Fabrication and characterization of gelatin-based test materials for verification of trace contraband vapor detectors

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This work describes a method to produce inexpensive and field deployable test materials that can be used to verify the performance of trace contraband vapor detection systems such as ion mobility spectrometers (IMS) currently deployed worldwide for explosives, narcotics, and chemical warfare agent (CWA) detection. Requirements for such field deployable test materials include long shelf life, portability, and low manufacturing costs. Reported here is a method for fabricating these test materials using encapsulation of high vapor pressure compounds, such as methyl salicylate (MS), into a gelatin matrix. Gelatin serves as a diffusion barrier allowing for controlled and sustained release of test vapors. Test materials were prepared by incorporating serial dilutions of MS into gelatin, which provide controlled analyte vapor release over 3 to 4 orders of magnitude of instrument response. The test materials are simple to prepare and have been shown to be stable for at least one year under controlled laboratory conditions.

Introduction

More than 60 000 portable, rapid, low cost instruments that can detect trace explosives and chemical warfare agents (CWAs) are currently deployed worldwide due to increased National Security concerns.[1] These systems utilize a variety of technologies for detection, including chromatography, mass spectrometry,[2] surface acoustic wavelength (SAW) detectors, flame photometric detectors (FPDs),[3] and ion mobility spectrometry (IMS). Ion mobility based systems are widely used and represent the bulk of the systems currently deployed for both explosives and CWA detection. IMS systems are often used in particle mode, where trace particulate contamination is collected by physically swiping and then thermally desorbed to produce analyte vapor. Alternatively, for CWAs and some of the more volatile explosives and explosive taggants, direct vapor sniffing is used.[4] When using either of these two operation modes, military, law enforcement, and security screeners require standard test materials to validate the performance of their detectors and ensure that they are working effectively. There are significant efforts underway to produce test materials for particle mode detectors,[5,6] as well as efforts to produce laboratory calibration systems for vapor detectors.[7] However, there are few field deployable vapor verification systems currently available. The vapor verification sample must be of appropriate size to allow the user to carry it easily at all times, be stable in various environmental conditions, and provide a reproducible signal throughout the life of the sample. The signal-producing analyte compound should also produce a strong and well characterized response in the detection system. Methyl salicylate (MS) is an example of one compound that is commonly used as a CWA simulant due to its physical properties and safety considerations.[8] Since MS also gives a suitable response in negative-ion explosives detection mode IMS, it is a very attractive material for a combined explosive and CWA simulant.

Home fragrance products that use gelatin or other encapsulant as a medium is one common way in which vapors may be continuously released over an extended period of time.[9,10] In these commercially available air fresheners, an aliquot of fragrance oil is incorporated into a gelatin matrix, emitting a relatively continuous level of vapor into the open air over several weeks time. Gelatin has also been used for vapor release of other volatile materials such as insect repellant and sanitizing agents.[11] In this work, the feasibility of using this same approach to produce a vapor test source for trace detectors is explored. Four commercially available fragrance oils including MS oil and two volatile explosives were chosen to incorporate into gelatin samples at variable concentrations. A procedure was developed to inexpensively fabricate these materials. The samples were then evaluated with a handheld vapor IMS instrument to determine the distinguishing IMS response for each analyte compound, the concentration dependence of the response, repeatability of the measurements, and the lifetime of the test material.

Experimental

Gelatin from porcine skin (Sigma-Aldrich, St Louis, MO),† a mixture of proteins with high molecular weights, was used for sample preparation. When this solid protein product is mixed with warm water and then allowed to cool, it produces a semi-solid gelatin containing 94% water. Fragrances in the form of aromatic oils can be mixed with gelatin at different volume concentrations before the gelatin solution begins to set. Four fragrance oils were combined with gelatin to determine the IMS

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† Certain commercial equipment, instruments, or materials are identified in this document. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products identified are necessarily the best available for the purpose.

