the taggant concentration will reach the same steady state concentration regardless of the taggant volatility and the amount of adsorptive surface. The significant effect of an adsorptive surface is to only slow the initial rate of taggant increase in the scenario, which is the most important time for most detection schemes.

2.5 L-4412 Taggant

The taggant L-4412 also exhibits a slight degree of adsorption loss as is indicated from the results displayed in Figure 2.5. The adsorption attenuation factor as obtained from the initial slopes is 1.63 ± 0.36 which indicates an initial 40% decrease in taggant concentration due to surface adsorption of L-4412 in the towel/suitcase scenario. As in the case for PFD, this does not necessarily preclude the use of PFD as a vapor taggant, provided this loss can be tolerated.

2.6 DFBP Taggant

A large adsorption loss was obtained for the DFBP taggant as is shown in Figure 2.6. The adsorption attenuation factor was determined to be 4.3 ± 1.0 indicating that approximately 80% of the taggant emitted from the taggant source is being adsorbed on the towel/suitcase surfaces. This adsorption loss is sufficiently great so as to remove DFBP as a potential vapor taggant.

L-4412 ADSORPTION EXPERIMENT SUITCASE/TOWEL ADSORBENT

ADSORPTION ATTENUATION = 1.63 ± 0.36

Figure 2.5

DFBP ADSORPTION EXPERIMENT
SUITCASE/TOWEL ADSORBENT

ADSORPTION ATTENUATION = 4.3 ± 1.0

Figure 2.6

2.7 OFN TAGGANT

OFN was also determined to have an adsorption attenuation (13.2 ± 2.0) sufficiently large probably to preclude its use as a vapor taggant. The results are displayed in Figure 2.7 and indicate that approximately 93% of the OFN is being adsorbed on the suitcase/towel surfaces at the start of the experiment.

2.8 OFT Taggant

Octafluorotoluene (OFT) was also determined to have a large adsorption loss, i.e., an observed adsorption attenuation factor of 13.5 ± 5.8 , as can be seen in Figure 2.8. This large degree of adsorption loss for OFT similarly probably precludes its use as a vapor taggant.

The result for the eight potential vapor taggants are summarized in table 2.2.

Table 2.2. Taggant Adsorption Losses		
Taggant	Adsorption Attenuation Factor	Vapor Taggant Suitability
PDCB	$\sim 1.0 \pm 0.2$	Yes
PMCH	$\sim 1.0 \pm 0.2$	Yes
PDCH	$\sim 1.0 \pm 0.2$	Yes
PFD	1.50 ± 0.21	Yes
L-4412	1.63 ± 0.36	Yes
DFBP	4.3 ± 1.0	questionable
OFN	13.2 ± 2.0	No
OFT	13.5 ± 5.8	No

The results indicate that PDCB, PMCH and PDCH will have a negligible degree of adsorption loss and PFD and L-4412 will have a slight degree of adsorption loss. These five compounds are thus suitable for use as vapor taggants. The other three compounds, OFN, OFT, and DFBP can be eliminated as vapor taggants due to their large scenario surface adsorption loss.

OFN ADSORPTION EXPERIMENT
SUITCASE/TOWEL ADSORBENT

ADSORPTION ATTENUATION = 13.2 ± 2.0

Figure 2.7

OFT ADSORPTION EXPERIMENT SUITCASE/TOWEL BARRIER

Figure 2.8

The suitcase/towel test scenario was considered to be a representative scenario that might introduce adsorption losses. There are other scenarios that might possibly be used deliberately to exploit the surface adsorption of taggants and thus hinder their detection. One such scenario which was examined was a box containing a pound of activated charcoal. Activated charcoal has an extremely large surface area (the term v_m in the expression for the adsorption attenuation) that increases the adsorptive area available to the taggants. All taggants regardless of their volatility will adsorb to some extent with the important criteria being besides volatility, the amount of adsorptive surface area present. A charcoal filled box with a taggant vapor source is an example of an extreme scenario with a large available adsorption area. This adsorption scenario was examined by the same method as described earlier but with only three of the more volatile taggants, i.e., PDCB, PMCH, and PDCH. The results are displayed in Figures 2.9, 2.10 and 2.11, respectively and the adsorption attenuation factors are tabulated in table 2.3.

Table 2.3. Adsorption Attenuation Factors

Taggant	Adsorption Attenuation Factor
PDCB	5.8 ± 0.8
PMCH	14.8 ± 1.6
PDCH	7.1 ± 0.8

There is a significant taggant adsorption loss in this scenario. This indicates a possible countermeasure, i.e. a method to hinder the detection of vapor taggant, by enclosing the tagged explosive with an extremely adsorptive surface.

PDCB ADSORPTION EXPERIMENT CHARCOAL ADSORBENT

ADSORPTION ATTENUATION = 5.77 ± 0.78

Figure 2.9

PMCH ADSORPTION EXPERIMENT CHARCOAL ADSORBENT

ADSORPTION ATTENUATION = 14.8 ± 1.6

Figure 2.10

PDCH ADSORPTION EXPERIMENT CHARCOAL ADSORBENT

ADSORPTION ATTENUATION = 7.1 ± 0.8

Figure 2.11

In conclusion, eight potential vapor taggants have been examined for their adsorption loss in a typical detection scenario. Only five of these taggants, namely, PDCB, PMCH, PDCH, PFD, and L-4412 have negligible or slight adsorption losses which allows their use as vapor taggants. Three taggants, DFBP, OFN, and OFT have substantial adsorption losses and thus are probably unsuitable as vapor taggants. If the available adsorption surface area is increased to an extreme, i.e., presence of a pound of activated charcoal, then even the most volatile taggant will exhibit adsorption losses sufficient to impede its detection significantly.

3.0 Scenario Taggant Concentrations from Barrier Enclosed Vapor Tagged

Explosives: Theoretical Model

The ultimate success of the vapor tagging of explosives is dependent on being able to detect the taggants in various detection scenarios. In order to realistically assess the detectability of tagged explosives, expressions have been derived that will predict the taggant concentrations in the various detection scenarios. The detectability will be dependent on the taggant emission rates from the tagged explosives and other scenario and barrier parameters. The expressions have been kept as general as possible in order to be applicable to the majority of realistic scenarios. The expected vapor taggant concentrations obtained with use of the derived expressions along the detection limits of the various taggant detection methods will quickly allow an assessment of the feasibility of detecting tagged explosives in various scenarios.

Conceptually, the detection of the vapor taggant is formulated as follows:

(1) a tagged explosive with a predetermined taggant emission rate is placed within an enclosure, realistic examples of which are boxes, cans, plastic bags,

suitcases etc., that acts as a barrier to detection of the vapor taggant; (2) this enclosure is then placed within a scenario. By a scenario, it is meant a defined space with a known volume and ventilation rate within which the taggant will be detected. Examples of scenarios are lockers, rooms, buildings, etc. A ventilation rate is included to reflect the constant exchange of air within the scenario with air from outside the scenario; (3) barriers will be considered with respect to their degree of "airtightness". A "tight" barrier will decrease the rate of taggant release into the scenario. It is convenient to compare the airtightness of various barrier enclosures to that of a reference barrier enclosure which is the case when there is no barrier present to enclose the tagged explosive. The no barrier situation will allow the fastest release of taggant into the scenario and thus represents the most detectable scenario. Eventually a steady state taggant concentration will be reached in the scenario regardless of the degree of airtightness of the barrier.

In most instances, the tagged explosive will be prepared and placed in a barrier and then subsequently placed in some scenario. This time delay between the introduction of the tagged explosive into the barrier and the introduction of the barrier into the final scenario will also affect the rate of taggant release into the scenario. This time delay may be on the order of an hour. The time delay will be taken into account in the derived expressions.

The derivation of the equations from the scenario taggant concentrations as a function of the various parameters is described in Section 3.1. Applications of the equations to predict the taggant concentrations inside a briefcase,

in a room containing a briefcase with tagged explosives and in a building or an airplane containing an enclosure with tagged explosives are described in Section 3.2.

3.1 Derivation of the Expressions

Expressions for the scenario taggant concentrations are derived with the following assumptions:

1. The taggant emission rate from the tagged explosive is constant over the time interval from the introduction of the tagged explosive into the barrier to the detection of the taggant in the scenario.
2. The emission of the taggant from the barrier is diffusion controlled, (best described by Fick's first law of diffusion).
3. There is uniform mixing of the taggant with the air in the barrier and in the scenario.
4. The air exchange rate due to ventilation of the scenario is constant with time.

