



IDEA

**Innovations Deserving
Exploratory Analysis Programs**

Transit IDEA Program

Counter Terrorism Chemical Detector for Transit Vehicles

Final Report for Transit IDEA Project 40

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Innovations Deserving Exploratory Analysis (IDEA) Programs Managed by the Transportation Research Board

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COUNTER TERRORISM CHEMICAL DETECTOR FOR TRANSIT VEHICLES
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Transportation Research Board
National Research Council

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Dr. Manuel Martinez Sanchez, Lead Scientist for MEMS-based Electrospray Generator at MIT

The panel for the Transit IDEA program, who selected this project for funding and provided oversight

Mr. Harvey Berlin, Senior Program Officer, TRB Transit IDEA Program

EXECUTIVE SUMMARY

This Transit IDEA project demonstrates a cost-effective electrospray technology employing an entirely different approach based on the remarkable effectiveness of small, highly charged liquid droplets formed from an electrospray source to “getter” both polarizable particles and polar molecules dispersed in a gas. This technology offers the smallest and most effective means to rapidly collect and detect the release of polar chemical species within a rail transit system.

This electrospray technique is more effective and inexpensive than collection system technologies that are generally based on stagnation of high volume, high velocity ambient airflow on a collecting surface. The momentum of particles and heavy molecules precludes their following gas streamlines during this stagnation. Instead, they concentrate and are trapped on the detector’s surface if the surface is “sticky,” or concentrated in the surface boundary layer, which can be separated from the mainstream flow and collected. Typically, the separation methodology collects about 50 percent of the particles between 1.0 and 10 microns in diameter from a flow of 500 L/min with a power consumption of up to 500 watts; i.e., about 1 watt of power is required for a small fan to compress 1 liter of air per minute to produce the high velocity, high volume airflow necessary for effective trapping of small bio-particles and heavy molecules. In contrast, our electrospray technology consumes negligible power and achieves virtually 100 percent particle collection. In fact, *we have demonstrated that the power efficiency of electrospray gettering for a single electrospray emitter to collect 100 percent of the particles, without a fan, at 10,000 times greater than the power efficiency of state of the art systems.*

The design offers a self-contained, battery operated (life of 1 year+) electrospray collector-detector which detects the target chemical agent or bioagent(s) using laser interrogation of specially developed Molecularly Imprinted Polymers (MIP's). MIP's are synthetic antibodies which possess all the advantages of antigen-antibody reactivity yet are more rugged than their natural counterparts. MIP's were developed by our one of our investigators at Virginia Commonwealth University. Experiments funded by the U.S. Army have demonstrated exceptional sensitivity in the range of picograms/liter in water! In contrast, delicate biological antibodies and their associated micro-assay technology often necessitate isothermal conditions for operation, have a finite shelf life, and are easily destroyed by ozone (ozone is created by sparks in subway tunnels and tubes from the commutators). Artificial MIP receptors are rugged, preferentially selective and, using a proprietary-based multiple MIP array, can accurately and rapidly identify a target chemical species or bio-agent. We call our concept an *Analytical Laboratory for Early Response to Terrorism*, abbreviated “ALERT”.

Contaminant species in ambient air can cause a broad spectrum of human ailments ranging from relatively mild reactions caused by allergens, e.g., "hay fever", to serious illness and death from diseases due to pathogens such as anthrax, small pox, botulinum, and the plagues of years past. Unfortunately, the epidemiologies of such contaminants and the afflictions attributed to them often lack reliable quantitative data on presence, vectors, cause and effect. Part of this lack is because the symptoms characteristic of an ailment may not emerge until long after exposure to its cause (i.e., incubation period and prodromal infection). Also, the nature and extent of exposure required to produce symptoms is rarely well defined. A further complication is that when a patient begins to show symptoms, it may be difficult if not impossible to determine either the contaminants that might have been involved or the nature and extent of the patient's exposure to those contaminants. Another major problem is that monitoring of air quality (extent and kind of pollution) is usually carried out only in a few "central" locations. The results are then considered representative of a large surrounding area. But within that area there may be tremendous diversity or heterogeneity in the composition of the air which individuals actually breathe. The more collector-samplers in a given area, the better the representation of possible contamination.

In the aftermath of 9/11, infection was caused by anthrax bacillus spores in envelopes sent through the mail system. Some of those spores became dispersed in the air at post offices, homes or offices where contaminated pieces of mail had been delivered. Since then, the reality of chem./bio-terrorism has underlined

the need for a variety of counter-measures, one of which is the air collector-detector which would make it possible to determine the actual representative air quality in real-time. The electrospray technology studied has demonstrated the capability to meet the need for a small, inexpensive, lightweight and effective collector-detector device. The device also has the ability to provide cumulative air contaminant sample data over periods of many months to years. The collection-detection system addresses the following:

- 1) Collecting samples for subsequent analysis
- 2) Providing identification of collected contaminants
- 3) Automatic notification of contaminant identification.

The most advanced devices currently in use reveal no application of electrospray, as does the disclosed technology in a “gettering” mode. While numerous applications exist where electrospray ionization is utilized to identify trace species that may be indicative of a polar molecule or biological agent of interest, such electrospray applications always require physical introduction of the analyte (sample) into the electrospray system. Furthermore, traditional electrospray ionization sources require that the solvent species and analyte be carefully fed by hydrostatic pressure into the source needle. The disclosed device obviates the need for hydrostatic feed and permits capture of polar species directly from the ambient air without the need for additional sample capture and introduction requirements.

The new technology stems from our experiments with charged droplets by the so-called electrospray dispersion of a conducting liquid into gas as a fine spray of tiny charged droplets. Evaporation of solvent from such droplets transforms polar solute species into free gas phase ions. This electrospray ionization is unique in being able to produce intact multiply-charged ions from large and complex organic molecules including peptides, viruses, proteins, nucleic acids and carbohydrates. Because such complex and fragile molecules and bio-species such as viruses, bacteria or spores cannot be vaporized without catastrophic decomposition, they cannot be ionized by the classical ionization methods. Consequently, they had long been "off limits" as subjects for mass spectrometric analysis. In the mid 1980's electrospray was one of two new techniques that led to revolutionary changes in the analytical chemistry scene by making possible the production of intact gaseous ions from such large polyatomic molecules.

The subject technology takes advantage of our discovery that the tiny charged droplets produced by electrospraying liquids are extremely effective "getters" for both particles and polar molecules in air and other gases. When a particle or molecule collides with a charged droplet it attaches to that droplet. If the attaching species is a polar molecule, it subsequently becomes a gas phase molecular ion just as if it had been a solute in the originally electrosprayed liquid. If the attaching species is a particle, it remains attached to the droplet and retains some of its charge becoming a charged particle when the last of the droplet solvent evaporates. Therefore, both particles and polar molecules that encounter such charged droplets become charged themselves and can thus be driven to a desired target surface by an appropriately directed electric field.

This gettering-charging process is quite effective. In one experiment, for example, a spray was produced by injecting a 50-50 mixture of propanol and water at a rate of 1.75 microliters/min through a short length of hypodermic needle tubing co-linear with the axis of a circular duct 2.2 cm in diameter and 8 cm in length maintained at 3.3 kV relative to the duct walls. A stream of room air flowed through the duct counter to the direction of liquid injection at a velocity of 12 cm/s which corresponds to a volume flow rate of 2.8 L/min. A particle counter indicated a number density of 5000 particles/mL in the entering air with diameters ranging from 0.3 to 3.5 microns, the size range of the counter. The spray current (needle to wall) was only 67 nA (10^{-9} Amp). The particle density in the exit air, measured by the same counter, indicated that the charged spray droplets had swept from 93 to 98 percent of the particles from the air!

1. IDEA PRODUCT, CONCEPT AND INNOVATION

1.1 IDEA PRODUCT

A key feature of our proprietary technology is the use of a wick feed system for the electrospray which overcomes the complexity, cost and potential unreliability of a hydrostatic feed system. It is this feature of wick flow that has been exploited in oil lamps and candles for millennia. In such devices, heat from the flame vaporizes the fuel which is then consumed by the flame to provide the heat that vaporizes the liquid fuel arriving at the end of the wick. In this way, capillarity maintains a steady state flame. The system is inherently self-stabilizing because the capillarity action cannot deliver liquid fuel to the end of the wick any faster than the flame can remove it. By the same token, the flame cannot consume the fuel any faster than the wick can supply it. We have successfully employed this feature under a NASA-JPL Phase II electrospray-based micro-thruster for miniature satellites. Eliminating a pump for the electrospray gettingting device leaves an easily regulated applied voltage as the only variable requiring control. Moreover, the nature of a wick is such that even very small particles are larger than the wick pores, but smaller than the area of porous surface. Therefore, the wick itself acts as a particle filter so that one doesn't have to worry so much about insuring the absence of particles in the liquid. We have even proven use of a wick feed system via our colleagues at MIT in a MEMS-based device in silicon! Recent environmental stress screening tests, undertaken during a Phase I USMC electrospray gettingting study, validate that the sampler also functions well in outdoor applications.

Electrospray collection is also ideally suited to the effective capture and analysis of target bio-agents. Electrostatic collectors, in addition to consuming higher power levels than electrospray, also produce copious amounts of ozone, which is sufficient to kill many if not most of the microbes and viruses that may be present in a sample collected by electrostatic precipitation. Such destruction of those organisms would negate any attempts to "amplify" any identifying "signal" that could be achieved from such organisms if they were allowed to grow and multiply in a culture of a collected sample. No ozone is produced during electrospray dispersion so that any living organisms in the collected sample can survive and multiply in a subsequent culture of that sample. In fact, experiments have shown that viruses in a solution that is electrosprayed into a vacuum system containing a mass analyzer, then removed from the vacuum system after passing through the mass analyzer, retain their viability and reproductive capacity.

Detector Suite

The electrospray-based sampler will be combined with a miniature chem./bio detector to provide a self-contained autonomous system capable of collecting and identifying trace species in air. Because no single detection technology is capable of identifying a broad range of biological and chemical pathogens, we have selected a unique combination of detectors based on laser induced fluorescence from molecularly imprinted polymers (MIP's) and a surface acoustic wave (SAW) arrays. Following is a brief description of these two complimentary detection technologies:

Laser Induced Fluorescence from MIP's

Detectors based on laser induced fluorescence (LIF) combine photo excitation with photo detection and represent one of the most widely used methods for detecting the presence of photoactive chemical and biological species. The popularity of this simple optical method stems from the convenience, low power consumption and potential for miniaturization. The primary drawback of LIF for species identification is the relatively broad and overlapping spectral emission range of most fluorophores. That is, many fluorescent species have common emission spectra that overlap. We have solved this problem through the use of MIP's to dramatically improve the selectivity of the LIF-based sensor. MIP's have been synthesized to exhibit preferential affinity to target chemical or biological agents. For biological agents, the MIP's are imprinted to specific associated chemical signatures. A patterned array of such MIP's are incorporated into the target of the electrospray sampler. Each component of the array was imprinted to a different, but specific chemical species. The MIP's are designed to change optically upon interaction with their target species. For example, the MIP/analyte interaction can produce an increase, decrease (quench) or spectral shift in the fluorescence emission spectra. The entire MIP array is periodically interrogated with a laser probe and the optical pattern from the array will be detected using a CCD array or photomultiplier tube. Each chemical species thus

produces a unique optical pattern allowing positive identification with LIF. The entire detector, therefore, consists of a light source and CCD detector with the MIP array incorporated into the target of the electrospray sampler.

Surface Acoustic Wave (SAW) Chemical Sensors

Polymer-coated SAW devices were investigated to be used as a complimentary chemical detection method. A SAW device is a solid-state micro scale piezoelectric transducer that converts the minute mass changes produced in a thin polymer film by vapor interactions into an electrical signal. Because a single polymer film is not selectively sensitive to a particular chemical species, an array of devices is used where each component of the array is coated with a different polymer. Just like the optical LIF detector described in the preceding section, the acoustic signal pattern of the SAW array is unique for each chemical species. SAW arrays have been developed and miniaturized by several companies and the technology has proven to be both robust and sensitive. Commercial SAW arrays are capable of detecting and identifying a wide range of chemical species including industrial toxins and chemical warfare agents. We believe that the unique combination of optical (LIF) and acoustic (SAW) detection strategies can provide an unprecedented level of performance and specificity in a small package and is particularly suited for the detection requirements of the transit environment.

Performance Goals

The ALERT system is capable of continuous 24/7-365 days per year operational capability. Sample collection and ionization by electrospray followed by detection and analysis via MIP and/or optional SAW devices, sensor cleaning, and waste disposal will be achieved through periodic thermal outgassing cycles. Alternatively, a large surface area detector may be employed with successive regions used for collection-detection over time.