response for each one. These included triethanolamine (TEA), methyl salicylate (MS or wintergreen oil) (both from Sigma-Adrich, St Louis, MO), agrunitrile, and musk oil (both from International Flavors and Fragrances, New York, NY). Propionic acid, cinnamon oil, chlorine bleach solution, and formaldehyde solution (37% weight in water) were purchased from Sigma-Aldrich (St Louis, MO) as preservatives of the gelatin. To make a large number of samples at once, gelatin and warm water were mixed in a ratio of 30 grams to 500 mL water. Once the gelatin was dissolved, a preservative was added. Twenty mL aliquots of the warm gelatin–water solution were placed in separate sample vials. Inexpensive 30 mL capacity plastic vials with a screw cap (Sigma-Aldrich, St Louis, MO) were used as sample containers. The aliquots of oil included 2 μL, 20 μL, 200 μL, and 2000 μL mixed with 20 mL gelatin to make samples with nominal oil volume fractions of 0.01%, 0.1%, 1%, and 10%, respectively. With this method, the oil typically separates from the gelatin and settles to the bottom of the sample vial before the gelatin fully solidifies, creating an oil layer capped by a gelatin diffusion barrier.

For another part of this study, gelatin samples were prepared by direct injection in order to study the effect of variable diffusion path lengths of the simulant. The gelatin solution was allowed to cool and set in the sample containers so that a 20 μL aliquot of fragrance oil could be injected at different locations throughout the sample. Injection locations were centered from the walls of the vial at 5 distinct distances from the surface of the gelatin (Fig. 1). A limited number of samples were made using trinitrotoluene (TNT) explosive crystals to test the use of real explosives in gelatin samples. A known mass of TNT was dissolved in ethanol so that the concentration of TNT in two gelatin samples would be mass fractions of 0.01% and 0.1%. For each batch of gelatin samples that was prepared, one blank sample without any fragrance oil or TNT was also placed in a sample container.

Once samples were prepared, they were analyzed primarily by using a Vapor Tracer 2 (General Electric, Bradenton, FL) handheld IMS instrument operated in negative-ion (explosives) mode. This instrument was operated in vapor mode with a heater temperature of 199 °C and a sampling time of 7 s. Dichloromethane was used as a dopant gas, and butylated hydroxytoluene (BHT) was used as an internal calibration compound to determine corrections to measured drift times which can shift over time and depend on environmental conditions. The handheld trace vapor IMS was interfaced to a desktop computer for more detailed data analysis including determination of the drift times and peak amplitudes produced by each oil. Ideally, the simulant should produce a well defined and repeatable peak. The gelatin samples were analyzed by removing the cap and holding the vial in close proximity to the vapor inlet of the IMS instrument. As discussed later, the most reproducible method for analysis of these materials involves allowing the sample to equilibrate with the cap removed for 1 minute prior to data acquisition. This allows the initial vapor headspace to dissipate and gives a more consistent response from sample-to-sample. Once the sample was collected, the vial was recapped and stored at room temperature.

To compare the response of the vapor IMS, a Phocheck photo ionization detection (PID) analyzer (Ion Science, Waterbury, VT) was also used for several studies. The Phocheck is an analyzer that is designed to detect low concentrations of vapor in ambient air. It was used in this study to compare the level of vapor release of the gelatin samples, but not to identify the substance. This instrument works by drawing ambient air through a probe where analyte molecules are ionized by a UV lamp. These ions are neutralized by a small photoionization current, which is proportional to the gas concentration. This instrument is calibrated against isobutylene in the factory, giving response factors equivalent to this gas, in volume fraction μL L^{-1}. Although the calibration gas can be changed, it was kept at factory settings for this study. Before running a set of analyses, the instrument was zeroed to remove any background signal, which tends to have an additive effect.

Results and discussion

IMS analysis of methyl salicylate

The majority of oils tested were not suitable as simulants for the explosives vapor IMS instrument operating in negative-ion detection mode. Two of them, TEA and musk oil, produced no peaks above background. The complex spectrum of agrunitrile was deemed unsatisfactory due to many confounding peaks in its IMS response. The MS oil performed ideally as a chemical simulant; it produced two IMS peaks, neither of which was within an existing threat channel for the Vapor Tracer 2. Fig. 2 shows a plasmagram for an analytical sample of MS oil in gelatin. The two negative ion mode IMS peaks are located at drift times 5.0 ms and 5.5 ms. While all MS-doped gelatin samples

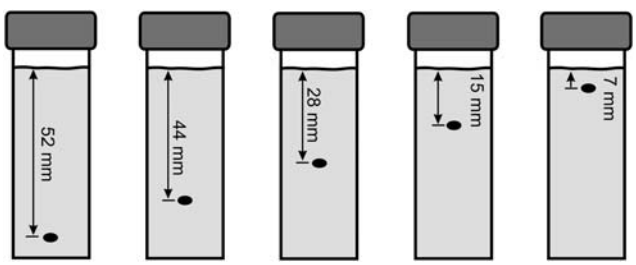

Fig. 1 Illustration showing the locations of MS oil (black dots) injected in gelatin sample vials once the gelatin was solidified.