Three separate examples can now be derived.

3.1.1 The No-Barrier or Reference Case

The method for the derivation of an expression for the taggant concentration in a scenario containing no barrier is derived below. Let $V_0(t)$ be the volume of taggant present in the scenario at time (t) , with $V_0(t = 0) = 0$. The volume of taggant $V_0(t)$ is affected by two rate processes, namely, the emission of taggant from the tagged explosive in the scenario (taggant source) and the removal of the taggant from the scenario by the ventilation (a taggant sink).

This is conveniently expressed as a balance between the various rate processes:

$$dV_o(t)/dt = \underbrace{R_{cap}}_{\text{Source}} - \underbrace{f R_{ex}}_{\text{Sink}} \quad (3.1)$$

in which R_{cap} is the taggant emission rate from a tagged explosive present in the scenario (units: liters/min), R_{ex} is the ventilation rate of the scenario and f is defined as the volume fraction of the taggant in the air leaving the scenario:

$$f = V_o(t)/V_{ch} \quad (3.2)$$

and V_{ch} is the volume of the scenario. Substituting for the volume fraction and noting the time independence of R_{cap} and R_{ex} we obtain

$$dV_o(t)/dt = R_{cap} - (R_{ex}/V_{ch})V_o(t) \quad (3.3)$$

with the initial condition

$$V_o(t = 0) = 0. \quad (3.4)$$

The solution of this differential equation is

$$V_o(t) = (R_{cap}V_{ch}/R_{ex}) (1 - \exp [-(R_{ex}/V_{ch})t]). \quad (3.5)$$

This may also be re-expressed in terms of a taggant concentration (units: parts per part) and in terms of a characteristic ventilation time (t_v), where:

$$t_v = V_{ch}/R_{ex}, \quad (3.6)$$

as

$$C_o(t) = (R_{cap}/R_{ex}) [1 - \exp (-t/t_v)] \quad (3.7)$$

in which $C_o(t)$ is the concentration of taggant in the scenario. Two comments are made about this result. First, the characteristic time t_v is simply the time required to completely exchange the total volume of air in the scenario by

ventilation, i.e., the turnover time. This turnover time, t_v , is generally 1/2 to 1 hr for most rooms and buildings as recommended by various building ventilation standards. Secondly, the steady state taggant concentration in the scenario is simply

$$C_o(t \rightarrow \infty) = R_{cap}/R_{ex} \quad (3.8)$$

i.e., the taggant emission rate divided by the scenario ventilation rate.

Thus for the no barrier case, we see that in one turnover time (t_v), the taggant concentration in the scenario is approximately 63% of its steady state value.

3.1.2 The Barrier Case

The method for the derivation of expressions for the taggant concentration in a scenario with the tagged explosives enclosed in a barrier is similar to the previous example. In this case, define two taggant volumes; $V_{en}(t)$, the volume of taggant inside the barrier and $V(t)$, the volume of the taggant inside the scenario. Similarly we can express the balances for the various rates in the barrier and scenario respectively as:

$$dV_{cn}(t)/dt = \underbrace{R_{cap}}_{\text{source}} - \underbrace{R_{en}(t)}_{\text{sink}} \quad (3.9)$$

and

$$dV(t)/dt = \underbrace{R_{en}(t)}_{\text{source}} - \underbrace{f R_{ex}}_{\text{sink}} \quad (3.10)$$

in which $R_{en}(t)$ is the taggant emission rate from the barrier into the scenario and f is the volume fraction as defined earlier. Substituting for the volume

fraction and noting which rates are time independent, we obtain

$$dV_{en}(t)/dt = R_{cap} - R_{en}(t) \quad (3.11)$$

$$dV(t)/dt = R_{en}(t) - (R_{ex}/V_{ch})V(t) \quad (3.12)$$

Now using the assumption that the taggant emission rate from the barrier is diffusion controlled and best described by Fick's first law, we obtain

$$R_{en}(t) = k (V_{en}(t)/V_{en} - V(t)/V_{ch}) \quad (3.13)$$

in which V_{en} is the volume of the barrier and k is a constant dependent only on the barrier. This barrier constant, k , can be thought of as an "air exchange" rate between the air in the barrier and the air surrounding the barrier. This air exchange rate, k , is due solely to diffusion of air in and out of the barrier through any minute openings in the barrier. This can be made more apparent by considering the example when the air surrounding the barrier has no taggant concentration, i.e., $V(t) = 0$; the taggant emission rate from the barrier becomes

$$R_{en}(t) = k V_{en}(t)/V_{en} \quad , \quad (3.13a)$$

i.e., the product of the air exchange rate, k , and the taggant concentration in the air. When there is a taggant concentration present in the scenario, equation (3.13) becomes appropriate. The units for k are liters/minute.

Substituting the expression for $R_{en}(t)$ into the two mass balance equations we have:

$$dV_{en}(t)/dt = R_{cap} - (k/V_{en}) V_{en}(t) + (k/V_{ch}) V(t) \quad (3.14)$$

and

$$dV(t)/dt = (k/V_{en}) V_{en}(t) - (k/V_{ch}) V(t) - (R_{ex}/V_{ch}) V(t) \quad (3.15)$$

The associated initial conditions are

$$V_{en}(t = 0) = 0 \quad (3.16)$$

and

$$V(t = 0) = 0 \quad (3.17)$$

i.e., the taggant concentrations in the barrier and scenario are zero at the time of introduction of the explosive into the scenario and the barrier.

The solution of these coupled differential equations is given in Appendix B and the solution for $V(t)$ is:

$$V(t) = \frac{R_{cap} V_{ch}}{R_{ex}} \left[1 - \frac{r_2 \exp[-r_1 t] - r_1 \exp[-r_2 t]}{r_2 - r_1} \right] \quad (3.18)$$

in which

$$\begin{aligned} r_1 &= \frac{R_{ex}}{V_{ch}} \left[(\beta + \beta/\gamma + 1) + ([\beta + \beta/\gamma + 1]^2 - 4\beta/\gamma)^{1/2} \right] / 2 \\ r_2 &= \frac{R_{ex}}{V_{ch}} \left[(\beta + \beta/\gamma + 1) - ([\beta + \beta/\gamma + 1]^2 - 4\beta/\gamma)^{1/2} \right] / 2 \end{aligned} \quad (3.19)$$

and $\beta = k/R_{ex}$, the ratio of the barrier air exchange rate to the scenario ventilation rate and $\gamma = V_{en}/V_{ch}$, the ratio of the barrier volume to the scenario volume. The taggant concentration inside the scenario is simply

$$C(t) = V(t)/V_{ch} \quad (3.20)$$

Several important limits of $C(t)$ can be derived. As $t \rightarrow \infty$, the taggant concentration in the scenario approaches the steady state concentration:

$$C(t \rightarrow \infty) = R_{cap}/R_{ex} \quad (3.21)$$

a result identical to that for the no barrier case. Thus the steady state concentration is independent of the degree of barrier airtightness. The effect

of a barrier is to attenuate the rate of taggant release into the scenario. This effect is dependent on the value of k , the barrier parameter, with smaller values of k corresponding to a more airtight barrier.

As mentioned earlier, the barrier parameter or air exchange rate, k , is related in some way to the size of the air leaks of a barrier. Two visualizations of the barrier parameter are available. The first interpretation is a barrier consisting of holes, cracks or microcracks. The barrier parameter can then be expressed as

$$k = AD/L \quad (3.22)$$

in which A is the total area of the cracks in the barrier, L is an average depth of the crack and D is the taggant-air diffusion constant. This barrier parameter visualization is consistent with barriers such as boxes, briefcases, pipebombs, etc. In this visualization it can be seen that the barrier parameter is nearly independent with respect to the taggant because D , the taggant-air diffusion constant, differs very slightly from taggant to taggant.

The other visualization is that of a barrier in which the taggant permeates through the barrier. In this instance the barrier parameter can be expressed as

$$k = QA/L \quad (3.23)$$

in which A is the total area of the barrier, L the average thickness of the barrier, and Q is the permeability coefficient of the taggant through the barrier expressed in appropriate units. This visualization is consistent with barriers such as extremely well sealed plastic bags, various waxes, and other material which coat the barrier. Also, in this visualization there should be little dependence of k on the taggant chemical due to the near constancy of Q with respect to differing taggants.