It is important to note that the AC line (if available) can power the proposed system, because of the low current requirements, with battery backup or by battery alone for periods in excess of a year. RF notification & telemetry system will mimic Emergency Locator Transmitters or ELTs, except that event information will be added to the signal. If desired, the technology also has the demonstrated capacity to identify gaseous polar species such as nerve and blister agents. Acquisition and operational cost will definitely be far below the maximum listed in the solicitation. In fact, the technology lends itself to disposability.

We have been most fortunate to have the cooperation of Dr. Charles Burrus, Director of System Safety, MTA Subway system of New York City Transit. Under TRB support from the National Academy of Science, we have conducted field studies in the dynamic transit system environment to establish a baseline for chem/bio sensors in the field. Dr. Burrus has been instrumental in arranging this field testing.

Note: We are also very fortunate that Dr. John Fenn, the inventor of the electrospray process employed in virtually all applications of biomedical mass spectrometry. Dr. Fenn, 2002 Nobel Laureate in chemistry, is our principal consultant on the collection-detection system. The principal investigator, Joseph Bango, has collaborated with Dr. Fenn in electrospray for nearly 24 years. Mr. Bango, a scientist and engineer, was also a Naval Reservist tasked with analyzing potential terrorist threats.

Personnel & Performer Qualifications

Joseph J. Bango	President, Connecticut Analytical Corporation (NASA, Air Force & USMC P.I.)
Dr. John Fenn	Inventor of Electrospray and the 2002 Nobel Laureate in Chemistry
Dr. Gary Tepper	Lead Scientist for MIPS/SAW Development at VCU & SenTor, Inc.

The design criterion is based on additional ambient aerosol studies performed on-site in NYC under the support of Dr. Charles Burrus.

1.2 CONCEPT AND INNOVATION

ES ionization investigated by mass spectrometry

A natural generalization of the studies undertaken on particulate detection via ES is to analyze and detect vapors present in ambient air by previously charging them with ES ions. This idea is to expose ambient air to an electrospray region so that vapors and aerosolized particles contained within it would come into contact with either the charged liquid drops or the associated ES ions, thus becoming charged and available for detection by mass spectrometry (MS), ion mobility spectrometry (IMS) or other similar techniques. The approach was initially developed by Fuerstenau and Fenn, Consultants on this investigation, whom introduced controlled quantities of vapors into a ES-MS system and were able to detect parts per billion (PPB) of certain analyses, including narcotics and explosives. ES charging of volatile species offers important advantages in principle over conventional charging techniques used in IMS. The main reason is that coronal, UV, or radioactive charging all involve hyper thermal energies, which lead to highly reactive ionic environments. ES, on the other hand, operates under mild or “soft” thermal conditions that produce a much simpler and cleaner charging environment. For instance, ES of water/methanol with small quantities of ammonium acetate yield primarily the protonated ammonium acetate ion, in the complete absence of other ions or radical species. Proton transfer from this ion to other vapor species present would then cleanly yield their ions. The interest of this charging scheme is not restricted to mass spectrometry, as shown also by the recent IMS work of Hill and colleagues.

In the early work of Fenn and Fuerstenau, the trace vapor to be detected was introduced into the ES charging region in the same counter-flow configuration ordinarily used in ES-MS. In other words, the drying counter flow gas used by Fenn and colleagues to dry the ES drops was seeded with the trace vapor. This is optimal from the point of view of efficient analyte charging. However, it cannot generally be implemented directly with humid ambient air, since the mass spectrometer needs to ingest a relatively dry gas. In addition, since the security applications pursued at CAC will often not rely on large and expensive instruments such as mass spectrometers, the objective of this exploration was to evaluate ES charging as a general tool for the analysis of ambient trace vapor species. Our strategy has been to build a clean ES chamber where the air to be analyzed is mixed with the ES, and its trace vapors are charged separately from the mass spectrometer inlet and its counter flow drying system.

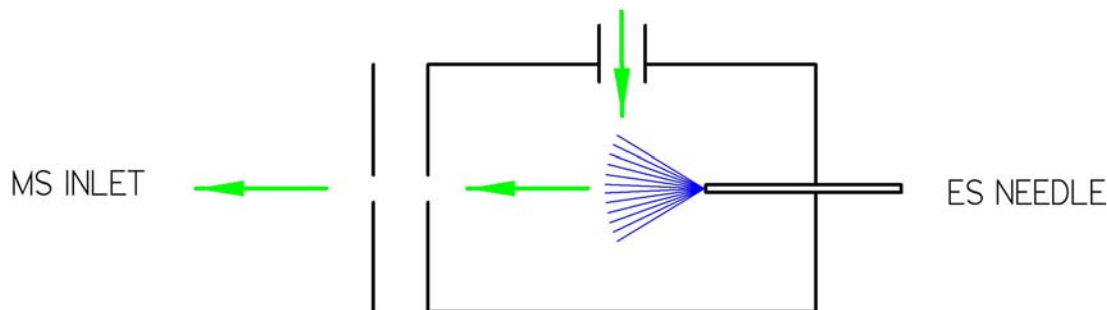


Figure 1

Figure 1: Schematic of the electrospray (ES) chamber. The liquid is introduced through the right into the spraying needle. The gas bearing trace volatile vapors enters from the top, goes through the spray and exits through the left in the form of a jet directed right into the MS inlet

Experimental

The simple ES chamber sketched in figure 1 was built with SS, glass windows and Teflon washers. The ES was formed by spraying within the chamber a solution of water-methanol (50/50 vol) with a small concentration of ammonium acetate (~ 10 mM) from a silica needle (40 μm ID). The needle was covered with a polyimide film, which was removed from the sharpened spraying end, but not from the solution end. The liquid was driven by compressed air pressure through the needle interior from the solution, held in a polypropylene vial, into the spraying end. The vial contained an o-ring on its top, but care was taken to avoid contact between the solution and the o-ring. Bottled dry air at several lit/min was introduced into the ES chamber, flew over the spray, was sampled through an orifice facing the spraying needle, and was blown into the inlet orifice of the mass spectrometer. Vapors were seeded into this gas by passing it through a gas cell (not shown) containing a small volume of liquid of the volatile material to be analyzed.

Results

Initially the ES chamber was thoroughly cleaned with solvents. In spite of this, the MS was dominated by dibutyl phthalate (figure 2), evidently from contamination of either the ES chamber or the gas supply line. It is striking that no original ES ions survive, almost all attaching to the DBP vapors. ES charging is therefore a vastly cleaner approach than the traditional radioactive chargers. A different type experiment was based on removing entirely the ES chamber, and electro spraying into the open lab, with the ES needle at a distance of a few cm from the inlet of the MS. The ES ions then had a chance to enter in contact with volatile substances in the laboratory, and become ions. Figure 3 shows that the corresponding spectra contain a sizeable amount of the original ES ions, also the three DBP peaks seen in figure 1, but at much smaller intensity, and a host of other peaks associated to unidentified substances. Once again, the effectiveness with which almost all ES ions are transferred to trace volatile species is striking.

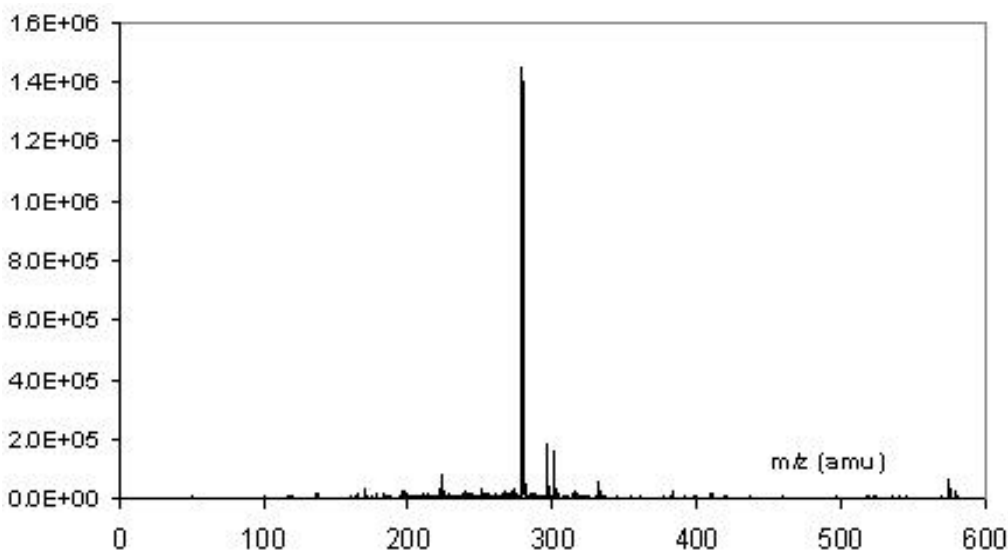


Figure 2

Figure 2: Typical spectrum for “clean” air contaminated by Dibutyl phthalate (DBP), showing a dominant DBP-H⁺ peak at 279.2 amu, followed by DBP-NH₄⁺ (296.4 amu) and DBP-Na⁺ (301.23). The largest peak to the right at 574.8 amu is DBP₂-NH₄⁺. Two unidentified small additional peaks are seen at 223.2 amu and 332.4 amu

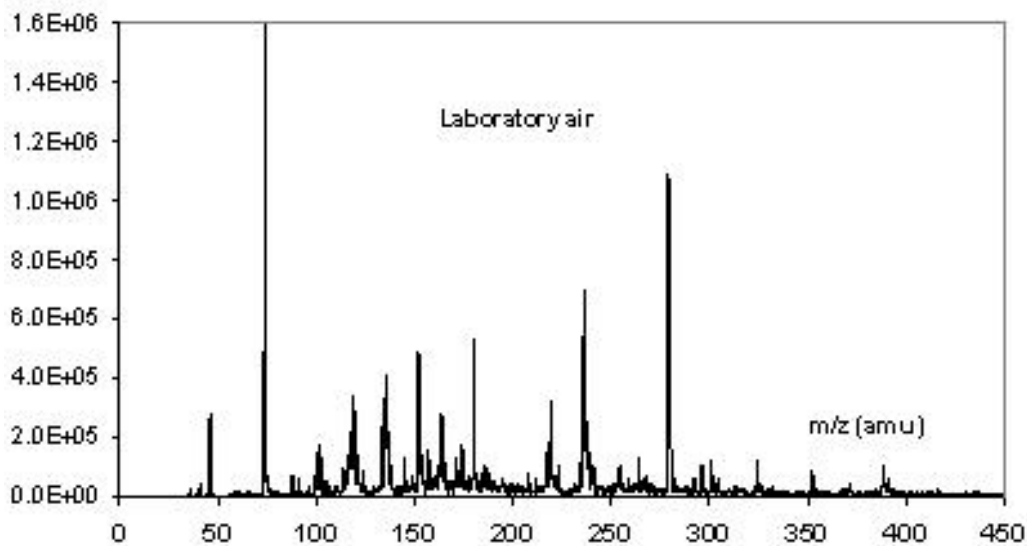


Figure 3

Figure 3: Typical spectrum for laboratory air. Small identifiable peaks appear at 36.054 ($\text{H}_2\text{O-NH}_4^+$), and 41 amu ($\text{H}_2\text{O-Na}^+$). More prominent unidentified peaks are at 46, 74, 119.2, 136, 152, 180, 219.2, 236, 279.2; 324.4, 352.4, and 388.4 amu. The three small peaks at about 300 amu correspond to DBP. The levels of these laboratory contaminants are well below those of those in figure 1 (for DBP), as evident from the fact that small amounts of ES ions survive

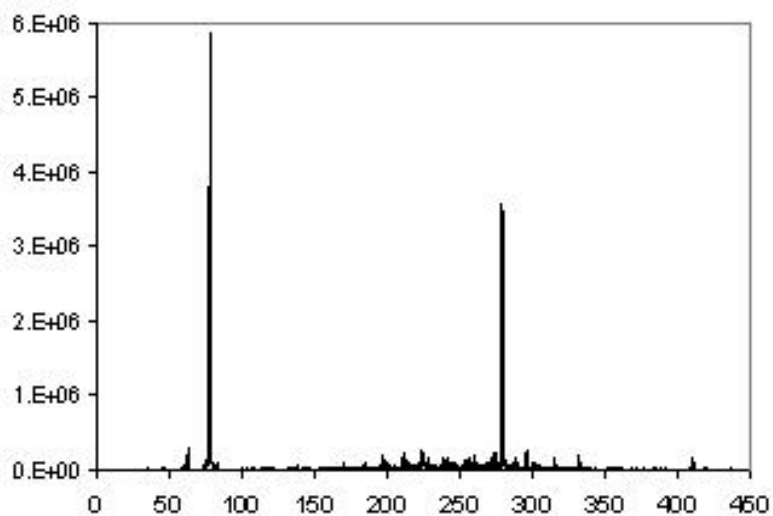


Figure 4

Figure 4: Result of a thorough cleaning of the ES chamber: The peak at 78 amu, corresponds to protonated ammonium acetate from the ammonium acetate buffer. The DBP peak is still visible

This second experiment indicated that the main source of DBP contamination was not associated to the gas line, but to the ES chamber. It was then purged with clean gas under heating. The o-rings used initially were also traded for Teflon gaskets. Finally this led to mass spectra such as that of figure 4, where the DBP peak is not suppressed, but the contaminant concentration does not consume all the charge available. This important point is evident from the large peak at 78 amu, corresponding to protonated ammonium acetate from the ammonium acetate buffer.