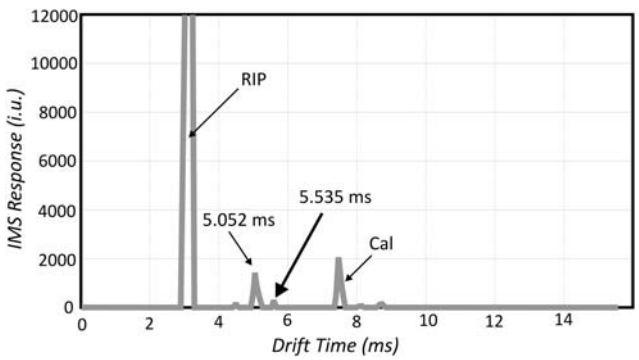

Fig. 2 Vapor IMS plasmagram for 1% MS oil vapors. The two main peaks produced by MS are noted. Other peaks are the reactant ion peak (RIP), calibrant (Cal), and some background peaks.

produced the peak at 5.0 ms, the 5.5 ms peak was produced only 64.0% of the time. Therefore, this peak should be considered a secondary channel for MS, not a primary identification peak. For a more simplified explanation of the experiment results, only the 5.0 ms peak will be discussed for the remaining data analysis.

Because drift times can vary, a more common way to define the mobility of a particular ion is to determine its reduced mobility (K_0). Ion mobility calculations are dependent on the drift tube length, drift gas, pressure, and temperature as well as the timing of ion injection and drift time.[12] All of these parameters differ from one instrument to another; therefore calculating experimental reduced mobility values can be complicated. Using a reduced mobility value is a more accurate way to describe the drift behavior of a compound compared to raw drift times, which can be variable due to environmental factors. Typically, the calibrant would be used as a reference for calculating experimental reduced mobility values. However, information on the K_0 of BHT is sparse in the open literature so TNT was chosen as a reference. TNT is a common test sample provided by most IMS manufacturers and is typically set up in alarm reference libraries. To calculate the experimental reduced mobility value for MS oil with the Vapor Tracer 2, a K_0 reference value of 1.55 $cm^2\ V^{-1}\ s^{-1}$ was used for TNT. This was determined by Spangler *et al.*[13] for a membrane-based IMS instrument operated at 200 °C, which used similar technology to that used for the Vapor Tracer 2 for these experiments. Based on this literature value for TNT, a reduced mobility value for MS oil can be calculated by using the following equation

$$K_{0u} = K_{0_{ref}} \times \frac{t_{d_{ref}}}{t_{du}} \quad (1)$$

where K_{0u} is the reduced mobility of the unknown, K_{0ref} and t_{dref} are the reduced mobility and drift times of the reference compound respectively, and t_{du} is the drift time of the unknown. By using the literature value of 1.55 $cm^2\ V^{-1}\ s^{-1}$ and the experimental drift time of 6.0 ms for TNT, it was calculated that the experimental value of 5.0 ms peak for MS oil has reduced mobility value of 1.86 $cm^2\ V^{-1}\ s^{-1}$. This approach of using a reference K_0 value is useful for determining a more accurate drift time for each individual instrument, which can vary. For example, one reduced mobility value previously cited for MS oil analyzed with a different type of IMS instrument was 1.62 $cm^2\ V^{-1}\ s^{-1}$,[14] which differs somewhat from the 1.86 $cm^2\ V^{-1}\ s^{-1}$ calculated for this particular instrument.