These expressions for k (eq. 3.22 and 3.23) are appropriate for obtaining an order of magnitude value of k for various barriers. It is more convenient, however, to determine k experimentally for a series of barriers with the use of the derived expressions and an experimentally measured taggant concentration in a scenario from a tagged source inserted in a barrier.

Another important point with regard to this example is that we have assumed both the barrier and scenario taggant concentrations are zero at the time of introduction ($t = 0$) of the barrier into the scenario (eq. 3.16 and 3.17). In most realistic scenarios the tagged explosive will be placed in the barrier and subsequently placed in the scenario, consequently, there may be several hours delay between placing the tagged explosive in the barrier and placing the barrier in the scenario. Thus a more realistic initial condition for $V_{en}(t)$ is

$$V_{en}(t = 0) = V_{en}^* \quad (3.24)$$

where the concentration of taggant in the enclosure is some non-zero value. The situation where both concentrations are zero at $t = 0$ is convenient to analyze and is experimentally realizable in the laboratory for the determination of the barrier parameter for the various barriers. The situation with

$$V_{en}(t = 0) = V_{en}^* \quad (3.25)$$

will be treated in the next section (3.13) where V_{en}^* is in the taggant concentration inside the barrier when the barrier enclosed explosive is placed in the scenario.

3.1.3 Barrier with Time Delay Case

The more realistic situation of a non-zero initial taggant concentration in the barrier will be considered here. The coupled differential equations for

the taggant volume in the scenario are the same; however, an additional term, the initial taggant volume inside the barrier, is added to the differential equation for $V_{en}(t)$. An estimation of the initial taggant concentration in the barrier can be derived from the first of the coupled differential equations. Assume $V(t) = 0$ for all times, i.e., the barrier enclosure is in an environment in which the taggant concentration is effectively zero, then the concentration of taggant inside the barrier is given by:

$$C_{en}(t) = V_{en}(t)/V_{en} = (R_{cap}/k)[1 - \exp(-kt/V_{en})] \quad (3.26)$$

Thus, an appropriate initial taggant concentration is

$$V_{en}^* = V_{en}(t = 0) = V_{en}C_{en}(t = t_{delay}) \quad (3.27)$$

in which t_{delay} is the time between the placing of the tagged explosive in the barrier and the placing of the barrier in the scenario.

The coupled differential equations can now be solved with the inclusion of the initial barrier taggant volume. The explicit solution is given in Appendix B as:

$$V(t) = \frac{R_{cap}V_{ch}}{R_{ex}} \left[1 - \frac{r_2 \exp(-r_1 t) - r_1 \exp(-r_2 t)}{r_2 - r_1} \right] + k C_{en}(t_{delay}) \left[\frac{\exp(-r_1 t) - \exp(-r_2 t)}{r_2 - r_1} \right] \quad (3.28)$$

The taggant concentration in the scenario, $V(t)/V_{ch}$, with time delay, is composed of two terms; the taggant concentration in the scenario without time delay (the case considered in Section 3.12) and an additional term. This additional term is positive for all times. Thus the effect of a time delay or, equivalently, an initial taggant concentration inside the barrier

is to increase the rate of taggant release into the scenario. Note that this additional term is proportional to the derivative of the first term, i.e., this additional increase is greatest when the taggant concentration (for the no time delay case) is rapidly increasing, i.e., at a time when the barrier has just been placed in the scenario. All of these physical conclusions are reasonable because the emission rate of taggant from the barrier enclosure is dependent on the concentration inside the barrier enclosure; thus the rate of taggant release into the scenario should be increased.

The taggant concentration in the scenario for this case has the same steady-state value as found for the other cases

$$C(t \rightarrow \infty) = V(t \rightarrow \infty)/V_{ch} = R_{cap}/R_{ex} \quad (3.29)$$

3.2 Application and Discussion of the Equations

The expressions for the scenario taggant concentrations as derived in the previous section will be discussed generally and then applied to various scenarios.

3.2.1 No Barrier Case

The scenario taggant concentration is given by

$$C_o(t) = (R_{cap}/R_{ex}) [1 - \exp(-t/t_v)] \quad (3.30)$$

in which $t_v = V_{ch}/R_{ex}$. The approach to the steady-state concentration of R_{cap}/R_{ex} is exponential in nature. The quantity t_v is simply the turnover time of the scenario: the time required to completely exchange the air in the scenario with fresh air.

3.2.2 Barrier Case

An estimation of k , the barrier parameter, has to be made before any further discussion can take place. The following ranges shall be defined for the barrier parameter, k , as based on the experimental evidence

<u>Degree of Barrier Severity</u>	<u>Barrier Parameter k (L/min)</u>
Severe	2×10^{-4}
Moderate	2×10^{-2}
Slight	2

A physical interpretation for these barrier parameters can be derived from the expression

$$k = AD/L$$

defined earlier. We obtain the following total area of cracks in the barrier for the various degrees of barrier severity. Assuming the taggant-air diffusion constant to be approximately $5 \text{ cm}^2/\text{min}$ and the cracks, to be 1 mm in depth the relationship would be

<u>Degree</u>	<u>Total Crack Area</u>
Severe	0.04 cm^2
Moderate	0.4 cm^2
Slight	40 cm^2

An example of a severe microcrack barrier is a 6-inch paint can with a 1 micron ($1 \times 10^{-6} \text{ m}$) crack about the circumference of the lid. In this instance, the crack area is 0.048 cm^2 . An increase in the crack depth will correspondingly decrease the total crack areas for equal degrees of barrier severity.

An estimation of the barrier parameter for the permeation mode can also be made. This again corresponds to a barrier enclosure such as a well-sealed plastic bag, in this mode:

$$k = QA/L$$

as defined earlier. Assuming a permeation coefficient of 0.1×10^{-10} cc(STP) cm/sec-cm² Δ torr such as for polyethylene with a thickness of 2 mil, we obtain $k = 1 \times 10^{-10}$ L/min, a value several orders of magnitude lower than for a severe microcrack barrier. In most instances, however, small cracks in the seal of the plastic bag and pinhole leaks will be the predominant mode of taggant loss from plastic bags. For example, a single pinhole with a diameter of 0.16 mm in a polyethylene bag will give a barrier parameter of 2×10^{-4} L/min, several orders of magnitude greater than the barrier parameter that results from permeation alone.

The effect of a barrier on the scenario taggant concentration in the no time delay case is displayed in Figure 3.1, a plot of the normalized scenario taggant concentration (normalized with respect to the steady state concentration, R_{cap}/R_{ex}) versus time. The various curves correspond to differing values of the barrier parameter k , expressed in the figure as the dimensionless parameter $\beta = k/R_{ex}$, with $\beta = \infty$ corresponding to the no barrier situation and decreasing β corresponding to an increased airtightness of the barrier. As expected, the effect of the barrier is to decrease the rate of taggant release into the scenario from the barrier enclosed explosive. Note that β has to be less than γ before there is any noticeable effect of the barrier on the rate of taggant release into the scenario. This means when $k/V_{en} < R_{ex}/V_{ch}$, i.e., the turnover time for the air in the scenario is greater than the turnover time for the air in the barrier, then the taggant will be removed at a rate from the scenario faster than the barrier can release taggant. Consequently the rate of taggant release in the scenario will be attenuated.

Figure 3.1

There is also a dependence of the scenario taggant concentration on γ , the ratio of the volume of the barrier enclosure to the volume of the scenario ($\gamma = V_{en}/V_{ch}$). Figure 3.2 represents the situation where the barrier enclosure volume has been decreased by a factor of 10 compared to that in Figure 3.1. It can be seen in comparing Figures 1 and 2 that for equivalent values of the barrier parameter the attenuation in the taggant emission rate from the barrier is less with the smaller barrier enclosure volume. In the limit, as β goes to zero, i.e., the barrier becoming more airtight, a decrease in barrier enclosure volume by a factor of 10, will increase the rate of taggant release into the scenario by a factor of 10. This is physically reasonable because the taggant emission rate from the barrier enclosure is dependent on the taggant concentration inside the enclosure which will increase with decreasing barrier enclosure volume. In the other limit, that of no barrier, the volume of the barrier is not consequential.

Several other observations for the no time delay barrier case can be made in the limit of a severe barrier. In this limit, $\gamma > \beta$, or equivalently $k/V_{en} < R_{ex}/V_{ch}$, then

- a. The taggant emission rate from the barrier enclosure is more or less constant after an initial period (normalized taggant concentration more than 0.1). The scenario taggant concentration increases linearly with time. However, the taggant emission rate during this initial period is approximately linear with time, i.e., the scenario taggant concentration increases quadratically with time. This can best be seen in Figure 3.3, an expanded version of Figure 3.1.