We next introduced 1 uL of trihexylamine (268.5 amu) in the glass seeding cell. This led to a spectrum with only the protonated amine peak (270.4 amu), with complete suppression of the ES ions as well as the DBP signal. We then cleaned up the glass cell with alcohol, and added 1uL of trioctylamine (353.7 amu). But the signal from the trihexylamine remained overwhelmingly dominant. After a far more thorough purging of the lines attached to the cell with clean gas under heated conditions, the spectrum of figure 5 was obtained. It is still dominated by a protonated trihexylamine peak, but shows additional peaks at 312.44 and 354.5 amu, the later being from protonated trioctylamine.

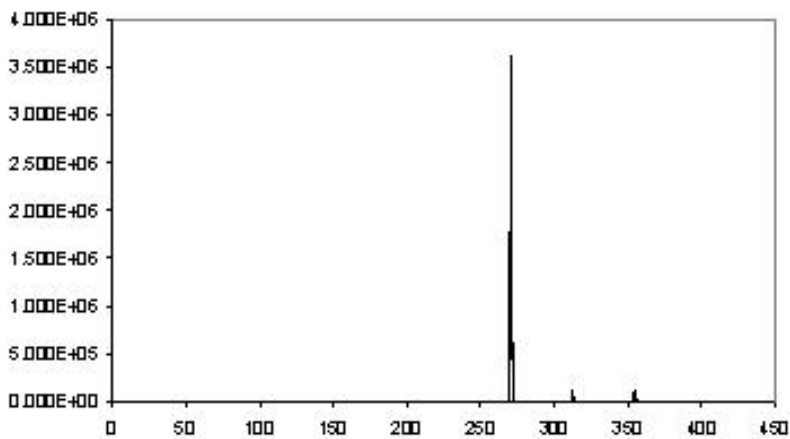


Figure 5

Figure 5: A more thorough cleaning of the glass cell finally yields the spectrum showing now a sizeable current of ES ions, as well as DBP and the two amines

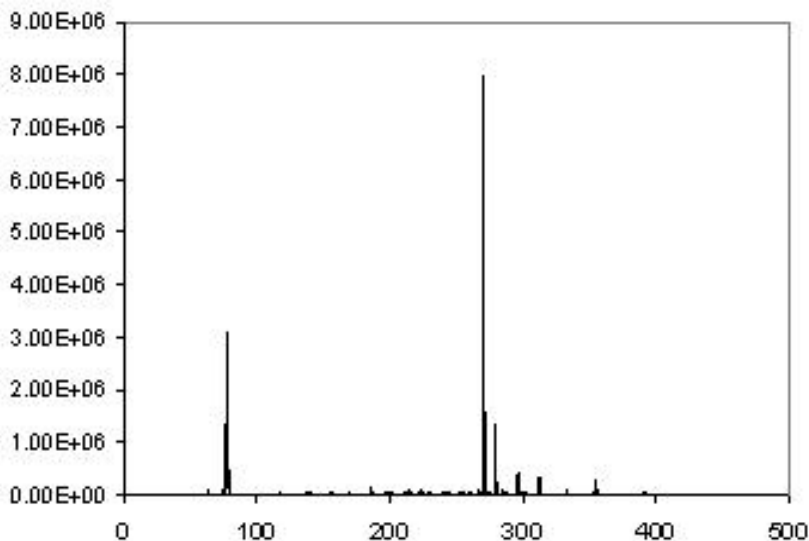


Figure 6

Figure 6: We finally tested also triodecylamine (TDA), but did not detect any signal. It is therefore clear that the minimum vapor pressure that can be detected by this scheme is intermediate between trioctyl and tridodecyl amine

A further test was made to test for the purity of the TDA. In this case, a 10^{-5} vol fraction was sprayed from a methanol solution, leading to the spectrum of figure 6. This confirming the intrinsic lack of sensitivity of the charging method to this low vapor pressure level. As a future test, we plan to pursue ES charging of this amine from ES of methanol, rather than methanol water (in which this amine is insoluble). This would

provide some interesting mechanistic information on whether the charging mechanism involves prior dissolution of the vapor on the drops, or direct charging from the ES ions

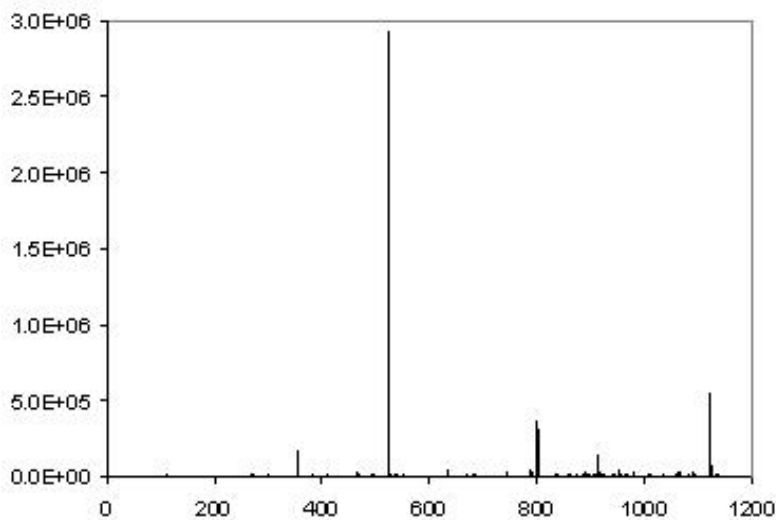


Figure 7

Figure 7: ES spectrum tridodecylamine ionized from the solution, showing that the sample is quite pure, and confirming the intrinsic lack of sensitivity of the charging method to this low vapor pressure level

ES ionization of Explosives, Narcotics, and Chemical Species

In experiments conducted by Fenn while at Yale, remarkable open air collection and detection sensitivities of explosives and narcotics were achieved using electrospray. In one case, the spectrum obtained with chloroform sprayed into open air, 1.5 ppb of RDX was detected. In another case, the air contained only 0.15 ppb of HMX and a peak was readily obtained. For narcotics, the air contained only 1.5 ppb of cocaine hydrochloride and the sprays were 1:1 methanol:water, acetone and chloroform respectively.

ES ionization of Particulate Species

A series of electrospray CDC particulate collection experiments were carried out during a CAC Phase I SBIR investigation under support from the USMC and Office of Naval Research this past year (M67854-03-C-5016). In these experiments, fluorescent polystyrene microspheres (Duke Scientific) ranging in diameter from 0.7 to 5 microns were aerosolized using a Collison nebulizer and introduced into a controlled glove box environment. A known particulate concentration was established and verified using a GT-521 Met-One Laser Particle Counter. Removal of the residual particles was achieved via a HEPA filter placed in the chamber. A separate 0.1 cubic meter enclosure which incorporated a single wick-fed electrospray source and laser particle counter was placed within the large chamber. A convective air flow was established within the small box so that the particle concentration matched that external to the electrospray test enclosure. Upon activation of the electrospray, the particle concentration dropped precipitously, achieving over 80%+ particulate removal in minutes with a non-optimized co-current spray. Shutting off the electrospray resulted in rapid increase of particle concentration.

2. INVESTIGATION

The subway aerosol environment was simulated as a controlled environment in the glove box shown below. Chemical and particulate species were aerosolized and introduced into this chamber for subsequent electro spray collection and detection.

Aerosol ES Getter Experimental Setup

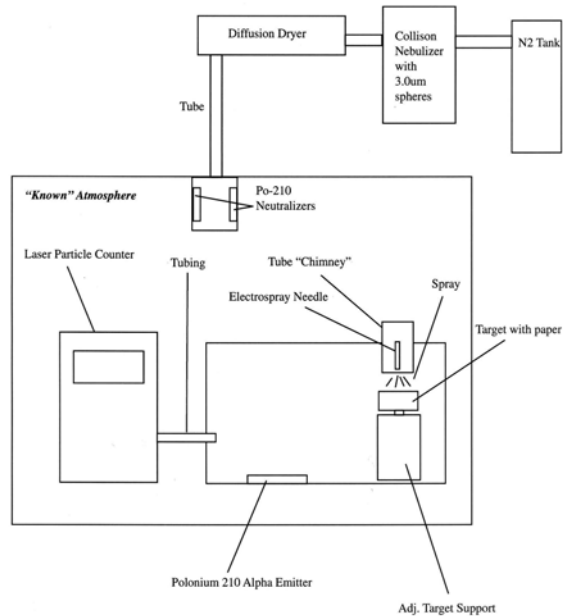


Figure 8: Schematic diagram of the glove box containing the ES test apparatus

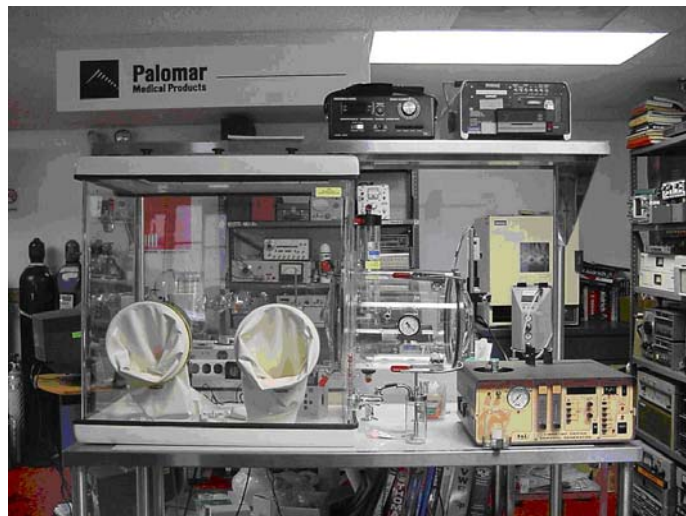
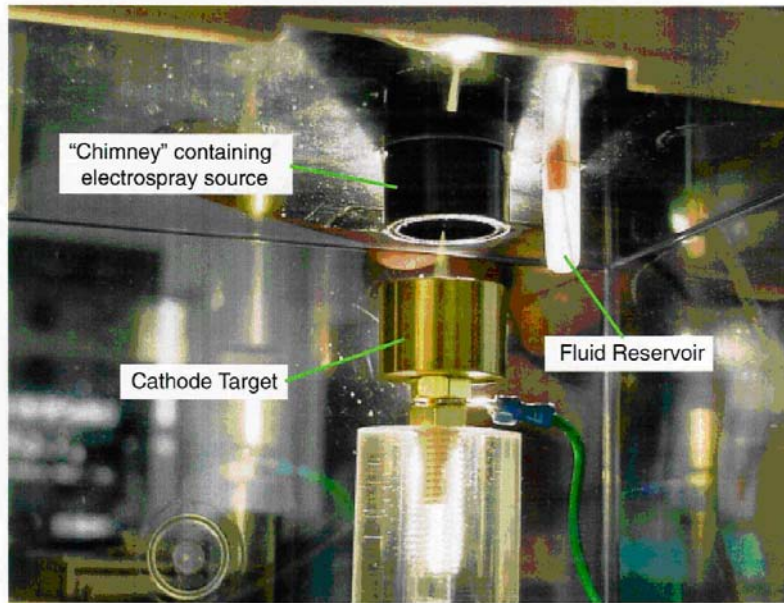


Figure 8

Figure 9: Photograph of the actual glove box used for testing



Note Tyndall Light Scattering effect of the electro spray... The efficacy of the electro spray is especially significant given that the spray "fan" shown here does not encompass the entire cross-sectional area of the incoming air stream. Even so, the incoming particulate media was attracted to, and captured by, the electro spray jet.