The drift time for the peaks can vary from day to day, depending on the environment and calibration of the instrument. For example, the drift time of the 5.0 ms peak throughout this study ranged from 4.936 ms to 5.293 ms (average 5.073 ms ± 0.061 ms), an approximate 1.2% deviation, which is within most analyte detection windows. It was found that even though the instrument was kept and used in the same laboratory everyday, the daily shift was quite significant, and the vapor IMS did need to be calibrated before each use to calculate the offset. Regular maintenance such as changing the dryer cartridge of the instrument at least once a week helped to reduce this shift. It is possible that frequent daily use of water based gelatin test samples will introduce water into the system, thus creating this daily shift and a saturated dryer unit. The gelatin samples were used many times during the evaluation phase of this study; however, normal use will require only one or two analyses per day and the humidity of the samples should not cause such a large shift or the need for frequent dryer cartridge replacement.

The concentration of fragrance oil incorporated into the gelatin samples was varied to determine the correlation between prepared oil concentration and IMS response. Ideally, the concentration of oil in gelatin could be varied to produce any desired IMS response level. Fig. 3 illustrates the average IMS response as intensity units (i.u.) and the average PID response for each oil concentration in gelatin tested. Each data point is the average of at least three analyses, and the error bars represent one standard deviation. These results were expected and indicate that the concentration of oil in gelatin correlates with the vapor detection response levels, and can be tailored to the individual detection levels of each instrument.

Repeatability of gelatin

Once it was determined that each concentration of MS oil in gelatin produced different IMS response levels, the samples were analyzed on a weekly basis to determine how repeatable the IMS measurement was for each sample over time. When the samples were not in use, they were kept tightly sealed in vials in a laboratory at room temperature without exposure to sun or UV light. The temperature and humidity of the buildings that house the laboratories are strictly regulated, so samples left at room temperature are not exposed to ambient weather conditions. Currently these studies only consist of samples remaining at the regulated temperature of 22.0 °C ± 0.11 °C and 38.0% ± 3.59% relative humidity (mean ± the standard deviation). Fig. 4 shows the IMS response of three different MS–gelatin samples over a 4 week period. Each data point represents at least 3 analyses, and the error bars are the standard deviation. These results indicate that the simulant gelatin samples produce analyte signals with a consistent and repeatable IMS response over time.

Lifetime studies

In addition to reproducibility, the shelf life of the gelatin and the vapor it releases is an important characteristic of these gelatin

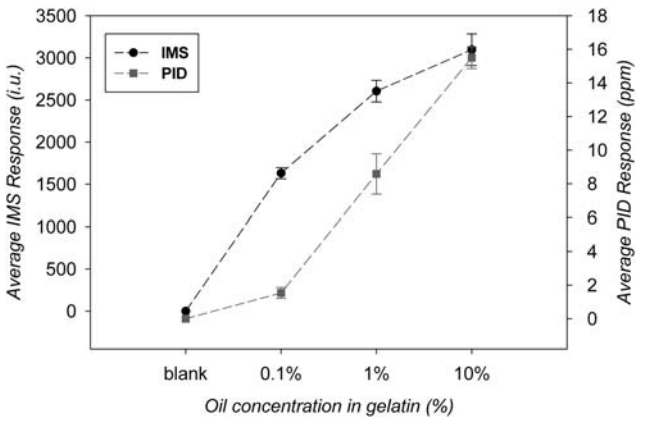

Fig. 3 PID and IMS response curves for increasing MS oil concentrations in gelatin vial samples. Left *y*-axis represents the IMS response (filled circles) in intensity units (i.u.). Right *y*-axis represents the PID response (grey squares) in μg g^{-1}. All error bars are one standard deviation.

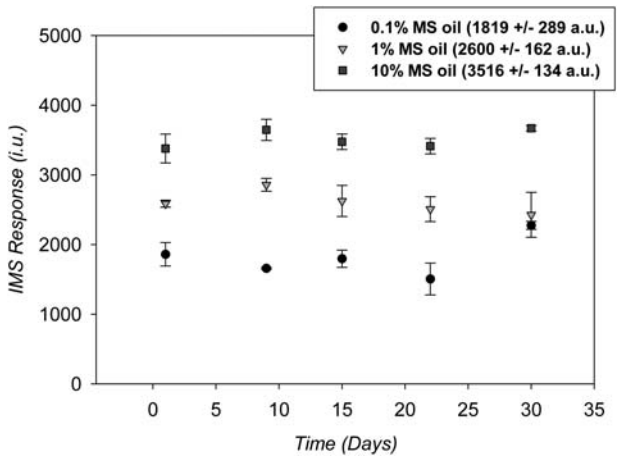

Fig. 4 Vapor detection levels for MS oil in tightly capped vials remain steady after 30 days of analysis with the IMS instrument. Each data point is the average of at least 3 analyses, and the error bars are the standard deviation.