Figure 3.2

Figure 3.3

- b. The taggant emission rate after the initial period is approximately linearly proportional to the barrier parameter k , i.e., a factor of 2 decrease in k will decrease the emission rate from the barrier by a factor of 2. This again can be seen in comparing the slopes in Figure 3.3.

These observations lead to the conclusion that for a barrier scenario with no time delay; namely, that in the limit of a severe barrier, the taggant emission rate from the barrier is proportional to $kV_{ch}/R_{ex}V_{en}$.

Another interesting observation is that the taggant scenario concentration always approaches the steady state concentration, R_{cap}/R_{ex} , regardless of the degree of airtightness of the barrier. The principal effect of a barrier is to delay the approach of the taggant concentration towards its steady state concentration as illustrated in Figure 3.4. The more airtight a barrier is, the greater the delay in the approach of the taggant concentration towards its steady state concentration. This is consonant with the idea of a lag time before the appearance of taggant concentration in the scenario.

3.3 Specific Examples

3.3.1 Taggant Concentrations Inside a Briefcase

This scenario is relevant in sampling of briefcases, suitcases etc. The assumption here is that a tagged explosive has been placed within a luggage item and that the luggage is not exposed for any length of time to any defined volume in which the taggant concentration can accumulate, i.e., the briefcase is constantly in an environment that is well ventilated. The only assumed mechanism for the loss of taggant vapors from the briefcase is diffusion through its

Figure 3.4

seams. The relevant equation for the taggant concentration inside the briefcase is then equation (3.26). Table 3.1 gives the results of the calculation for a standard size briefcase for three levels of airtightness.

Table 3.1
Taggant Concentration Inside a Briefcase
having Various Degrees of Barrier Airtightness

Time Elapsed	Taggant Concentration, parts per billion		
	Severe Barrier $k = 2 \times 10^{-4}$ L/min	Moderate Barrier $k = 2 \times 10^{-2}$ L/min	Slight Barrier $k = 2$ L/min
15 min	1.32	1.31	0.46
30 min	2.65	2.58	0.50
1 hr	5.29	5.02	0.50
2 hr	10.6	9.54	0.50
5 hr	26.4	20.6	0.50
10 hr	52.7	32.7	0.50
1 day	125	46.1	0.50
2 days	248	49.1	0.50
$R_{cap} = 1 \times 10^{-9}$ L/min			
$V_{en} = 11.33$ liters			

The results show that the taggant concentrations inside a briefcase are at least in the ppb range. Thus, if the taggant vapors are diluted by a factor of 1000 by some sort of briefcase/suitcase sampling scheme, it is possible to detect the taggant vapors with a real time continuous instrument that has a taggant lower limit of detectability of 1 ppt. Naturally, the dilution factor will be greater for a severe barrier enclosure than for a slight one. This calculation neglects the effects of taggant adsorption onto material that might be present in the briefcase, but this can be neglected if the taggants are sufficiently volatile.

Experimental verification of this is discussed in another chapter and is fully described in an experiment using the U.S. Customs baggage examiner in conjunction with the Brookhaven continuous electron capture detector (CECD)^{3,4}.

3.3.2 Volume Sampling (A moderately sized room)

A moderately sized room (10 x 20 x 8 ft or 1600 ft³) has been chosen as a volume sampling scenario. The scenario is described as a tagged explosive contained within a briefcase barrier which is placed into the room. The calculation is performed assuming various time delays ranging from 0 to 24 hours between the introduction of the tagged explosive into the briefcase and the introduction of the briefcase into the scenario. The calculation is performed with the use of equation 3.28, the barrier with time delay equation, and equation 3.26 for the taggant concentration inside the briefcase. Various degrees of barrier airtightness and a ventilation rate corresponding to a complete turnover time of 30 minutes with fresh air are assumed. The calculated results for a severe barrier ($k = 2 \times 10^{-4}$ L/min) containing tagged explosives with an emission rate of 1 nL per min are given in Table 3.2. The columns in Table 3.2 are described as follows: the first column is the length of time the briefcase enclosed tagged explosive has been in the detection scenario, i.e., the room; the second column is the room taggant concentration assuming no barrier enclosed the tagged explosive; the third column is the room taggant concentration with the briefcase enclosed tagged explosive assuming no time delay between placing the tagged explosive into the briefcase and placing the briefcase into the scenario. The remaining columns are for various time delays from 1 hour up to 24 hours. A typical time delay is 1/2 to 1 hour. As can be seen in the table, all of the

Table 3.2
Scenario Taggant Concentrations in a
Moderately Sized Room with a Severe Barrier

Time after Introduction of Barrier into Scenario	Taggant Concentration, $\text{pp}10^{12}$ (ppt)						
	No Barrier	Barrier With No Time Delay	Barrier with Time Delay				
			1 hr	2 hr	4 hr	10 hr	24 hr
15 min	0.260	.0000374	.000313	.000589	.00113	.00279	.00658
30 min	0.418	.000129	.000572	.00102	.00189	.00456	.0106
1 hr	0.572	.000398	.00100	.00161	.00282	.00646	.0148
2 hr	0.650	.00106	.00174	.00247	.00386	.00792	.0162
4 hr	0.662	.00245	.00315	.00385	.00525	.00944	.0191
10 hr	0.662	.00663	.00732	.00802	.00941	.0136	.0231
1 day	0.662	.0163	.0169	.0176	.0190	.0231	.0325
2 days	0.662	.0325	.0332	.0338	.0352	.0392	.0483

Taggant Concentration
inside the Barrier at
the Time of Introduction
into the Scenario

0	5290	10,600	21,100	52,700	125,500
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Emission Rate of Tagged Cap = 1×10^{-9} L/min
Volume of the Scenario = 1600 ft^3
Volume of the Barrier Enclosure = 0.4 ft^3
Barrier Parameter = 2×10^{-4} L/min
Turnover Time = 30 min
Ventilation Rate = $53.3 \text{ cu. ft}^3/\text{min}$

calculated taggant concentrations require utilization of a concentrating taggant detection system with a lower limit of detection greater than parts per 10^{17} . The greater the time delay the faster the initial approach to the taggant steady state concentrations.

Table 3.3 presents the results for the same briefcase scenario assuming moderate airtightness with all other conditions the same as considered in Table 3.2. In this instance, the scenario taggant concentrations are almost in the range of the real-time taggant detectors, such as the Brookhaven CECD, i.e., a part per 10^{12} . This would be especially so if the taggant emission rate from the cap were a factor of 2 or 3 higher, i.e., 2 or 3 nL/min. The scenario taggant concentrations are simply proportional to the taggant emission rates of the tagged explosives.

TABLE 3.3

Scenario Taggant Concentrations in a
Moderately Sized Room with a Moderate Barrier

Time after Introduction of Barrier Into Scenario	Taggant Concentration, pp 10^{12} (ppt)						
	No Barrier	Barrier With No Time Delay	Barrier with Time Delay				
			1 hr	2 hr	4 hr	10 hr	24 hr
15 min	0.260	.00370	.0295	.0527	.0924	.172	0.240
30 min	0.418	.0127	.0535	.0902	.153	.278	0.387
1 hr	0.572	.0382	.0919	.140	.223	.387	0.531
2 hr	0.650	.910	.147	.196	.282	.458	0.607
4 hr	0.662	.204	.250	.291	.362	.503	0.626
10 hr	0.662	.420	.444	.466	.504	.578	0.643
1 day	0.662	.607	.613	.618	.626	.643	0.658
2 days	0.662	.658	.658	.659	.659	.661	0.662

Taggant Concentration
inside the Barrier at
Time of Intro-
duction into the
Scenario

0	5020	9530	17,300	32,700	46,100
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Emission Rate of Tagged Cap = 1×10^{-9} L/min
Volume of the Scenario = 1600 ft^3
Volume of the Barrier Enclosure = 0.4 ft^3
Barrier Parameter = 2×10^{-2} L/min
Turnover Time = 30 minutes
Ventilation Rate = $53.3 \text{ ft}^3/\text{min}$

Table 3.4 contains the results for the same briefcase with a slight airtightness again assuming all other conditions are the same as in Tables 3.2 and 3.3. The taggant concentrations are nearly in the range for real-time continuous taggant detector. In this instance the taggant release rate is essentially as though there were no barrier present at all, especially when the time delay is greater than 1 hour.