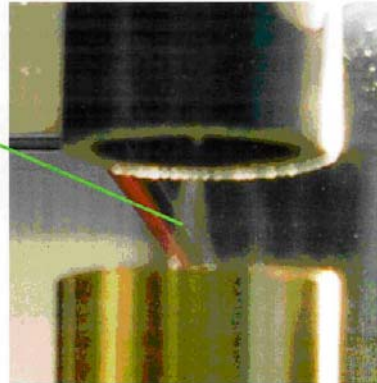


Figure 9

Figure 10: Photograph of the actual ES produced by the test unit

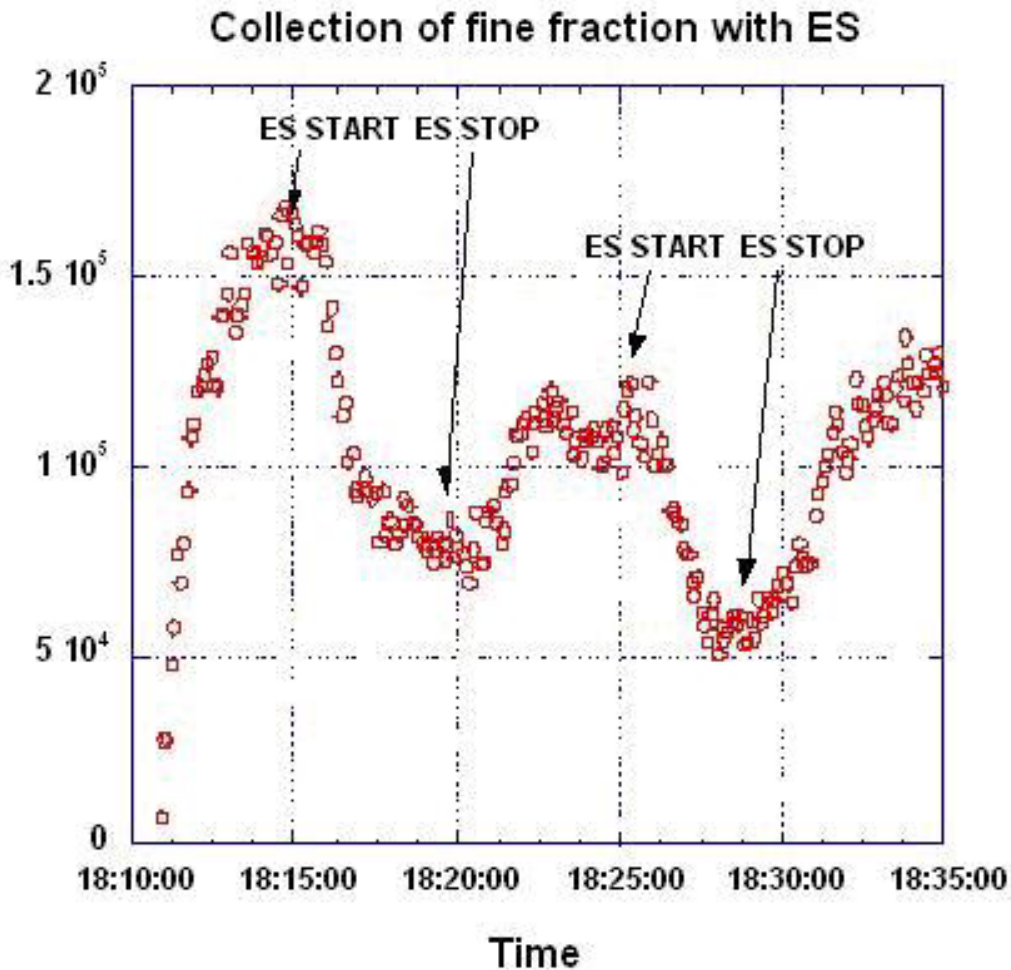


Figure 10

Figure 11: Plot of particle count vs. time to illustrate capture efficiency of the test unit

Applications of the Charged Droplet Detector (CDC)

The development of the Electro spray CDC prototype serves three purposes for the transit work, namely a means to effectively collect polar chemical and biological airborne species with minimal power requirements and essentially zero acoustical or RF emissions over a wide size range in ambient aerosols, a means to collect BWAs in a viable state, including directly onto culture media devoid of ozone, and an ability to combine the CDC with other detection instruments.

Data analysis and User Benefit of Prototype

The development of the CDC prototype serves two purposes for the proposed work, namely a means to effectively collect potentially dangerous chemical and biological agents in ambient aerosols and a feasibility study on integrating the CDC with detection instruments or methodologies. Whether the CDC can also serve as an effective means not only to sample the ambient air, but also to effectively clean contaminated air remains to be seen. The question rests on the level of particles that can be swept away from aerosol particles in the air, and the effects of a hostile background. This will be an important question to answer if the CDC is used in an environment such as the MTA, where a dirt and dust could overwhelm any air filtration technology.

Potential Interference to and Circumvention of the Collection Method

It is possible that a terrorist would attempt to design a spray system that does not create a charged aerosol by adding a spray of ions downstream of the spray nozzle. Any electric field applied to the nozzle will likely result in higher charge states and sprays from electrically grounded spray nozzles have been shown to generate highly charged droplets and particulates as well. The addition of an anti-static additive to the spray solution could result in a weakly charged aerosol, which needs to be recognized.

The CDC component of the prototype is known to be highly reliable. During the past two years of intermittent operation at CAC it has not clogged, failed, and required only minimal maintenance. Sources other than sprays can introduce highly charged particles into the environment due to tribo-electric effects. High charge states have been observed for particles of wind blown dust. Fogs and haze, which form by condensation processes, do not belong to this category and will not be investigated.

Operational Limits and Implications for Detection of BWAs

The collection method is emphasized with regard to chemical and biological airborne species, as the majority of aerosolized warfare agents will be chemical or biological in nature. Bio-species in particular, can remain lethal over vast distances from the point of release whereas toxic gases released from a point source will suffer rapid dilution by the ambient air convection currents resulting in an increasingly benign state. More research and information from those more knowledgeable in the field of BWA defense will be required before the proposers can offer definitive opinions on this subject. Smoke is a neutral entity that can impede ES droplets, so care must be undertaken to account for this. Many commercial smoke detectors have special filters that allow them to be used in harsh environments while still maintaining their sensitivity to smoke or smoke-like aerosols.



Figure 11

Figure 12: Our aerosol investigation was continued this fall at the Church Street Station where the ‘F’ train passes through the station



Figure 12

Figure 13: Shows a photograph of some of the research team members from Connecticut Analytical Corporation (in addition to Dr. Chuck Burrus) taking aerosol particle measurements using a MET-ONE GT-521 particle analyzer

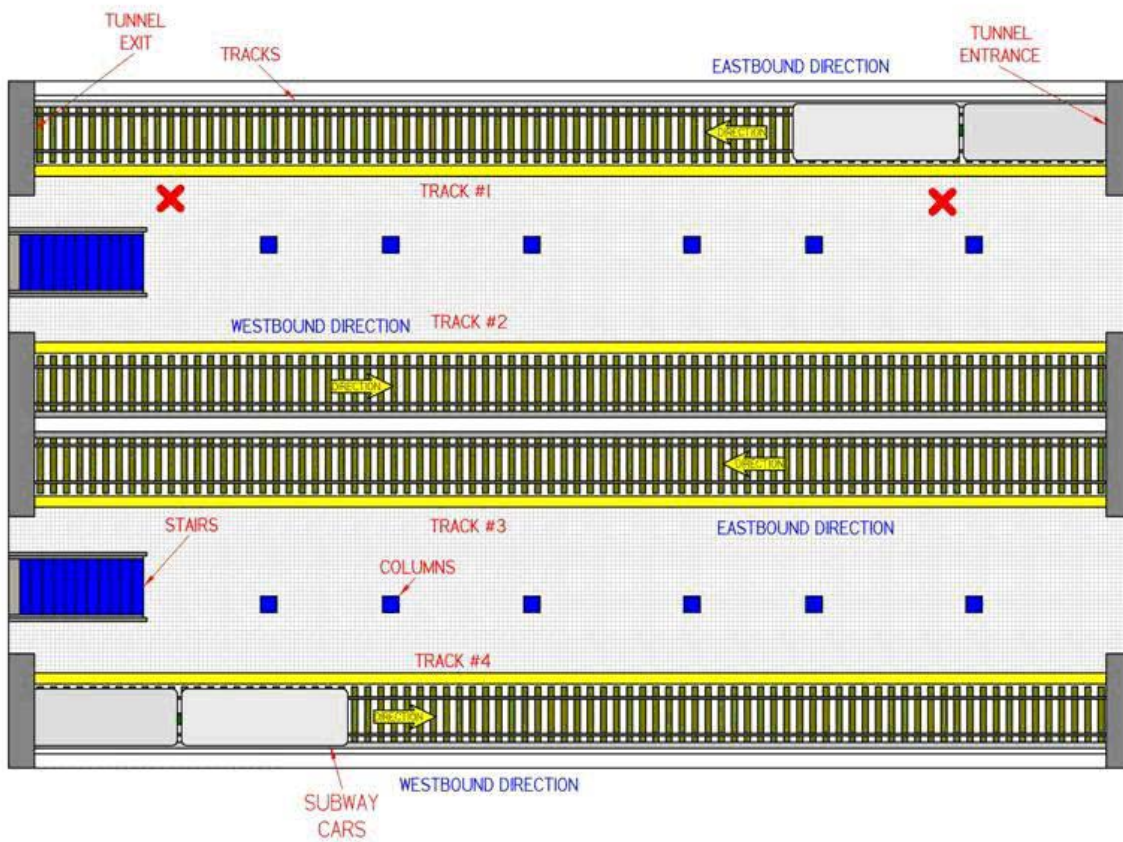


Figure 13

Figure 14: Shows an image of relative placement of the MET-ONE Laser Particle Counter. The two red X's indicate the relative position related to the tunnel entrance (Right) and tunnel exit (Left) at the

Church Street station. All references to Eastbound and westbound trains are related to track numbers 1 and 2

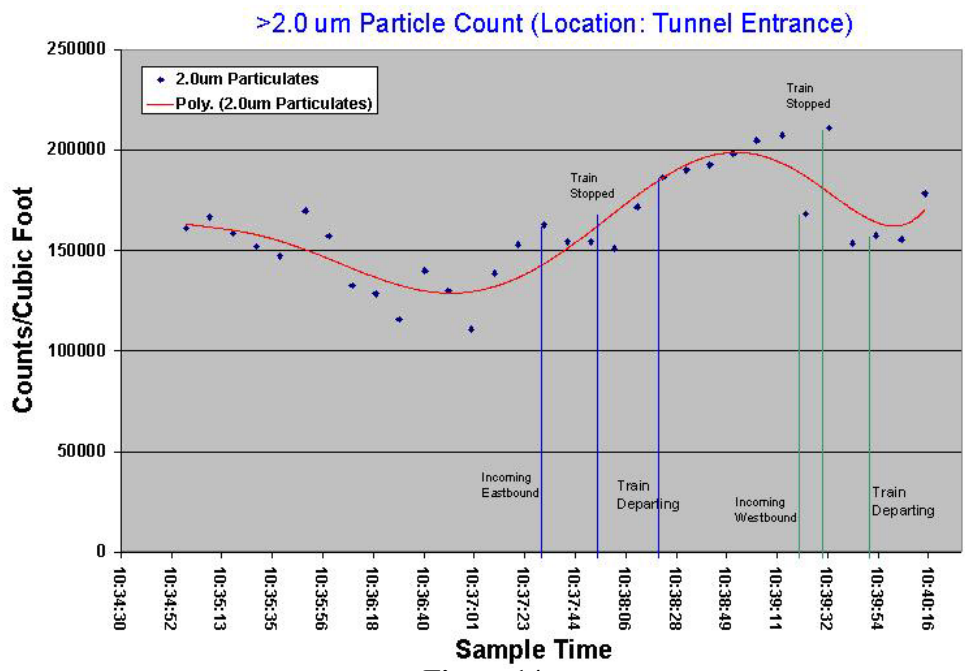


Figure 14

Figure 15: Illustrated here is the resultant graph of a respirable particle plume. The graph shows the resultant action of particles equal to or greater than 2.0 um. The vertical axis is absolute particle count per cubic foot, and the horizontal axis is actual time of the sample. The variation of the particle count is dependent upon train motion