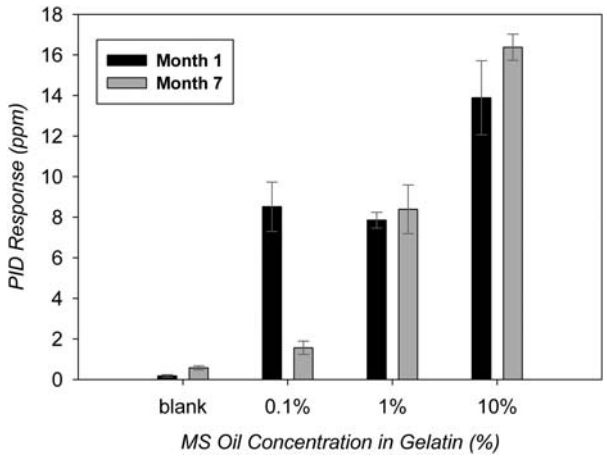

Fig. 6 Results of the PID response for a range of MS oil gelatin samples in vials in a 7 month span. Each bar is the average of at least 6 analyses, and error bars are one standard deviation.

samples for field use as verification of vapor detectors. A selected number of gelatin samples were analyzed with IMS as well as the PID at the early stages of this study and then again after 7 months. The samples were analyzed several times a month and otherwise they remained tightly closed at room temperature during that time span. Fig. 5 shows the IMS responses of three MS oil gelatin concentrations for April 2009 and October 2009, and Fig. 6 shows the PID responses for the same samples and time frame. The vapor response remained high after at least 7 months, which suggests a promising shelf life for the gelatin samples. The vapor response of the volume fraction 0.1% MS concentration sample did decrease after 7 months, which indicates that the lower MS concentration samples may have a shorter shelf life than the higher MS concentration samples. The vapor response of the volume fraction 10% MS concentration sample increased slightly over the 7 month span. A plausible explanation for this effect has not yet been developed. However, keeping the vials tightly sealed is very important for a long lasting sample. This was evident by some gelatin samples that were not sealed properly when not in use lost their vapor response after just a few weeks.

Initially, it was not clear whether the IMS was detecting vapors that had built up in the headspace of the vial or if the gelatin was continuously producing vapors detectable by IMS. To examine this, a MS–gelatin sample was opened and analyzed immediately, and then the vial was left open at room temperature and analyzed again every few minutes. Fig. 7 shows the average IMS response from five different vials of 1% MS oil in gelatin analyzed periodically over 30 min, with the vial being uncapped during this time. This demonstrates that there is an initial spike in vapor release, but after 1 min the response decreases at a slower rate potentially reaching a steady state of vapor release and the sample appears to continue producing sufficient vapor for

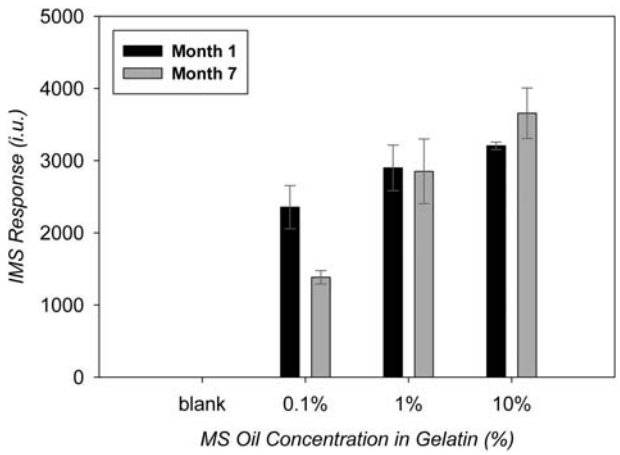

Fig. 5 Lifetime study of the IMS response for MS gelatin samples over a 7 month period. Each bar represents the average of at least six analyses, and the error bars are one standard deviation. Note that the response for 0.1% MS sample decreases by almost half after 7 months. This indicates that samples with concentrations of 0.1% MS oil or less may have a shorter shelf life than higher MS oil concentrations.