TABLE 3.4

Scenario Taggant Concentrations in a
Moderately Sized Room with a Slight Barrier

Time after Introduction of Barrier into the Scenario	Taggant Concentration, pp 10 ¹² (ppt)				
	No Barrier	Barrier with No Time Delay	Barrier with Time Delay		
			1 hr	2 hr	4 hr
15 min	.260	.178	.260	.260	.260
30 min	.418	.363	.418	.418	.418
1 hr	.572	.552	.572	.572	.572
2 hr	.650	.647	.650	.650	.650
4 hr	.662	.662	.662	.662	.662
Barrier Taggant Concentration at Time of Introduction into the Scenario		0	500	500	500

Emission Rate of Tagged Cap = 1×10^{-9} L/min
Volume of the Scenario = 1600 ft³
Volume of the Barrier Enclosure = 0.4 ft³
Barrier Parameter = 2 L/min
Turnover Time = 30 minutes
Ventilation Rate = 53.3 ft³/min

In all three instances, the taggant concentrations in the scenario will approach the steady-state value of 0.66 ppt given sufficient time. This steady state concentration, $C(\infty)$, is equal to R_{cap}/R_{ex} . In all detection scenarios,

although it is not possible to change R_{cap} , the taggant emission rate from the explosive, it is possible to change R_{ex} , the ventilation rate of the scenario. Thus, a very good detection strategy is to shut off the ventilation system in the area where detection of vapor tagged explosives is being attempted. The scenario taggant concentration will then be higher than those given in the examples because the taggant emission rate from the barrier enclosure will approach a constant rate when the ventilation of the scenario is stopped.

3.3.3 Volume Sampling (A DC-8 Aircraft)

Another volume sampling scenario of interest is the detection of a tagged explosive that has been placed in an aircraft. The calculation for this scenario is performed for a tagged explosive (with a taggant emission rate of 1 nL/min) placed within a briefcase-sized barrier with varying degrees of barrier airtightness. Table 3.5 contains the results for a barrier with an airtightness of the order of a pipebomb. In almost all examples of time delay and time after placing the explosive on the aircraft, the taggant concentrations are of the order of <.001 ppt. However, the ambient taggant concentration is 0.03 ppt for PDCH. If the taggant emission rate were increased by two orders of magnitude then it would be conceivable to detect the explosives in this scenario with a concentrating off-line discrete sample taggant detection system.

The results for a barrier of moderate airtightness (a very tightly sealed box, etc.) is given in Table 3.6. In this case it is possible to detect the explosives with a concentrating detection system. If the taggant emission rate was increased by two orders of magnitude, it would then be possible to detect the taggant with a real-time detection instrument such as the Brookhaven CECD.

TABLE 3.5

Taggant Concentrations in a DC-8 from a
Tagged Explosive Enclosed in a Severe Barrier

Time after Introduction of Barrier into Scenario	Taggant Concentration, parts per part						
	No Barrier	Barrier With No Time Delay	Barrier with Time Delay				
			1 hr	2 hr	4 hr	10 hr	24 hr
5 min	1.47(-14)	7.03(-19)	1.63(-17)	3.19(-17)	6.27(-17)	1.56(-16)	3.70(-16)
10 min	2.33(-14)	2.41(-18)	2.70(-17)	5.17(-17)	1.01(-16)	2.47(-16)	5.86(-16)
15 min	2.83(-14)	4.70(-18)	3.46(-17)	6.46(-17)	1.24(-16)	3.02(-16)	7.14(-16)
30 min	3.39(-14)	1.31(-17)	4.90(-17)	8.50(-17)	1.56(-16)	3.70(-16)	8.64(-16)
1 hr	3.52(-14)	3.16(-17)	6.88(-17)	1.06(-16)	1.80(-16)	4.03(-16)	9.15(-15)
2 hr	3.57(-14)	6.89(-17)	1.06(-16)	1.44(-16)	2.18(-16)	4.40(-16)	9.54(-16)
5 hr	3.53(-14)	1.80(-16)	2.17(-16)	2.54(-16)	3.28(-16)	5.50(-16)	1.06(-15)
12 hr	3.53(-14)	4.41(-16)	4.78(-16)	5.15(-16)	5.88(-16)	8.08(-16)	1.32(-15)
Barrier Taggant Concentration at Time of Introduction into the Scenario		0	5.29(- 9)	10.6 (- 9)	21.1 (- 9)	52.7 (- 9)	12.5 (- 8)

Taggant Emission Rate = 1×10^{-9} L/min
Volume of the DC-8 = 9,300 ft³
Volume of the Barrier Enclosure = 0.4 ft³
Barrier Parameter = 2×10^{-4} L/min
Turnover Time = 9.3 min
Ventilation Rate = 1000 ft³/min
7.03(-19) = 7.03×10^{-19}

TABLE 3.6

Taggant Concentrations in a DC-8 from a
Tagged Explosive Enclosed in a Moderate Barrier

Time after Introduction of Barrier into Scenario	Taggant Concentration, parts per part						
	No Barrier	Barrier With No Time Delay	Barrier with Time Delay				
			1 hr	2 hr	4 hr	10 hr	24 hr
5 min	1.47(-14)	7.03(-19)	1.54(-15)	2.85(-15)	5.12(-15)	9.62(-15)	1.35(-14)
10 min	2.33(-14)	2.39(-16)	2.55(-15)	4.62(-15)	8.20(-15)	1.53(-14)	2.14(-14)
15 min	2.83(-14)	4.66(-16)	3.26(-15)	5.76(-15)	1.01(-15)	1.86(-14)	2.61(-14)
30 min	3.39(-14)	1.29(-15)	4.56(-15)	4.50(-15)	1.26(-14)	2.26(-14)	3.13(-14)
1 hr	3.52(-14)	3.02(-15)	6.26(-15)	9.14(-15)	1.42(-14)	2.41(-14)	3.28(-14)
2 hr	3.57(-14)	6.25(-15)	9.17(-15)	1.18(-14)	1.63(-14)	2.52(-14)	3.30(-14)
5 hr	3.53(-14)	1.42(-14)	1.63(-14)	1.82(-14)	2.15(-14)	2.80(-14)	3.37(-14)
12 hr	3.53(-14)	2.52(-14)	2.67(-14)	2.71(-14)	2.87(-14)	3.18(-14)	3.45(-14)
Barrier Taggant Concentration at Time of Introduction into the Scenario		0	5.02(- 9)	9.53(- 9)	1.73(- 8)	3.27(- 8)	4.61(- 8)

Taggant Emission Rate = 1×10^{-9} L/min
Volume of the DC-8 = 9,300 ft³
Volume of the Barrier Enclosure = 0.4 ft³
Barrier Parameter = 2×10^{-2} L/min
Turnover Time = 9.3 min
Ventilation Rate = 1000 ft³/min
7.03(-19) = 7.03×10^{-17}

The results for a slight barrier (briefcases, suitcases, etc.) are presented in Table 3.7. Here the barrier provides a negligible attenuation on the taggant emission rate, and it is possible to detect the tagged explosive within 5 min with the use of a vapor taggant concentrating instrument.

As in the other volume detection scenarios, if the ventilation rate could be reduced then it would be possible to detect the taggant because the taggant concentrations are increased. An experimental verification of these calculated results will be mentioned in Section 4.0. The airplane detection taggant concentration profiles for a DC-9 and a Boeing 727 aircraft have been measured in another work^{5,6}.