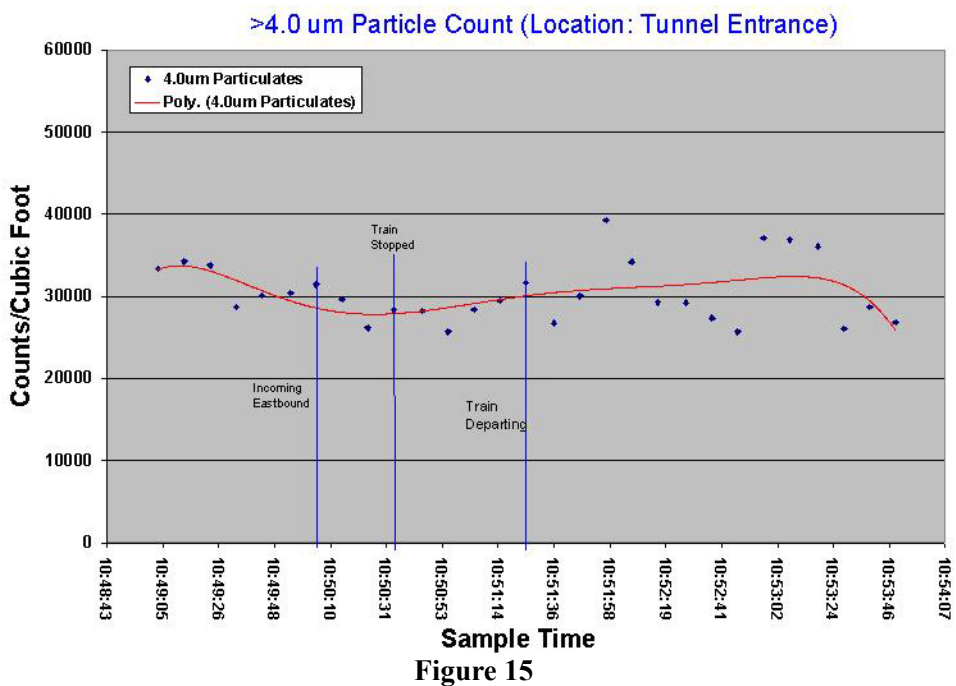


Figure 15

Figure 16: Illustrated above is another graph showing a respirable particle plume. The graph shows the resultant action of particles equal to or greater than 4.0 um. The vertical axis is absolute particle count

per cubic foot, and the horizontal axis is actual time of the sample. The variation of the particle count is dependent upon train motion

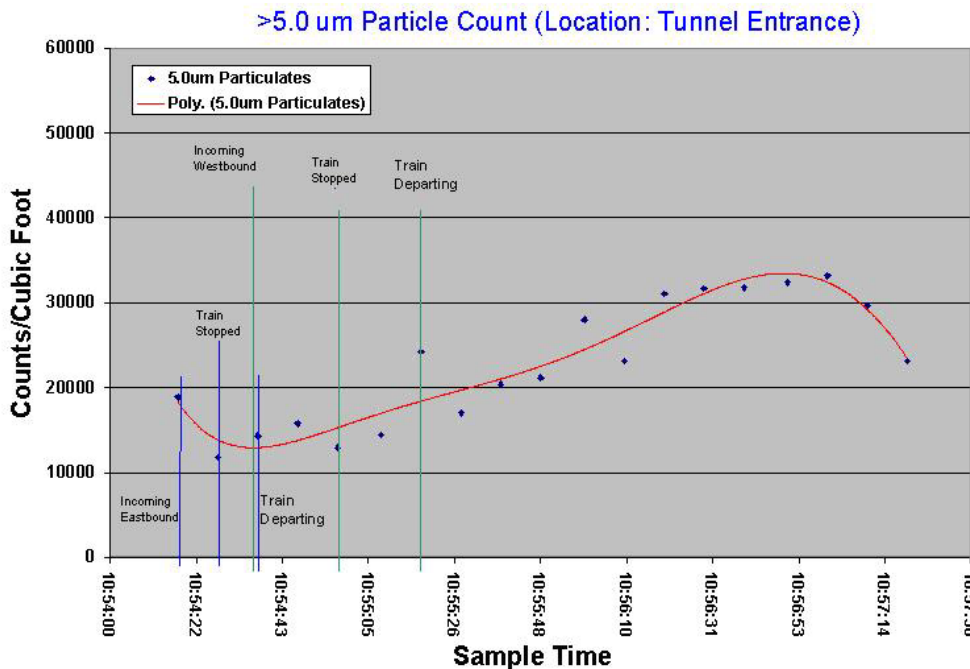


Figure 16

Figure 17: This is a graph showing a respirable particle plume. The graph shows the resultant action of particles equal to or greater than 5.0 um. The vertical axis is absolute particle count per cubic foot, and the horizontal axis is actual time of the sample. The variation of the particle count is dependent upon train motion

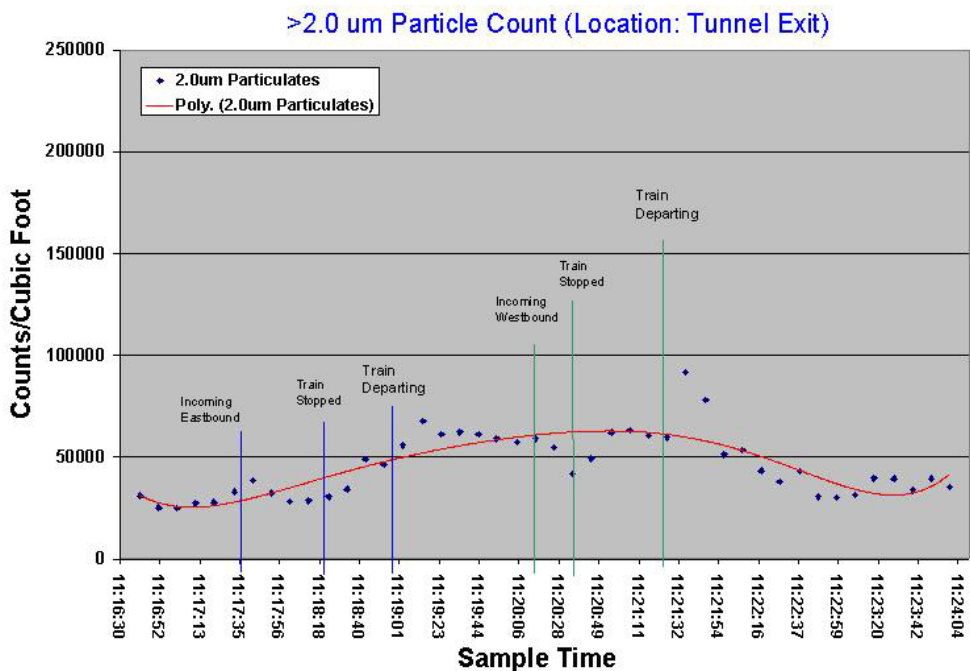


Figure 17

Figure 18: Shown here is another graph which displays a respirable particle plume at the exit of the tunnel. The graph shows the resultant action of particles equal to or greater than 2.0 um. The vertical

axis is absolute particle count per cubic foot, and the horizontal axis is actual time of the sample. The variation of the particle count is dependent upon train motion

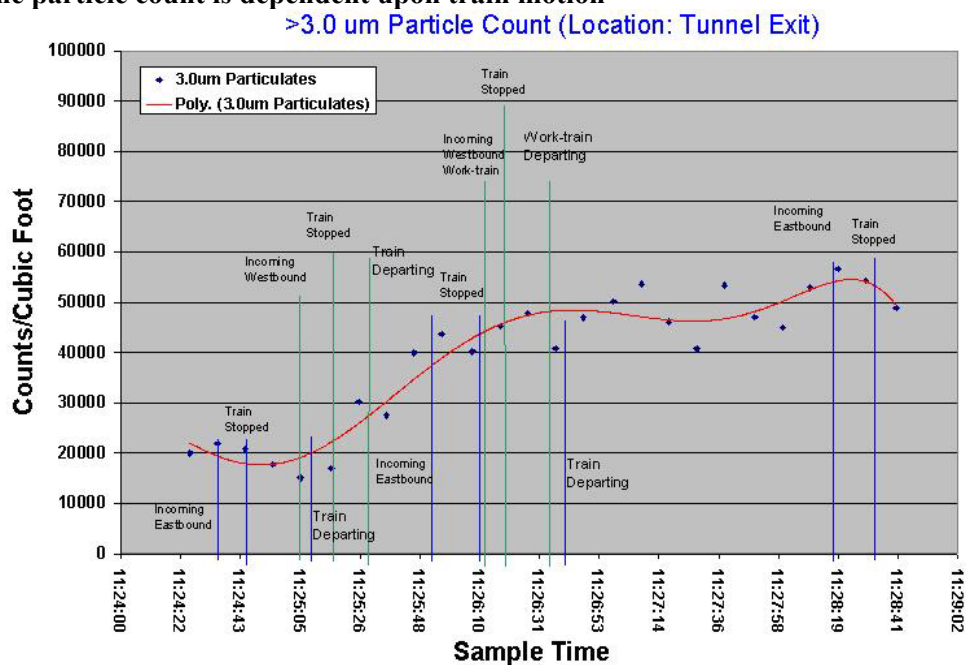


Figure 18

Figure 19: Shown above is a graph showing a respirable particle plume at the exit of the tunnel. The graph shows the resultant action of particles equal to or greater than 3.0 um. The vertical axis is absolute particle count per cubic foot, and the horizontal axis is actual time of the sample. The variation of the particle count is dependent upon train motion

All recorded data supports the supposition that the subway cars have a major effect on particle plume behavior. This was expected, and validates CAC’s initial assumptions. The larger size particles were chosen to be analyzed in this particular exercise as the smaller sub-micron particles would remain aloft for a greater amount of time, and thus would not show such a well organized plume growth and decay. The larger respirable particles would exhibit a greater correlation with transient events, such as a train entering or leaving a station. All graphs indicate an increase in absolute particle count as the train enters the station. It is extremely difficult to characterize plume behavior based on relatively few measurements done in a single trip, as many factors need to be considered, such as, humidity, temperature, time of year (pollen count, etc), number and movement of people in the station, the type of train passing through the station (i.e. a work train with vacuum equipment cleaning the tracks, etc.), time of day (rush hour, early morning, late night, etc.), external weather conditions (snow, rain, hot, humid, smog, etc.), along with many other difficult to categorize events, such as work done for station maintenance (i.e. welding, painting, cleaning, sandblasting, etc.), along with various pest control measures.

To make a very detailed study to characterize all possible conditions would require a large quantity of sensors placed throughout each individual station for many months, since each individual station would have its own unique characteristics or “behavioral response” to varying conditions. In addition to this data, it would have to be correlated with routine maintenance to determine any unusual sensor responses based upon interaction with cleaning agents, paint fumes, welding fumes, pest sprays, etc.

In spite of all these difficulties, CAC feels that it is possible to eventually develop a “normal” background behavior for stations, and also be able to modify this “normal” background to account for transient events that could be mistaken as an anomaly. The purpose of this exercise was to determine the behavior of non-buoyant

particle plumes caused by train movement. In addition to this, the interior and exterior of subway cars was studied to determine an effective collector/detector placement.

CAC has been studying several methods for detection of the presence of chemical and biological compounds. Some of these incorporate the usage of aforementioned MIP's (Molecularly Imprinted Polymers) that are highly selective and will target only a specific chemical compound. CAC has already shown that the MIP's can detect a variety of chemical compounds and biological agents such as Anthrax. By placing a long strip of MIP coated tape inside a subway tunnel, a relatively simple laser interrogation system could be used to determine for the presence of chemical or biological agents. Below is a diagram showing an image of one possible scenario. The MIP coated tape is indicated as item 40 in figure 20.

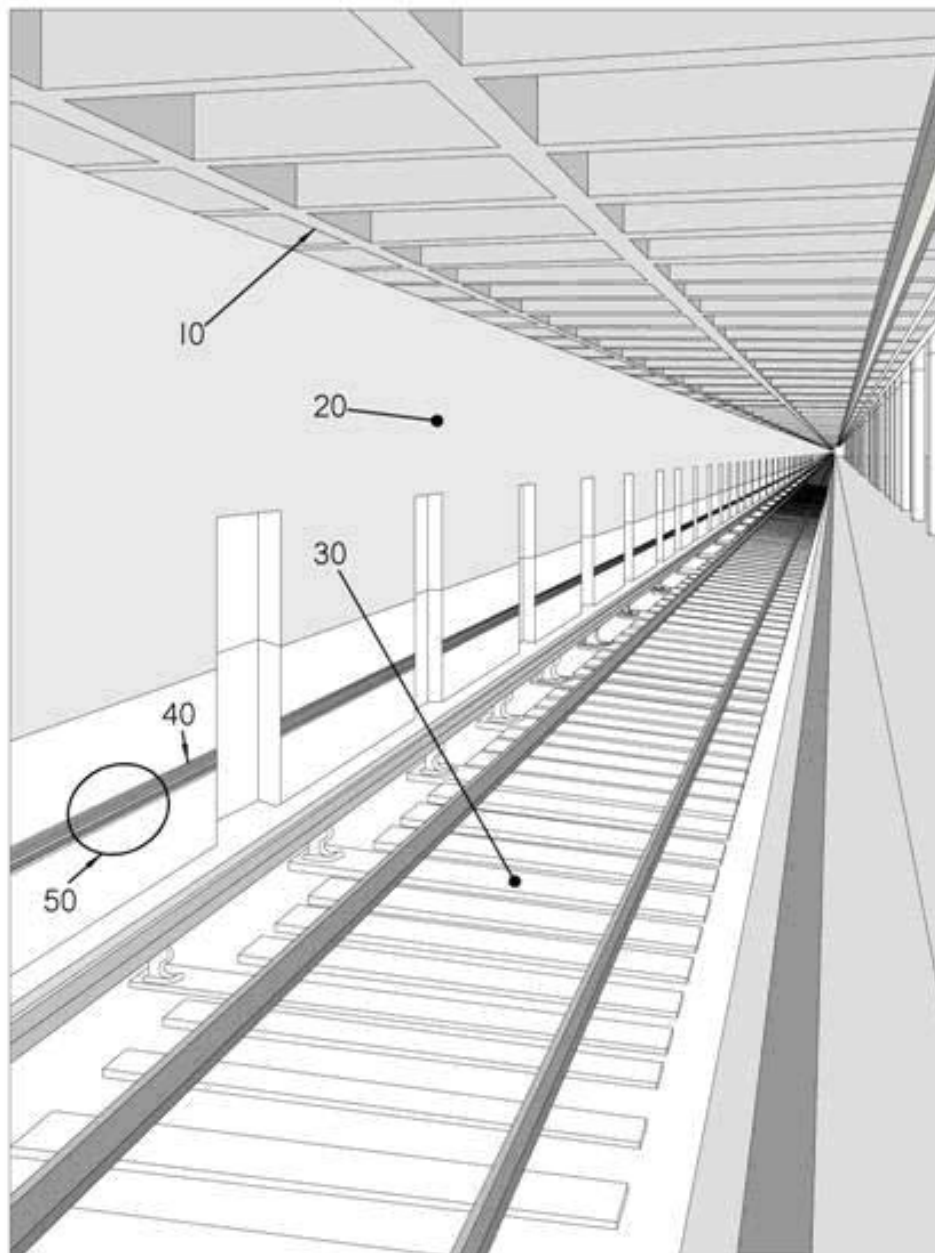


Figure 19

Figure 20: A diagram showing a long strip of MIP coated tape inside a subway tunnel that could be interrogated by a relatively simple laser interrogation system for the presence of chemical or biological agents. The MIP coated tape is indicated as item 40