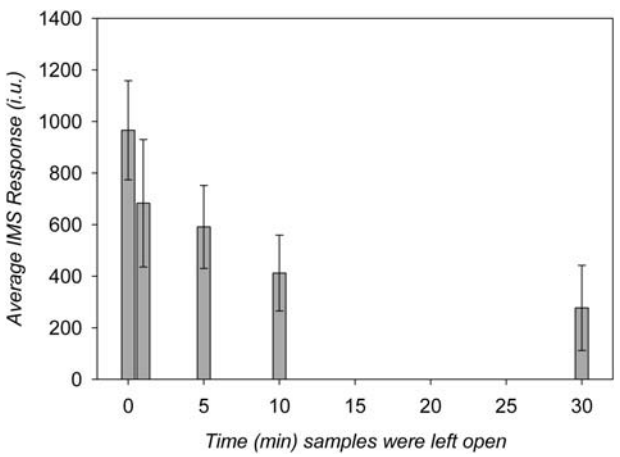

Fig. 7 Average IMS response to gelatin vapor test materials as a function of time after the vial was opened. These data suggest that a buildup of headspace vapor is released upon opening the vial. If the vial is left open, the vapor released by the gelatin approaches a constant level.

a considerable IMS response after 30 min. This observation is important because having a continuous vapor source is likely to produce more repeatable vapor concentration than simply analyzing the headspace vapors which could take some time to replenish. Based on these results, standard operating procedures to use the gelatin samples were developed that are based on allowing the original headspace vapor spike to deplete before conducting the analysis. The operating procedures include opening the vial and allowing it to stand open for one minute before analyzing the sample with a trace contraband detector. This procedure was used for all data recorded in this paper.

Injected samples

It was noted that when the MS oil and a liquid gelatin solution are mixed, they can phase-separate, creating a large diffusion path length with the oil settled on the bottom of the vial. This created samples with variable concentration of MS oil topped with a gelatin diffusion barrier consisting of equal path lengths. As an alternate fabrication procedure, gelatin samples that contained distinct injection sites of MS oil were analyzed to determine how factors such as vapor diffusion path length and volume ratio of oil to gelatin in each sample affect the instrument response. This method provided samples with a constant concentration of oil and a variable diffusion path length. Fig. 8 shows the results of these samples analyzed by IMS over a 1 month period. These results indicate that the initial instrument response is much lower for the oil that is furthest from the gelatin surface and a much stronger response is generated for the oil that is closest to the surface. This suggests that the rate of diffusion of the MS vapors is relatively slow, since less vapor is reaching the IMS inlet in the samples that have the oil at a farther distance. However, after 1 month the response begins to trend in the opposite direction; the response for the smallest distance of MS is reduced and fluctuates over time, and the response for the largest distance of MS is increased. This indicates that the closer the oil is to the surface, the faster the vapors are depleted. By keeping the MS oil closer to the bottom of the container, the vapor takes longer to reach a steady response level. The response for the samples where the MS oil was near the center (28 mm) had the least amount of variation from day-to-day. It is likely that such samples reach a steady diffusion rate fairly quickly without the MS vapors depleting too quickly.

Gelatin preservatives

Since gelatin is commonly used as a bacterial culture medium, a potential concern is the growth of mold.[15] Propionic acid and cinnamon oil are two common additives used to prevent mold growth when making ballistics gelatin.[16] Therefore small aliquots of either cinnamon oil or propionic acid, as well as a chlorine bleach solution (Sigma-Aldrich, St Louis, MO) were added to some gelatin samples to determine how well they prevented mold growth. As a precautionary measure, blank samples with preservative only were analyzed with IMS to ensure they didn't interfere with the MS oil signal or produce peaks in real threat channels. A formaldehyde solution was also considered as preservative, but it tends to reduce the gelling capacity of the gelatin and should be avoided.[16] The propionic acid and cinnamon oil prevented mold growth in gelatin for at least one year. However, the cinnamon oil produced extra peaks in positive mode IMS which could negatively impact dual mode vapor detection systems, therefore propionic acid was determined to be the best preservative for this purpose. The bleach prevented mold growth for a longer time period compared to gelatin with no preservative, but mold did begin to grow after 6 months. Fig. 9 shows two vials of gelatin 20 days after being produced. Without any preservative, small spots of microbes begin to grow. It is important to prevent this growth to keep a long lasting gelatin sample.