TABLE 3.7

Taggant Concentrations in a DC-8 from a
Tagged Explosive Enclosed in a Slight Barrier

Time after Introduction of Barrier into the Scenario	Taggant Concentration, parts per part				
	No Barrier	Barrier With No Time Delay	Barrier with Time Delay		
			15 min	30 min	1 hr
5 min	1.47(-14)	5.30(-15)	1.39(-14)	1.47(-14)	1.47(-14)
10 min	2.33(-14)	1.39(-14)	2.25(-14)	2.33(-14)	2.33(-14)
15 min	2.83(-14)	2.12(-14)	2.77(-14)	2.83(-14)	2.83(-14)
30 min	3.39(-14)	3.20(-14)	3.38(-14)	3.39(-14)	3.39(-14)
1 hr	3.52(-14)	3.52(-14)	3.52(-14)	3.52(-14)	3.52(-14)
2 hr	3.53(-14)	3.53(-14)	3.53(-14)	3.53(-14)	3.53(-14)

Barrier Taggant Concentration at Time of Introduction into the Scenario

0	0.46×10^{-9}	0.50×10^{-10}	0.50×10^{-10}
---	-----------------------	------------------------	------------------------

Taggant Emission Rate = 1×10^{-9} L/min
Volume of the DC-8 = $9,300 \text{ ft}^3$
Volume of the Barrier Enclosure = 0.4 ft^3
Barrier Parameter = 2 L/min
Turnover Time = 9.3 min
Ventilation Rate = $1000 \text{ ft}^3/\text{min}$
 $5.30(-15) = 5.03 \times 10^{-15}$

3.4 Conclusions

Several general and specific conclusions can be made

1. The scenario taggant concentrations will always approach a steady state concentration of R_{cap}/R_{ex} , the taggant emission rate from the tagged explosive divided by the ventilation rate of the scenario, regardless of any barrier. The effect of a barrier is to delay the approach to this steady state concentration. The more severe the barrier, the longer this delay.
2. The effect of a time interval between the introduction of the tagged explosive into the barrier enclosure and placing the barrier enclosure into the scenario, is to hasten the initial approach to the steady state concentration. The longer the time interval, the greater is the rate of initial increase in the scenario taggant concentration.
3. The taggant concentration within briefcases/suitcases from a 1 nanoliter per minute tagged explosive is of the order of ppb for almost all degrees of briefcase/suitcase barrier airtightness. This will allow real-time continuous detection of the taggants with a sampling system having a dilution factor up to 1000.
4. The taggant concentrations attained in a moderately sized room 15 min following introduction of a severe barrier containing a taggant source of emission rate, 1 nanoliter per minute placed in it 1 hour earlier, is sufficient to make possible detection by a concentrating detection scheme. A moderate barrier will almost allow real-time continuous detection under the same circumstances.
5. The taggant concentrations attained in a DC-8 will allow the detection of a 1 nL/min emission-rate tagged explosive contained in a slight to moderate airtightness barrier within 15 minutes, using a vapor concentrating taggant detection system.

4.0 Scenario Taggant Concentration from Barrier Enclosed Vapor Tagged

Explosives: Experimental Results

The rate of taggant release from a barrier enclosed tagged explosive is dependent on two parameters as described in Section 3.0. Specifically, these are β , the ratio of the barrier constant k to the scenario ventilation rate (R_{ex}), and γ the ratio of the barrier enclosed volume (V_{en}) to the volume of the scenario (V_{ch}). Of these, only k , the barrier constant, is unknown for various common barriers, e.g., suitcases, boxes, plastic bags, etc., in which tagged explosives might be enclosed. An order of magnitude estimate of the barrier constant can be made with the use of equations (3.22) and (3.23) which are derived for the microcrack and permeation mechanisms of taggant emission through a barrier. However, the purpose of this chapter is to report on an experimental determination of the barrier constants, k , for a range of various barriers, specifically, a suitcase, an attache case, an average size box containing styrofoam chip filler, a 1 gal paint can, a heat sealed plastic bag, and a zip-lock plastic bag. The barriers were chosen as average representations of barriers that might be used to conceal bombs.

The experimental procedure was designed to use equation (3.18) in the analysis of the experimental results. This was accomplished by enclosing a constant source of vapor taggant in one of the barriers that in turn was placed in a scenario, a 422 liter chamber, with a controlled ventilation rate. The scenario taggant concentration was then recorded as a function of the elapsed time. The constant source of vapor taggant was a tagged blasting cap with a predetermined taggant emission rate. The tagged caps were old enough, i.e., several months since their preparation, so as to have a nearly constant emission rate over the 2 to 3 day experimental period. Before the start of each experiment, it was ascertained that there was no initial taggant concentration inside

either the scenario or the barrier to ensure that the conditions for which equation (3.18) was derived would be satisfied. With this procedure, the barrier constant for each barrier can be extracted from the results of the experiment.

The vapor taggants used, PDCB, PMCH, and PDCH, were those which would have a negligible barrier adsorption loss (see Section 2.0). Barrier adsorption loss would unnecessarily complicate the experimental results. In each experiment the three taggant sources were enclosed in the barrier to be tested. The scenario ventilation exhaust was sampled periodically for the three taggants and the scenario taggant concentrations determined chromatographically. For comparison, the resulting scenario taggant concentrations for each barrier enclosed taggant source were compared against the no barrier situation. The time dependence of the scenario taggant concentration for the no barrier experiment is, as has been derived in the theoretical section (equation 3.7), an exponential dilution

$$C(t) = C(\infty)[1 - \exp(-t/t_v)] \quad (4.1)$$

in which

$$C(\infty) = R_{cap}/R_{ex} \quad (2.2)$$

and

$$t_v = V_{ch}/R_{ex} \quad (3.6)$$

$C(\infty)$ is the steady state taggant scenario concentration and t_v the chamber turnover time. A comparison between the barrier and no barrier parts of the experiment provided an immediate indication of whether there was any significant barrier effect for each tested barrier.

The experimental results were normalized in the same manner as the results of the adsorption experiment. The scenario taggant concentrations, $C(t)$, were normalized by dividing by the taggant steady state concentration, $C(\infty)$, and the elapsed time was normalized by dividing by the scenario turnover time t_v . These normalizations allowed direct comparison of the results between the various barriers.

The experimental results for each barrier will be discussed individually as follows.

4.1 A Box Filled with Styrofoam Packing

Several vapor tagged blasting caps were placed inside a 7" x 9" x 12" box filled with a polystyrene chip packing material. The box barrier was then sealed securely with sealing tape and placed inside the scenario chamber. The blasting caps provided the source of PDCB, PMCH, and PDCH vapor taggants. The results are displayed in Figures 4.1 through 4.3 for each of the three taggants. As is evidenced by the coincidence of the no-barrier and barrier results, there is a negligible barrier effect exerted by the styrofoam filled box.

The barrier constant, k , for this barrier is very large because this is a negligible barrier, i.e. the box is not at all air tight. The precision of the experimental results does not allow a numerical value for the barrier constant to be extracted. Therefore, k can be said simply to be large, i.e. infinite, which signifies that this barrier is equivalent to the no-barrier situation, a conclusion clearly indicated in Figures 1 through 3.

4.2 Suitcase

A zippered cloth suitcase (22 x 8 x 16 in.) was examined in a similar manner. This is the same suitcase which had been used in the adsorption studies. As is seen in results presented in Figures 4.4 through 4.6, the suitcase has a negligible barrier effect for the three taggants. The results also show higher taggant concentration for all three taggants for the barrier situation when compared to the no-barrier situation, even though this is theoretically impossible. This is due, as in similar instances in the adsorption experiments, to a ± 20 percent difference in the chamber ventilation rate between the no barrier and

Figure 4.1

Figure 4.2

Figure 4.3

Figure 4.4

Figure 4.5

Figure 4.6

barrier parts of the experiment. Although it was attempted to use the same ventilation rate in both parts of the experiments, the ventilation rate changed throughout the experiment because of insufficient flow regulation over the 2 to 3 day period required for the experiment. A decrease in the chamber ventilation rate proportionally increased the chamber taggant concentrations as was the case for the barrier situation in this experiment.

Nonetheless, the results indicate a negligible barrier effect exerted by the suitcase barrier. As in the sealed box barrier, the barrier constant for the suitcase is very large and can be assigned a value of infinity.

4.3 Heat Sealed Polyethylene Bag

The PDCB, PMCH, and PDCH taggant sources were placed inside a 1 x 1 ft polyethylene bag that was heat sealed several times with a small, portable heat sealer. Surprisingly, the results as displayed in Figures 4.7 to 4.9 indicate that this is also a negligible barrier towards taggant release. The lack of airtightness of the heat-sealed bag is due to either imperfections in the heat sealing that leaves air gaps or small pinhole leaks. The barrier constant, k , for the heat sealed polyethylene bag is very large and is set at infinity, similar to the two other negligible barriers.

4.4 Attache Case

The three taggant sources were placed in an empty attache case (4-1/2 x 17-1/2 x 13 in.) which was placed in the experimental chamber. The resulting taggant concentrations in the chamber are displayed in Figures 4.10 to 4.12. The results indicate a lack of airtightness for the attache case barrier, so much that the attache case can be considered to have no barrier effect at all, i.e., a large k value.