In addition to using having a system wide MIP coated passive sensor tape throughout the subway system, each train itself could be used to actively collect and detect for the presence of chemical and biological agents. MIP's can be thought of as synthetic antigens, with the ability to be programmed for specific target species. A matrix of different MIP's could enable a highly selective chemical "fingerprint" to be produced, thereby eliminating any false positives or false alarms. The diagram below indicates how train motion could be used to enable active sampling.

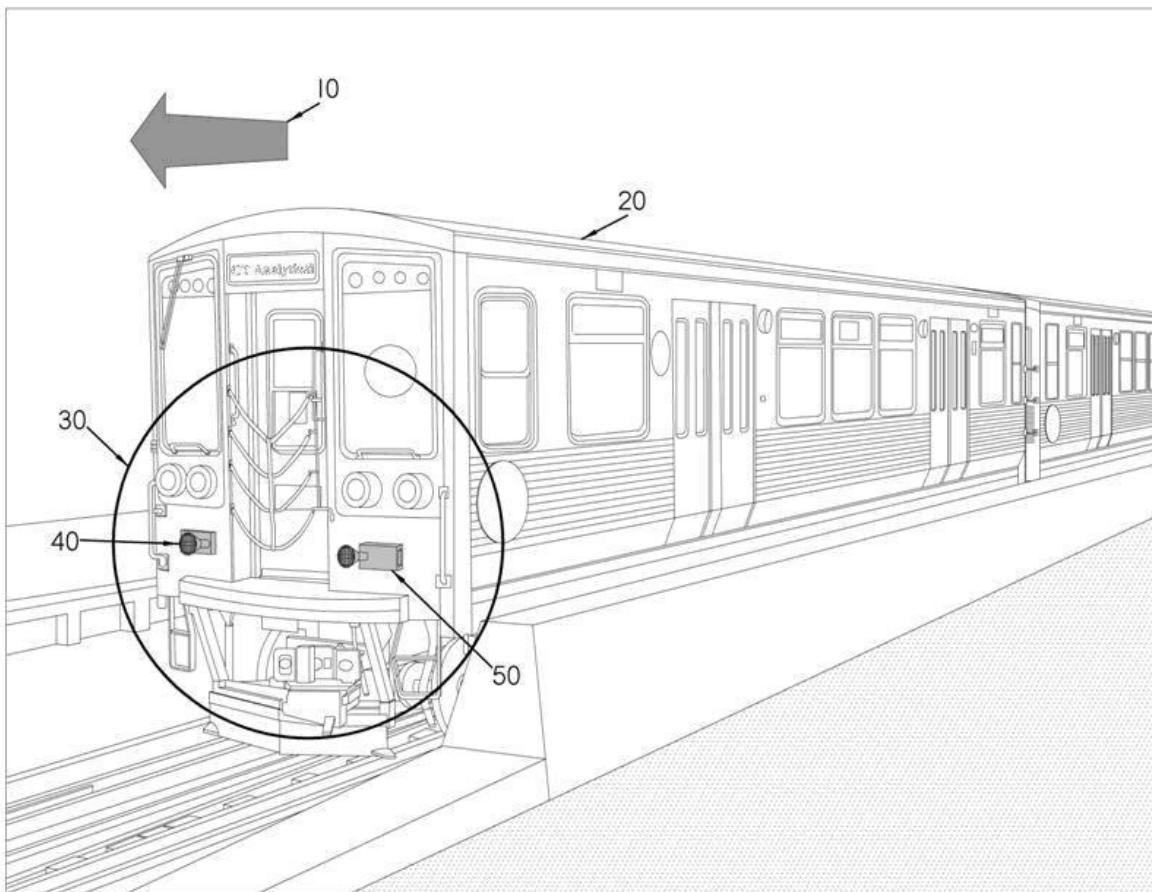


Figure 20

Figure 21: A diagram showing placement of collection units on a subway car. The collection units are identified as items 40 and 50

As each subway car travels throughout the subway system, an active sampling and detection scheme could be realized. This data could then be signaled to a specific monitoring agency via. Wireless transmission and/or carrier current modulation through the tracks. By utilizing this method, a real-time active system-wide chemical and biological monitoring system could be done effectively and efficiently. If wanted, the train engineer could be informed of an "anomaly" as it happens in real-time. This should be discussed as it may cause undue stress and panic. This subject will have to be further discussed.

The individual train sensors would be placed at the front of the first car, with additional sensor placed underneath to give an immediate indication of any chemical or biological agents that are placed at track level.

Some compounds, such as Anthrax could be simply placed at track level and dispersed throughout the system by the motion of each subway car.

Below is a close-up diagram of the front part of a subway car equipped with a collector/detector. The collector/detector uses the forward motion of the train to sample large quantities of air without the need for complicated and expensive air pumps. This feature makes this detection methodology more reliable and will reduce any routine maintenance involved.

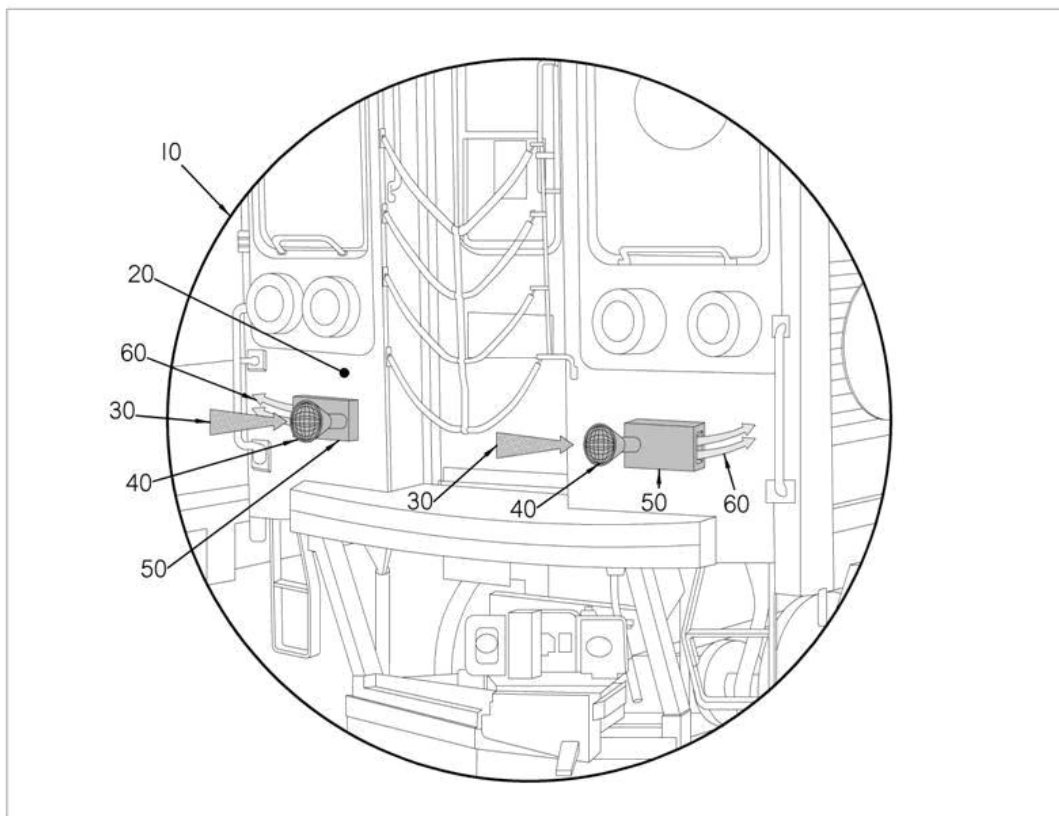


Figure 21

Figure 22: Shown is a diagram of a close-up diagram of the front part of a subway car equipped with a collector/detector. The collection units are identified as items 40 and 50

The forward motion of the subway car would act as an active air-sampling pump. By using the forward motion of the subway car, any additional air pumps could be eliminated, and reduce the size, cost and complexity of the collector/detector while increasing its reliability and efficiency.

Earlier electrospray collection system did not extract all particulate and chemical species from the incoming air stream as the ES jet plume or fan did not expand enough to provide charge transfer to the air flow. Instead, we propose using an ES jet source charged HV+ with respect to an annulus or grid that is at ground potential with respect to the ES source. At a point further downstream, we propose a MIP detector target that is small in area, charged HV- with respect to the annulus or housing structure. By doing so, all incoming air with polarizable species (chemical and biological) will be captured by the electrospray droplets and refocused and deposited onto the target which contains the MIP detector polymer. Utilizing selective laser interrogation, the fluorescence signature can be observed using suitable CCD or other optical detector. See below.

3. PLANS FOR IMPLEMENTATION

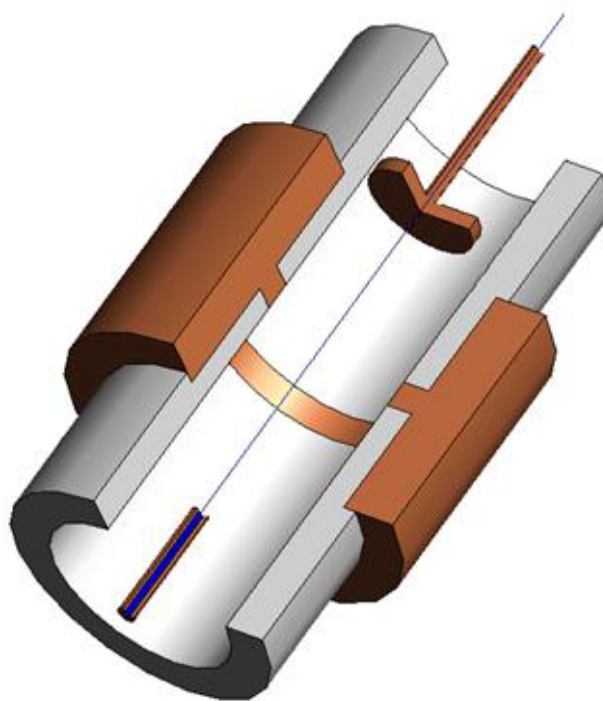
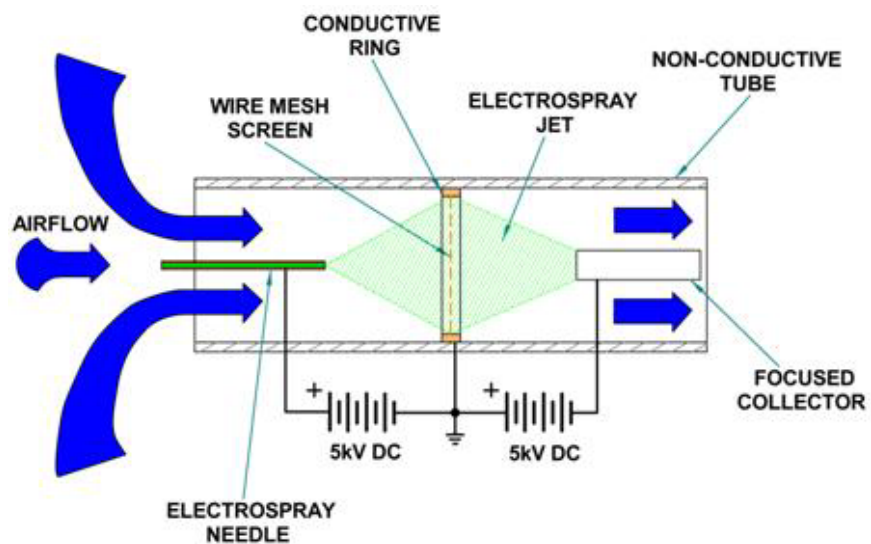