Explosives in gelatin

In addition to producing simulant vapor test materials for explosives and CWAs, there is also great interest in the ability to

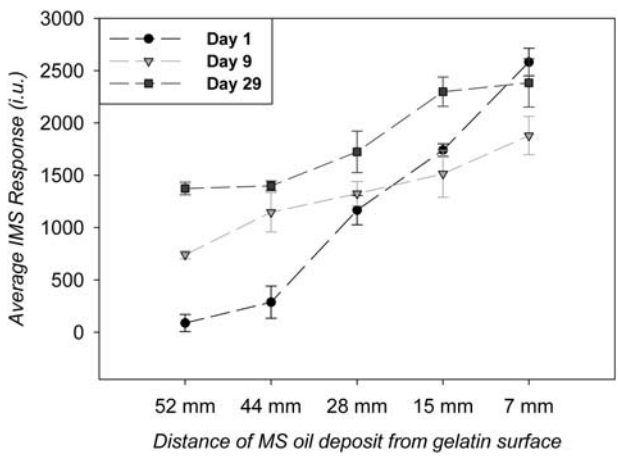

Fig. 8 Comparison of initial IMS response for injected MS oil samples to the response after 9 days and 29 days. Note that the sample where MS is furthest from the surface produces a much higher slope over time, while the MS closest to the surface fluctuates unsteadily.

Fig. 9 The vial on the left contains no preservative, and is growing small spots of mold after 20 days. Vial on the right has a volume fraction of 0.12% propionic acid and contains no mold.

Table 1 The average response ($n = 18$) and standard deviation (SD) for TNT gelatin IMS results

	Response	
Sample	Average	SD
0.01% TNT	2538	322.7
0.1% TNT	4219	407.4

incorporate real explosives into vapor verification samples, which would be useful for confirming that a trace vapor instrument produces a correct alarm for a high explosive. To demonstrate the feasibility of this, trinitrotoluene (TNT) was chosen to add to a gelatin sample. TNT has a vapor pressure of 9.49 nV V^{-1} at room temperature,[17] which is relatively large compared to other high explosives and makes it a good candidate for a vapor verification source. TNT gelatin samples were analyzed in the same manner as the MS oil samples. The average response and relative standard deviation for both concentrations are listed in Table 1.

Both TNT gelatin samples provided sufficient vapors to produce an alarm IMS response above the default threshold settings. The samples have been stored at room temperature and have provided a steady IMS response for at least 6 months.

Conclusions

These preliminary studies of oil-encapsulated gelatin-based vapor test materials demonstrate that this method of delivering vapor simulants to a trace vapor detector is very promising. Of the four fragrance oils tested, it was determined that MS oil is an ideal material for vapor testing. It produces consistent IMS peaks that do not overlap with any real threat channels. The main MS peak produced an experimental K_0 value of 1.86 cm^2 V^{-1} s^{-1} and is produced by all samples examined regardless of the concentration. The other peak produced by MS oil is a secondary peak seen less often. Real explosives can also be incorporated into the gelatin matrices which produce an IMS response above the default threshold settings as shown with TNT. A preservative is needed to prevent mold growth in the gelatin over time, and the best one was found to be propionic acid. By varying the concentration of oil incorporated into gelatin samples, instruments can be checked over 3 to 4 orders of dynamic range in vapor concentration. It has also been determined that a plastic vial and a screw cap with a tight seal is important for making the sample long lasting. Standard operating procedures for these samples have been developed which include removing the cap of the sample for one minute before analyzing. These MS fragrance oil infused gelatin vapor samples have a shelf life of at least 7 months depending on the concentration, and have proven to be a very useful tool as vapor detector verification samples.

Future work

Additional studies will be conducted to better test the lifetime and temperature ranges these samples can endure. The evaluation of other types of encapsulant matrices such as a polyamide polymer or a stearate to form a gel will be performed. These may be used to improve the vapor release or the lifetime of the samples. Altering the chemistry of the gelatin may also help it to withstand higher temperatures. Future efforts will focus on determining the rate of diffusion of vapor from gelatin samples, especially for the difference of injected fragrance oil at varying distances from the surface of the gelatin. Calibration of the vapor response will be conducted with a vapor jet instrument.[7] These ideas will be tested in the near future.

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