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Trace Vapor Generator for Explosives and Narcotics (TV-GEN)

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14. ABSTRACT

The Trace Vapor Generator for Explosives and Narcotics (TV-Gen) is a portable and compact instrument designed to deliver a continuous source of trace-level vapors and vapor mixtures. It was developed to evaluate new materials and sensors under development for explosives and narcotics detection. It consists of a vapor generation system utilizing the nebulization of solution-based analytes, an oven to promote efficient transport, and a control box that provides dedicated computer control with logging capabilities. The TV-Gen provides a single vapor output with a dual manifold that can be easily switched between clean air and trace levels of analytes. The humidity and analyte introduction is provided using the custom nebulizer system that reproducibly and accurately generates trace vapors of low vapor pressure compounds from parts per quadrillion to parts per million levels. The TV-Gen has been demonstrated for explosives, including nitromethane, nitroglycerine, ethylene glycol dinitrate, triacetone triperoxide, 2,4,6-trinitrotoluene, pentaerythritol tetran, and hexahydro-1,3,5-trinitro-1,3,5-triazine.

15. SUBJECT TERMS

vapor generator, trace explosive vapor, dual manifold, trace analytes, custom nebulizer system, oven, control box, single vapor outlet port, nitromethane, nitroglycerine, ethylene glycol dinitrate, TATP, TNT, PETN and RDX

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Contents

Table of Figures

Tables

I. EXECUTIVE SUMMARY

The Trace Vapor Generator for Explosives and Narcotics (TV-Gen) is a portable and compact instrument designed to deliver a continuous source of trace- level vapors and vapor mixtures. It was developed to provide the Department of Homeland Security Science and Technology Directorate (DHS) with independent validation and verification (IV&V) of the new materials and sensors under development for explosives and narcotics detection. The design was conceived for use with a broad range of analytes, detection systems, materials and sensors, and to switch easily between clean and analyte vapor streams. It consists of a vapor generation system utilizing the nebulization of solution-based analytes, an oven to promote efficient transport, and a control box that provides dedicated computer control with logging capabilities. Vapor concentrations exiting from the TV-Gen are analytically quantitated.

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II. INTRODUCTION

The most commonly employed method for detection of trace explosive material involves particle detection by direct contact sampling of the subject or item of interest, typically with analysis by ion mobility spectrometry (IMS). An alternate approach to trace explosive detection is via vapor detection as it allows for non-contact sampling methods that are less invasive, relieving logistic and security concerns associated with direct contact sampling, and benefitting from an improved potential for detecting wrapped or obscured materials [1]. These inherent benefits have been the impetus for the development of explosive and narcotics vapor detection capabilities, and for this purpose, it is imperative that reliable methods for the evaluation of new and potential detectors and sensing materials be available. It is also crucial that such methods be characterized using vapor streams that are easily adjustable over a wide concentration range, stable over time, and reproducible. Furthermore, vapor generation methodologies must also meet the demand for low concentration vapor streams across a variety of potential chemical analytes.

The greatest challenge faced in the vapor generation of explosives is the exceedingly low vapor pressures of many explosives, often requiring vapor concentrations as low as the parts-per-quadrillion level in air (ppq by volume; fmol/mol of air) for realistic detection scenarios [2]. Additionally, many explosive analyte molecules exhibit strong interactions with many surfaces, making them appear to be "sticky." For this reason, all surfaces that have contact with analyte vapor must be maintained at an elevated temperature in order to prevent any loss of analyte in cold spots encountered along the vapor path [3, 4].

There have been a number of trace vapor generation methods developed for explosives analytes. These have been previously reviewed in works by Grate et. al. [3] and Collins et. al. [4]. To summarize, the most common method of vapor generation is direct sampling from a bulk energetic/static source. In this approach, reproducibility and stability of the vapor stream concentration can be challenging and is not easily amenable to varying concentration levels. Ideally, the source vapor is allowed to reach equilibrium prior to sampling, though rate of evaporation and, thus, time to equilibrium, is often unknown for many target analytes. Additionally, equilibrium is disrupted when the headspace is sampled. One must also consider safety / regulatory limitations for handling bulk explosives as well when implementing this mode of vapor generation. Alternatively, analyte material may be deposited onto a solid substrate. A