Figure 22

Figure 23: Shown is a schematic diagram and cutaway three dimensional image of the ES collection/detection unit

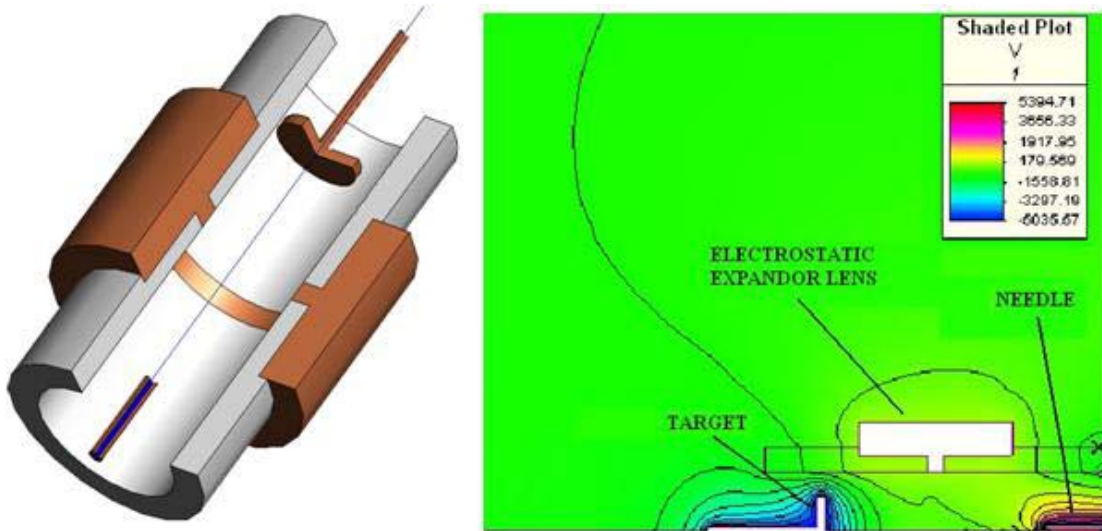


Figure 23

Figure 24: Illustration of proposed electrostatic aerosol collector is shown on the left. The wick-fed needle source is shown at the bottom of the cylindrical structure, and is charged high voltage positive with respect to a grounded annular ring in the cylinder midsection. This ring will serve to expand the spray droplet jet so that incoming particle laden air encounters the droplet cloud. The cloud, after particle capture, is focused to a negatively charged high voltage collector shown at the left of the flight tube. This collector may serve as a witness plate where laser interrogation of collected species may be performed. The field diagram is shown in the right hand image

Potential Electrostatic collector locations were reviewed after examining rolling stock at the MTA repair facility in Coney Island. This review was again made possible through the invaluable interaction of Dr. Charles Burrus.



Figure 24

Figure 25: Shown is a photograph of some possible locations inside the subway car to place a detection/collection unit



Figure 25

Figure 26: Shown is a photograph of some possible locations inside the subway car to place a detection/collection unit



Figure 26

Figure 27: Shown is a photograph of some possible locations inside the subway car to place a detection/collection unit. This photograph indicates a view of the subway cars air handling duct

Telemetry Design & Computer Interface:

In the event of a chemical release and activation of the chemical collector-detector, a means will be needed to notify the appropriate authorities. It is proposed that this be accomplished via a wireless radio telemetry system. We investigated several methods to achieve this goal, including cellular radio transmission and high frequency spread spectrum telemetry. This task will also develop a method to communicate central office notification of the nature and magnitude of the hazard detected.

Chemical Alarm Telemetry & Notification

The chemical sensors can be designed for fully autonomous functionality, providing battery backup in case of a system AC power failure. Fire reporting equipment has for some time had the ability to make use of wireless notification appliances (i.e. Smoke Detectors and Pull-Stations). Each wireless device can communicate its status at a predetermined interval or immediately on a change of state (Alarm, Tamper condition, Low Battery, Maintenance condition, etc.). Without extra effort in installing sensors (i.e. no hard wiring necessary), the chemical sensors could employ this same technology. A wireless chemical detector can be easily installed in any train car or station, with a typical range of several hundred feet. Existing battery technology will also enable operation for several years before a new cell must be installed. For more station security and fail-safe operation, a wired version could be realized, with battery backup. Each method has advantages and disadvantages. Each chemical detector can be assigned its own unique serial or I.D. number, and this number can be correlated with a specific installation location to give rapid regional assessments to the location and severity of a given event. The current status of each chemical sensor can be communicated wirelessly, or over the AC power lines by carrier current to give a rapid indication of an approaching subway train that has been contaminated with some type of chemical weapon. With a pooling of information by various agencies, a quick determination can be made as to the source of a chemical attack if more than one vehicle is contaminated.

NFPA 130 specifies fire protection and life safety requirements for underground, surface, and elevated fixed guideway transit systems including trainways, vehicles, passenger rail transit stations and vehicle areas. Since smoke is composed of a plurality of micron sized particles, the movement of smoke can be applied to chemical sensors.

Potential causes of disruption of airflow in vehicles, such as rolling stock, are as follows:

- a) Motion or change in movement of vehicle.
- b) Movement of occupants inside vehicle.
- c) Movement of airflow due to heating (occupant body heat, heaters, etc.).
- d) Opening and closing of doors or windows.
- e) Pressure changes with change in elevation, or change in aboveground or underground movement.
- f) Any change in pressurization of vehicle.

Potential causes of disruption of airflow in structures are as follows:

- a) HVAC air movement.
- b) Air pressure changes due to elevator operation or train motion through station (Piston effect).
- c) Movement of occupants (to a lesser extent than previously discussed).
- d) Opening and closing of doors or windows.

Note: Consideration to gas density is required since a heavier than air toxin may escape overhead detection schemes or technologies.

Significant research has been accumulated modeling airflow inside closed structures by many organizations; one of particular note is NIST (National Institute of Standards and Technology). NIST has done work on a computer-modeling program called FDS (Fire Dynamics Simulator). The FDS program has the capability of describing the transport of mass, momentum, and energy from fire induced flows. Although a program that models air movement/modification based on a localized heat source such as a fire is not a direct analogue to toxic gas dispersal, it can easily be used to determine normal airflow based on static, or quasi-static conditions for determination of detector sensors for maximum efficiency. With the research already done in the field of smoke/fire detection, a thorough comprehensive model can be developed for mass transit systems. Shown below is a picture of a computer-generated image of the Smithsonian Institutes, Industry and Technology museum. The picture below depicts a CAD-modeled structure of the museum interior showing heat and airflow conditions if a fire was set at a specific location.

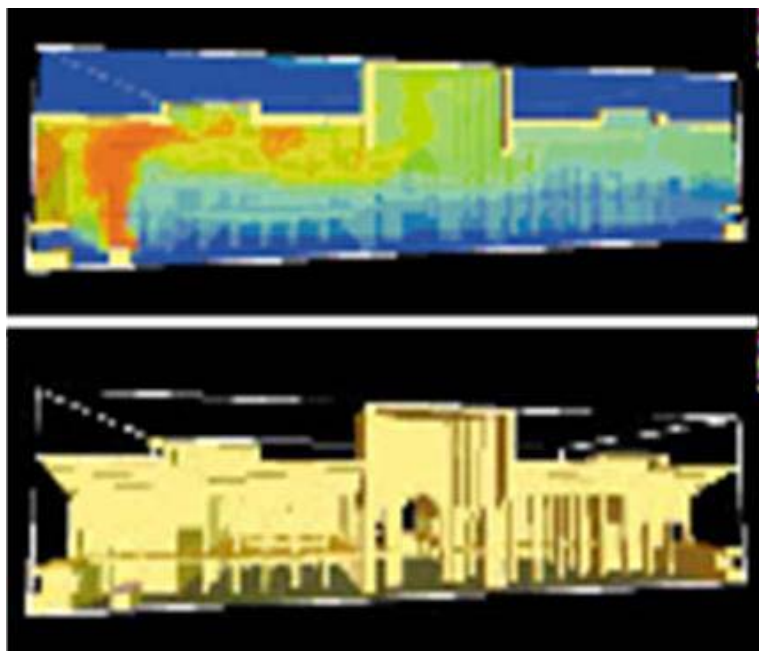


Figure 27

Figure 28: Shown is a computer generated image using CFD modeling to determine airflow conditions during a small fire

In addition to the aforementioned airflow modeling, care must be taken to account for non-buoyant plume flow. When air is heated, it becomes buoyant, and many chemical compounds are buoyant; however, some chemicals are non-buoyant (heavier than air) and must be modeled accordingly. This buoyant/non-buoyant modeling will assure that an entire station could be categorized based on sensor data, and the safest route of egress established.

Wireless Sensor Data Collection and Communication:

The wireless RF communication transceiver would be a highly “Jam resistant”, spread spectrum radio transceiver designed for license-free operation in the 902-928 MHz frequency band. The transceiver unit already investigated by CAC employs digital signal processing (DSP) technology that is highly reliable for long-distance communications, even in the presence of weak signals or interference. Excessive noise and electrical interference would be expected in Subway systems. Integrated DSP technology also makes it

possible to monitor radio operation and troubleshoot problems remotely, without going to the remote radio site. With appropriate software at the master station, diagnostic data can be obtained on any DSP radio in the system, even while sensor data is being transmitted. The transceiver is housed in a compact, rugged die-cast enclosure that need only be protected from direct exposure to the elements. No jumper settings or manual adjustments are required to configure the radio for operation. Each transceiver could be used as a wireless repeater utilizing the Store-and-Forward protocol, in which a networked transceiver receives RF data and retransmits it to the master. Store and forward is defined as a network using vertically adjacent sub-networks which alternate communicating upstream and downstream. The wireless transceivers perform store and forward at the internal data frame level (not the user data level) which allows the transceiver to stream data with minimal latency through each Extension/Repeater radio station. Listed below are several key features of the Spread Spectrum transceiver. These are designed to ease the installation and configuration of the radio, while retaining the ability to make changes in the future.

- 128 frequencies over 902–928 MHz, subdivided into eight frequency zones
- Fast Frequency Hopping Spread Spectrum (Fast FH-SS) communications
- Configurable operating zones to omit frequencies with constant interference
- 65,000 available network addresses
- Network-wide configuration from the master station; eliminates most trips to remote sites and enables remote diagnostics to be performed
- Ability to use encryption to ensure radio link security
- Peak-hold RSSI, averaged over eight hop cycles
- Optional bandpass filter to eliminate possible interference issues in highly RF congested urban locations
- Ability to use secure passwords to prevent system from being compromised
- Store-and-Forward repeater operation allows each individual wireless transceiver to function as a wireless repeater while maintaining synchronization with master, adding increased distance while still complying with FCC regulations
- Built in DSP to perform continuous self diagnostics and signal conditioning
- Same hardware for master or remote configuration
- Available Forward Error Correction (FER) and 16 bit CRC
- User programmable RF power output to allow for compliance with FCC regulations when changing to different “high gain” antenna such as a Yagi
- Low current consumption - less than 8 mA in “sleep” mode

The main difference between a traditional (licensed) radio and the Spread Spectrum transceiver is that this unit “hops” from channel to channel many times per second (fast hop) using a specific hop pattern applied to all radios in the network. A distinct hopping pattern is provided for each of the 65,000 available network addresses, thereby minimizing the chance of interference with other spread spectrum systems. In the USA, and certain other countries, no license is required to install and operate this type of radio system, provided that RF power and antenna gain restrictions are observed, this functionality will prove useful if these remote sensors are to be installed in U.S. embassy’s located in foreign countries. One key advantage in using Frequency Hopping Spread Spectrum as opposed to Direct Sequence Spread Spectrum is related to the so-called “near-far” problem. This problem arises when there are multiple transmitters that are geographically separated and transmitting in the same band. If receiver i is trying to receive the i th signal, but transmitter k is geographically much closer, receiver i will receive signal k at a much higher power level than signal i . If there is perfect synchronization between all users and all transmitters, the importance of this issue is decreased, because of the Pseudorandom Noise (PN) sequence, in which case the orthogonal code should remove the interference.