Figure 4.7

Figure 4.8

Figure 4.9

Figure 4.10

Figure 4.11

Figure 4.12

The chamber ventilation rates fluctuated due to a lack of sufficient controls during this experiment. This is especially evident in Figures 4.11 and 4.12. The ventilation rate would decrease for several hours, increasing the chamber taggant concentrations. Later, the ventilation rate returned to its earlier value with the consequent return of the taggant concentrations to their expected values. The source of the ventilation fluctuation was the in-house compressed air used to ventilate the chamber which varied in its supply pressure.

4.5 One Gallon Paint Can

The three taggant sources were placed inside a 1 gal paint can with the lid tightly closed. The paint can was placed inside the experimental chamber. The resulting taggant concentrations, as displayed in Figures 4.13 to 4.15, indicate that a paint can represents a significant barrier. Note in these figures that the vertical scale has been expanded by a factor of 10 and that the no barrier taggant concentration results are offscale.

The barrier constant, k , was determined to be 1.2×10^{-4} L/min with the use of the theoretical barrier model. The resulting agreement, as displayed in the figures as a solid line, is quite good for all three taggants. The cyclical perturbation in the measured taggant concentrations is the result of a slow expansion and contraction of the paint can which allowed more or less taggant to be emitted from the paint can. The expansions and contractions were a result of diurnal temperature fluctuations in the experimental room.

This significant barrier effect will hinder the detection of vapor tagged explosives placed in the paint can. A calculation of the expected taggant concentration in a moderately sized room from a paint can with enclosed tagged explosives is given in Table 4.2. At one ventilation turnover time, the expected taggant concentration is 0.03% of the taggant concentration expected for no barrier.

Figure 4.13

Figure 4.14

Figure 4.15

This experiment was conducted with an unused paint can and it could be expected that an emptied, used paint can will not impose as great a barrier effect, most likely it will impose no barrier.

4.6 A Zip-Lock Plastic Bag

A PDCB taggant source was placed inside a zip-lock plastic bag which was placed in the experimental chamber. The resulting PDCB chamber concentrations, displayed in Figure 4.16, indicate a significant barrier effect imposed by the zip-lock plastic bag. The vertical scale of the figure has been expanded by a factor of 10 and the no barrier PDCB chamber concentrations are off scale. The barrier constant, k , has been determined to be 2.7×10^{-6} L/min using the theoretical barrier model. The resulting fit is displayed as a solid line in the figure.

Again, as with the paint can barrier, this severe degree of barrier airtightness will hinder the detection of vapor tagged explosives enclosed in zip-lock plastic bags.

4.7 Conclusions

The principal result of these barrier experiments is that most boxes, luggage items, attache cases, and heat sealed plastic bags will impose no significant barrier to the release of a vapor taggant from within the barrier. This is due to the relative lack of airtightness of these barriers. Two other barriers, a sealed new paint can and a zip-locked plastic bag did have a significant degree of airtightness. Additional data on a variety of samples and information on the way such barriers might be treated in actual use would be needed before a firm conclusion about the seriousness of these findings could be made.

Figure 4.16

These results have been further corroborated by two field experiments involving the detection of vapor tagged explosives in various luggage items^{3,4}. The various types of baggage, ranging from a soft suitcase to an aluminum suitcase with a rubber gasket, did not exhibit any significant degree of airtightness to the vapor taggant. More experimental details can be found in the specific reports.

Appendix A: Taggant Concentrations in Detection Scenarios from Vapor Tagged
Explosives Enclosed in Various Barriers: Theoretical Modeling
of the Adsorption Losses

In vapor tagging of explosive products, there is a requirement that vapor taggants be volatile. This ensures that there will be negligible taggant adsorption losses on various surfaces present in scenarios, e.g., clothing inside suitcases, packing material in boxes, etc. This appendix describes a suitable adsorption loss term and determines the effect of adsorption losses on the detectability of nonvolatile taggants. This discussion is appropriate to the detection of explosive vapors, e.g., EGDN, TNT etc. from bulk explosives. These natural vapors are relatively nonvolatile and adsorption losses are an important sink for these vapors.

It is convenient to consider two cases of a detection scenario: one without any barrier, i.e., suitcase, boxes, and one with barriers.

A1. No Barrier case

The vapor concentration present in a detection scenario is result of a balance between the vapor sources and the vapor sinks (losses). Thus the rate of increase of the volume of vapor taggant in the scenario is simply

$$dV_o(t)/dt = (\text{sources}) - (\text{sinks}) \quad (\text{A1})$$

The only source present is the vapor emission rate from the vapor source, e.g., a tagged blasting cap, a permeation source in bulk explosive, or the inherent explosive vapors. For the explosive vapor, the emission rate would be equivalent to vapor evaporation rate from the explosives.

Define

$$(\text{sources}) = R_{\text{cap}} \quad (\text{A2})$$

There are two sinks. First is a loss of vapor from the scenario due to the ventilation of the scenario. This is simply $V_O(t) R_{ex}/V_{ch}$ in which R_{ex} is the ventilation rate. The quantity (V_{ch}/R_{ex}) is equal to the turnover time t_v of the scenario, i.e., the time required to completely replace the air in the scenario with fresh air. The second sink is a loss of taggant due to irreversible adsorption. This is best expressed using the Langmuir adsorption isotherm

$$V_{ad} = v_m c(p/P_O)/[1 + c(p/P_O)] \quad (A3)$$

in which V_{ad} is the amount of adsorbate, v_m is the volume of gas necessary to cover the entire surface with a completely adsorbed monolayer, c is an empirical constant, p is the partial pressure of the adsorbate, and P_O is the equilibrium vapor pressure of the adsorbate. This can be re-expressed in more familiar terms as

$$V_{ad} = v_m cV_O(t)/(P_{ext}/V_{ch}P_O)[1 + cV_O(t)P_{ext}/V_{ch}P_O] \quad (A4)$$

or more conveniently:

$$V_{ad} = av_m V_O(t)/(1 + aV_O(t)) \quad (A5)$$

The rate of loss due to adsorption is then:

$$R_{ad} = dV_{ad}/dt = \frac{av_m dV_O(t)/dt}{[1 + aV_O(t)]^2} \quad (A6)$$

Thus the complete equation is then:

$$dV_O(t)/dt = R_{cap} - V_O(t)/t_v - av_m/[1 + aV_O(t)]^2 \cdot dV_O(t)/dt \quad (A7)$$

This equation has a steady state solution of $R_{cap} t_v$, which is also the case without adsorption. The equation for $V_O(t)$ has to have this limit since the adsorption sites will be saturated and consequently adsorption loss will become negligible after a sufficient time.

This differential equation (eq. A7) can be solved explicitly to yield the following solution,

$$\ln\left(1 - \frac{V_o(t)}{t_v R_{cap}}\right) - \frac{a^2 v_m V_o(t)}{(1 + a t_v R_{cap})(1 + a V_o(t))} - \frac{a v_m}{(1 + a t_v R_{cap})^2} \ln\left[\frac{1 + a v_m V_o(t)}{1 - V_o(t)/t_v R_{cap}}\right] = -t/t_v \quad (A8)$$

however this exact solution is cumbersome. Another solution can be obtained for $V_o(t)$ in terms of a power series expansion:

$$V_o(t) = a_0 + a_1 t + a_2 t^2 + a_3 t^3 + \dots \quad (A9)$$

for which:

$$a_0 = 0 \quad (A10)$$

$$a_1 = R_{cap}/(1 + a v_m) \quad (A11)$$

$$a_2 = \frac{R_{cap}}{(1 + a v_m)^2} \left(\frac{2 v_m a^2}{1 + a v_m} - \frac{1}{t_v} \right) \quad (A12)$$

This solution is for the initial condition $V_o(t = 0) = 0$, a realistic condition for most laboratory experiments.

This is compared with solution for the no adsorption case:

$$V_o(t) = R_{cap} t + \dots$$

where the initial rate of taggant increase has been attenuated by the factor $(1 + a v_m)$. More explicitly:

$$(1 + a v_m) = (1 + v_m c P_{ext}/V_{ch} P_o) \quad (A13)$$

due to adsorption losses. The attenuation due to adsorption is greatest when

- (a) v_m is large, i.e., a large surface available for adsorption
- (b) P_o is small, i.e., the more non-volatile an adsorbate is.

The attenuation can be further quantified if v_m , c and p_0 are known for particular adsorbates and surfaces. The factors a and v_m can be obtained experimentally from a least squares fit of any experimental system if sufficient experimental detection precision is available at initial times.

A2. Barrier Case

The equations for the case with a non-negligible barrier enclosing the explosive vapor source is more complicated. The differential equations for this situation are:

$$dV_{en}(t)/dt = R_{cap} - kV_{en}(t)/V_{en} + kV(t)/V_{ch} - av_m/(1 + aV_{en}(t))^2 \cdot dV_{en}(t)/dt \quad (A14a)$$

$$dV(t)/dt = kV_{en}(t)/V_{en} - kV(t)/V_{ch} - V(t)/t_v - a'v'_m/(1 + a'V(t))^2 dV(t)/dt \quad (A14b)$$

These equations include an adsorption loss inside the barrier (eq. 14a) and an adsorption loss in the scenario and on the outside of the barrier (eq. 14b).

This last term can in most practical cases be neglected so that the relevant equations becomes

$$dV_{en}(t)/dt = R_{cap} - kV_{en}(t)/V_{en} + kV(t)/V_{ch} - av_m/(1 + aV_{en}(t))^2 dV_{en}(t)/dt \quad (A15a)$$

$$dV(t)/dt = kV_{en}(t)/V_{en} - kV(t)/V_{ch} - V(t)/t_v \quad (A15b)$$

Again, it is possible to obtain the few leading terms in the power series development for $V(t)$,

$$V(t) = a_0 + a_1 + a_2 t^2 + a_3 t^3 + \dots \quad (A16)$$

Specifically

$$a_0 = a_1 = 0 \quad (A17)$$

$$a_2 = \frac{k R_{cap}}{V_{en} (1 + av_m)} \quad (A18)$$

The same attenuation factor of the initial vapor emission rate, i.e., $(1 + av_m)$ occurs in the barrier case as in the no-barrier case. Thus the same conclusions can be applied here as stated for the no barrier case. These equations (both eq. A14 and A15) have the correct limiting values i.e., $V(t \rightarrow \infty) = t_v R_{cap}$.

A3. Conclusion

The effect of adsorption losses is to effectively attenuate the vapor emission rate R_{cap} by a factor $(1 + av_m)$ during the initial part of the detection period, i.e., $t < t_v$. This adsorption attenuation $(1 + av_m)$ can be related to known physical parameters and thus realistic estimates can be made regarding the detectability of explosives vapor. Almost all explosive vapors are exceedingly nonvolatile; thus, the attenuation due to adsorption should be large.

If the vapor taggants are fairly volatile, however, then the attenuation factor due to adsorption should be near unity, i.e., essentially no adsorption loss of the vapor taggant.

Appendix B: Scenario Taggant Concentrations from Barrier Enclosed Vapor
Tagged Explosives: Solution of the Two Coupled Differential
Equations.

As a result of the mathematical development for barriers were two coupled differential equations to be solved, that have two different initial conditions: zero initial taggant concentration or a non-zero initial taggant concentration inside the barrier.

B1. Zero Initial Taggant Concentration Inside the Barrier (no time delay).

The two coupled differential equations for the $V_{en}(t)$, the volume of the taggant inside the enclosure and $V(t)$, the volume of the taggant inside the barrier are:

$$dV_{en}(t)/dt = R_{cap} - (k/V_{en})V_{en}(t) + (k/V_{ch})V(t) \quad (B1)$$

and

$$dV(t)/dt = (k/V_{en})V_{en}(t) - (k/V_{ch} + R_{ex}/V_{ch})V(t) \quad (B2)$$

(equations (14) and (15) of the main text,) with the initial conditions:

$$V_{en}(t = 0) = 0 \quad (B3)$$

and

$$V(t = 0) = 0. \quad (B4)$$

The best method for solving these coupled equations is by Laplace transforms. Defining $f(s)$ and $g(s)$ as the Laplace transforms of $V(t)$ and $V_{en}(t)$ respectively, we obtain using the initial conditions and equations (B5) and (B6)

$$sg(s) = (R_{cap}/s) - (k/V_{en})g(s) + (k/V_{ch})f(s) \quad (B5)$$

and

$$sf(s) = (k/V_{en})g(s) - (k/V_{ch} + R_{ex}/V_{ch})f(s) \quad (B6)$$

Solving explicitly for $f(s)$ we obtain

$$f(s) = \frac{k R_{cap}}{V_{en}s[(s + k/V_{ch} + R_{ex}/V_{ch})(s + k/V_{en}) - k^2/(V_{en}V_{ch})]} \quad (B7)$$

The inverse Laplace transform of this expression for $f(s)$ is then simply the solution for $V(t)$.

Before explicitly writing the solution, it is convenient to define two dimensionless parameters:

$$\gamma = V_{en}/V_{ch} \quad (B8)$$

the ratio of the enclosure volume to the scenario volume and

$$\beta = k/R_{ex} \quad (B9)$$

the ratio of the barrier air exchange rate to the scenario ventilation rate.

The parameter γ is a known quantity for any defined system whereas β is unknown unless the barrier constant is known.

The solution for the scenario taggant concentration as obtained from the inverse Laplace transform is thus

$$V(t) = \frac{R_{cap} V_{ch}}{R_{ex}} \left[1 - \frac{r_2 \exp(-r_1 t) - r_1 \exp(-r_2 t)}{r_2 - r_1} \right] \quad (B10)$$

in which

$$\begin{aligned} r_1 &= (R_{ex}/V_{ch})[(\beta + \beta/\gamma + 1) + [(\beta + \beta/\gamma + 1)^2 - 4\beta/\gamma]^{1/2}]/2 \\ r_2 &= (R_{ex}/V_{ch})[(\beta + \beta/\gamma + 1) - [(\beta + \beta/\gamma + 1)^2 - 4\beta/\gamma]^{1/2}]/2 \end{aligned} \quad (B11)$$

B2. Non Zero Initial Taggant Concentrations

The differential equations for the non zero situation are the same but initial conditions are different:

$$V(t = 0) = 0 \quad (B12)$$

and

$$V_{en}(t = 0) = V$$

As before, defining $f(s)$ and $g(s)$ as the Laplace transforms of $V(t)$ and $V_{en}(t)$, respectively, we obtain:

$$sg(s) - V = R_{cap}/s - (k/V_{en}) g(s) + (k/V_{ch}) f(s) \quad (B14)$$

and

$$sf(s) = (k/V_{en})g(s) - (k/V_{ch} + R_{ex}/V_{ch})f(s) \quad (B15)$$

Again solving for $f(s)$ yields:

$$f(s) = \frac{(k/V_{en})(R_{cap}/s + V)}{(s + k/V_{en})(s + k/V_{en} + R_{ex}/V_{ch}) - k^2/V_{en}V_{ch}} \quad (B16)$$

Now $f(s)$ can be expressed as two terms:

$$f(s) = f_1(s) + f_2(s) \quad (B17)$$

where

$$f_1(s) = \frac{k R_{cap}}{sV_{en}[(s + k/V_{en})(s + k/V_{en} + R_{ex}/V_{ch}) - k^2/V_{en}V_{ch}]} \quad (B18)$$

and

$$f_2(s) = \frac{kV}{V_{en}[(s + k/V_{en})(s + k/V_{en} + R_{ex}/V_{ch}) - k^2/V_{en}V_{ch}]} \quad (B19)$$

The concentration of taggant $V(t)$ for the time delay case is expressed as a sum of two functions

$$V(t) = V_1(t) + V_2(t) \quad (B20)$$

in which $V_1(t)$ and $V_2(t)$ are the inverse Laplace transforms of $f_1(s)$ and $f_2(s)$, respectively. $V_1(t)$ is simply the expression for the taggant concentration without time delay:

$$V_1(t) = \frac{R_{cap} V_{ch}}{R_{ex}} \left[1 - \frac{r_2 \exp(-r_1 t) - r_1 \exp(-r_2 t)}{r_2 - r_1} \right] \quad (B21)$$

in which r_1 , r_2 , β , and γ have been defined previously.

$V_2(t)$ can also be determined from the inverse transform and it is found to be

$$V_2(t) = \frac{kV}{V_{en}} \left[\frac{\exp(-r_1 t) - \exp(-r_2 t)}{r_2 - r_1} \right] \quad (B22)$$

thus the taggant volume in a scenario with time delay is

$$V(t) = \frac{R_{cap} V_{ch}}{R_{ex}} \left[1 - \frac{r_2 \exp(-r_1 t) - r_1 \exp(-r_2 t)}{r_2 - r_1} \right] + \frac{kV}{V_{en}} \left[\frac{\exp(-r_1 t) - \exp(-r_2 t)}{r_2 - r_1} \right] \quad (B23)$$

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