In a real-world situation, where perfect synchronization can never be guaranteed, the near-far problem severely impacts DS-SS systems, whereas FH-SS systems, while impacted, can be designed to overcome this problem. In today’s systems, where the data rates are often high enough that the chip rate is not that much

higher than the data rate, this amount of processing gain is by no means assured, and thus DS-SS can suffer greatly from this problem. DS-SS systems have tried to combat this power problem by using a technique called “power-control”. The transmitter adaptively changes its transmitter power based on the distance to the receiver, so as not to interfere with other transmissions; however, this system is not perfect either. Reducing transmission power increases the vulnerability to corruption due to other sources (such as jammers), and also increases the complexity of the communication between the receiver and transmitter (some sort of constant monitor of distance is needed); thus this solution is far from perfect. In FH-SS, the situation is somewhat better. Again, for perfect orthogonality, this is not an issue, just as in DS-SS; however, FH-SS has advantages over DS-SS in a few respects. First of all, the fact that there are N frequency bands decreases the probability of this type of interference, i.e. the i th signal and k th signal have to overlap, and there is a one in N (or less) chance that they will overlap. In DS-SS, all the received signals are correlated equally, whereas in FH-SS, since the actual data still takes up the same bandwidth as it originally did, a bandpass filter limited to the width of the expected data signal will kill the signals in the $N-1$ other sub-bands. In order to cause destructive interference, the k th signal must be in the same sub-band as the i th signal at the time that the receiver correlates its received signal. The current wireless Spread Spectrum transceivers that will be used in this proposal overcome any acquisition and synchronization problems.

For remote interrogation, diagnostic data from a remote radio can be obtained by connecting a laptop or personal computer running proprietary diagnostics software to any radio in the network, including the master. If a PC is connected to any radio in the network, intrusive polling (polling which briefly interrupts sensor data transmission) can be performed, or non-intrusive polling can perform diagnostics without interrupting sensor data transmission. While the laptop is connected to the remote sensor unit, the wireless transceivers firmware could be easily upgraded without any special tools, just the proprietary software running on the laptop PC and a RJ-11 to DB-9 Adapter Cable. This will ensure that the latest and greatest software is running on each wireless transceiver.

The Master controls the synchronization for a given network for all modes by broadcasting a command from the Master to all radio units in the associated network either directly or through an Extension radio (repeater). Extensions or extension radios are single radios that serve as bridges between adjacent sub-network levels. Extensions will undertake a “remote” personality in one timeslot and a “master” personality in the alternate timeslot and provide communications with associated Remotes downstream. Extensions behave like two radios with their data ports tied together, first synchronizing with their upstream Master during their Remote personality period, and then providing synchronization signals to dependent Remotes downstream during its Master personality period. All Remotes must synchronize to a corresponding Master for communication to be realized.

For security concerns, the operation and management of a wireless network is becoming increasing dependent on electronic information flow. An accompanying concern becomes the security of the communication infrastructure and the security of the data itself. The wireless Spread Spectrum transceiver takes this matter seriously, and provides several means for protecting the data carried over its wireless products. The wireless transceivers address this issue primarily through the use of the following items:

- 1) A proprietary modem/data link layer—Data signals are processed using code and hardware specifically designed to handle this
- 2) A unique Network Address—This provides a unique identifier for each radio in a network. A radio is not addressable unless this unique code is included in the data string
- 3) An optional encryption value (code) could be used - Setting an encryption code scrambles the radio’s hop pattern and encrypts payload data content. A radio requires the correct Network Address and encryption code value in order to synchronize to the master

The items described above provide sufficient security for a typical wireless system. For even greater security for more highly sensitive applications, it is possible to employ application level encryption into the polling protocols to further protect their systems. Third party software tools are available for adding encryption, and these should be considered as part of any advanced encryption scheme.

4. CONCLUSIONS

The Transit-40 research project objective was to employ electrospray ionization methodologies toward transit counter-terror chemical detection. (It should be noted that a detector is in reality a combination of collection of a given analyte and a means of identification...the combination of collection-identification forms a “detector”).

During the course of this investigation, it became apparent that two solutions were required for an effective chemical detector for subway transit applications. Two detectors are required, one or more inside each piece of rolling stock with another outside. The latter requirement was initially perplexing since as the train moves through the tunnel, the amount of air disruption can disperse a terror agent rapidly. Dr. Burrus has pointed out that on an average day, the NYC subway moves over 5 million people and in so doing, the system breathes - drawing air behind trains, pushing air forward in front and up through the vents to the street. During 1966, the US Army conducted a covert operation where supposedly innocuous spores were placed in glass bulbs and dropped off select trains in the NYC subway, and the spores were spread throughout the system in a matter of hours.

Furthermore, if an “anomaly” is detected in the NYC system, it is required that an actual sample be taken (by whom is still a matter of debate). The sample is then taken to a laboratory, and conclusive identification accomplished, using PCR or Polymerase Chain Reaction. Only once a positive identification has been made and the Mayors Office so advised, can a decision be made to shut down the system if required. Regretfully, the current paradigm of events has a very long time constant, and by the time a positive attack has been made and the decision made to shut down the subways, millions of passengers could be afflicted.

How then, can we mitigate the spread of a chemical or biological agent, collect a representative sample of the agent without destroying it (necessary as if a terrorist develops novel destructive agents we need to reverse engineer these agents in order to mount a defense), reduce the time required to identify an agent and minimize false positives? While we were tasked with employing the gettering or collection capability of an electrospray (*a process developed by our friend and colleague Dr. John Fenn - a member of the National Academy of Sciences and 2002 Nobel Laureate in Chemistry*) we found we could apply the identification method used with our electrospray sampler inside a train in a new and novel way outside of the vehicle and solve the aforementioned problems. The identification method employed relies on the sensitivity and specificity of select chemical species whose molecular shape is custom imprinted onto the surface of a specially prepared polymer.

The species so adsorbed onto the surface of these Molecularly Imprinted Polymers or MIPs (First postulated by Nobel Laureate Dr. Linus Pauling) and “interrogated” by a suitable laser, results in a predicative and reproducible fluorescence signature indicative of the agent targeted. As a result of experiments under US Army support carried out by our colleague and consultant for this project Dr. Gary Tepper of Virginia Commonwealth University, chemicals indicative of Anthrax (dipicolinic acid) in a pond or berm were remotely detected at over 4,000 feet by an overflying aircraft using an ultraviolet laser. This success caused us to turn a bad thing into a good thing, as the adage goes.

We consider it highly effective in using a plurality of MIPs placed on a suitable panel placed on the front of a subway car and make the train into an aerosol impactor, collecting airborne species as the train moves along the track. We have filed a patent application on a process where a subway car equipped with an integral MIP chemical detector panel is scanned at every station upon arrival by an invisible UV laser. Data is

collected and processed, and if an “anomaly” is detected, the train is immobilized - thus precluding any further spread of the suspect agent. Passengers would then evacuate and a sample taken to confirm any hazardous nature of the anomaly. We can thus confirm what was detected (nerve agents, explosives, chemicals, bioagents, etc.), where it was collected, on which train it was collected, and where that train has been. This is our first solution and we conclude such an approach will be a highly effective and cost effective solution. Our second solution would entail placing a small electrospray collector and MIP-laser identifier combination (about the size of a pack of cigarettes) inside each piece of rolling stock, ideally near the return vent of the air handling system.

Comment of Expert Review Panel

The Expert Review Panel members consisted of Dr. John Fenn and Dr. Gary Tepper, both of Virginia Commonwealth University, and Dr. Charles Burrus, Director of MTA System Safety. After reviewing the Draft Final Report under Transit 40, the only comment raised by Dr. Fenn and corroborated by Dr. Tepper concerned the fact that at high speeds, laminar air flow over a subway car would preclude impaction and therefore detection of light molecular species when using a MIP panel alone. As a consequence, it was recommended that air samples be obtained using a pitot tube located on the front of rolling stock, where the air sample could be channeled into an electrospray sampler which employs MIP identification.

Comments by Transit IDEA Panel Members

Reviewer #1:

The final report for the project should note that additional sensors would be needed to check air samples outside and inside a rail transit vehicle. It strikes me that to deal with this issue, sensors would need to be widely distributed in a system to adequately detect chemicals released in the air in a rail transit system, including in tunnels.

Response:

The investigators agree that more sensors would be helpful inside a rail car, but that consideration was given to cost and complexity. The selection of a sensor location near a return vent for the air conditioning system was deemed the most economical and effective placement of an electrospray collector. Nevertheless, we are in the process of attempting to secure additional research support to field a number of collector-detectors on rolling stock to perform long term field tests to ascertain the minimum total number and placement of devices inside a given car. As for external detection, a pending patent application filed by the investigators does mention using MIP sensors with laser interrogation throughout transit tunnels. In addition, collaborative work with MIT has produced a silicon chip based Micro Electro Mechanical System (MEMS) electrospray source that consumes only microwatts of power. It is possible to field or "seed" hundreds or thousands of these devices throughout a transit environment to augment widespread system monitoring. Indeed, these devices can even be "disposable", having internal power for months or years sending telemetry about ambient conditions. We hope to begin testing with these devices in the next year given the necessary support.

Reviewer #2:

The consequences of shutting down a line will need to be considered by transit agencies. The probability of detecting to a high confidence level will need to be established and considered.

Response:

The consequences of shutting down a system have been extensively discussed by NYC MTA and other agencies. The principal problem is deciding what we are willing to accept as a minimum threshold of a contaminant before sounding the alarm as it were, and, if we can tolerate the possibility of a "false positive". For example, with regard to the former, no minimum "safe" level of anthrax has been established. At what point do we trip an alert? If we make the level very low, the potential for false positives can increase. Furthermore, an antagonist would then only need a small quantity of a given agent to create mass panic by triggering such a system shutdown. We need to dynamic and employ a multitude of collection and identification methodologies to stay ahead of our enemies. Reports produced by the IDEA program and other agencies are not classified and so we can expect terrorists to look for weaknesses in every system we try to deploy. In this sense, we need to address proper "OpSec" or Operational Security and classify how and what we in the transit community intend to do, what sensors we use and how and in what manner we plan to

respond. A system of mitigation measures and not just a single approach will be the best and perhaps offered by several firms.

Reviewer #3:

A problem concerning a biological agent contamination is the time factor; many people could be contaminated, and not show symptoms for hours. I believe that a "real-time" reliable capability would be important.

Response:

Ideally, we agree the Holy Grail would be a real-time detection system. In reality, other factors of a non technological, often political nature come into play. We have been informed that in the past, shutdown of a system requires virtually irrevocable proof positive of a contaminant. To achieve this, the process included keeping the transit system active, sending an individual to collect a sample of the chemical or biological agent, returning same to a laboratory operating under CDC oversight, and performing PCR or other suitable identification measures. Only until this sequence had produced a positive result would the political powers that be issue an alert and shut down a system. Obviously, this is not the ideal sequence of events and that a pathogen could be spread by passenger "vectors" far and wide before we knew what had transpired. In the process, potentially many lives could be lost.

We do not know what the NYC plan is in such a situation at present or for other systems. However, we feel the best plan would be to target containment even if a false positive occurs. It remains to be seen what the public can tolerate for a false positive before people stop using a system or lose confidence in the alerts, not to mention the panic that will ensue given such an alert. Perhaps establishing routine system "sweeps" by a special piece of chemical-biological sensing rolling stock can be implemented where random isolated shutdowns become the norm. As a consequence, neither the public nor the terrorist would know what is a real shutdown and if an agent had been detected. An obvious inconvenience, it is no more so than random searches at an airport which we have all come to expect as a sign of the times.

5. INVESTIGATOR PROFILE

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Mr. Bango received a B.S. degree in Electrical Engineering from the University of Bridgeport and will be completing in the Spring of 2006 a Masters in Electrical Engineering from the same institution and a Masters in Mechanical Engineering from Central Connecticut State University. Mr. Bango established Connecticut Analytical Corporation in 1989 as an instrument manufacturing firm and research facility, and has been awarded research contracts from the U.S. Navy, US Air Force, United States Marine Corps (USMC), and the National Aeronautics & Space Administration (NASA), to name a few.

Joseph Bango conducted research under the auspices of Dr. John Fenn (2002 Nobel Laureate in Chemistry) in Chemical Engineering at Yale over twenty years ago during the initial landmark experiments in electrospray ionization mass spectrometry. Collaboration with Dr. Fenn has increased substantially over the ensuing years and joint research conducted by the PI, Joseph Bango, with Dr. Fenn, includes electrospray propulsion for NASA-JPL and aerosol studies for the USMC and National Academy of Science.

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21. Provisional Patent Application of Bango et al, for METHOD OF CHEMICAL AND BIOLOGICAL DETECTION FOR MASS TRANSIT SYSTEMS, No. 60/634635, Filed 12-8-2004

Existing Intellectual Property

Dr. John Fenn has filed a patent application with the United States Patent Office (USPTO) on the electrospray collection instrument. The status of that application is pending, and Connecticut Analytical Corporation (CAC) has right of first refusal on the technology.