Manuscript approved December 8, 2018

flow of heated air is then swept across the substrate, carrying analyte vapor to the detector. In this method, the hazard of working with bulk material is reduced and there is a greater surface area for vaporization. This technique, however, still suffers from changing concentration due to a depletion of analyte vapor over time. Similarly, vaporization directly from analyte solution can be utilized, again, to reduce safety precautions and other drawbacks of working with bulk material. The drawback of this method is the introduction of an organic solvent into the vapor stream. Finally, some assemblies utilize syringes or sample pumps to move analyte vapor from a source to a sensor. These approaches tend to provide a pulsed or non-continuous delivery of analyte vapor [2, 3, 4].

An optimal vapor generation system should allow for the reproducible and continuous delivery of analytes (i.e. no pulsing effect) of varying vapor pressures in a vapor stream free of organic solvents. The concentration of the analyte stream should be adjustable across a large range of vapor concentrations, and the pathway from the analyte source to the detector should be passivated and free of cold spots to minimize attenuation of the analyte vapor. Scientists and engineers at the Transportation Safety Laboratory (Atlantic City, NJ) developed a first generation explosive vapor generator with modifications by the U.S. Naval Research Laboratory (NRL) addressing these requirements [4]. The liquid injection vapor generator (LIVG) uses a hypodermic injection needle set coaxially in a stainless steel tube (Figure 1). Warm air flowing through this tube vaporizes drops of an aqueous solution of explosives delivered by the hypodermic needle. The internal surfaces of the LIVG are heated and SilcoNert-coated to minimize loss to adsorption. The placement of the syringe needle allows analyte solutions to be injected into the heated stainless steel tube, and the placement of the air inlet encourages optimal mixing. The LIVG was designed to deliver a continuous stream of explosive vapor when introduced to large atmospheric domes, with vapor concentration adjustable over three orders of magnitude. Additionally, it was shown to be amenable to low vapor pressure analytes with relatively stable concentration output over multiple days.

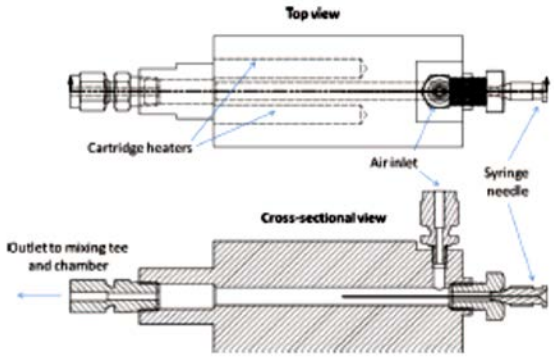

Figure 1. Liquid injection vapor generator, from Collins et. al. [4].

While the LIVG is capable of generating explosives vapor, the drops do not readily vaporize in the air stream, but instead form a droplet that falls onto a heated tube surface and then vaporizes sequentially as the droplets are generated. This phenomenon results in lower than expected efficiencies and a slight pulsing of the vapor concentration. NRL designed a second generation system, replacing the LIVG with a pneumatically modulated liquid delivery system (PMLDS) [5] with a micro-flow nebulizer (Figure 2). The nebulizer uses the same air volume as the LIVG but instead of creating a single, large droplet, many micro-droplets with a greater total surface area are generated, enabling more rapid vaporization using cooler operating temperatures [6]. Additionally, the PMLDS incorporates a liquid flow meter to maintain constant liquid flow. The flow meter prevents changes in the liquid flow rate with time as the liquid volume in the reservoir vessel decreases [7]. The ability to precisely control the pressure for the liquid flow to the nebulizer using the PMLDS allows for pulse-free, continuous vapor generation limited only by the volume of liquid in the reservoir. As an example, Field et. al. compared the measured flow rates from a commercially available syringe pump to that of the PMLDS over 1 hour (Figure 3a), and also examined the continuous operation of the PMLDS over 24 hours (Figure 3b). The syringe pump was not capable of operating for more than 2 hours continuously and produced a flow rate with an RSD of 6.6%, while the PMLDS produced an uninterrupted flow over 24 hours with a RSD of 0.5% [7].

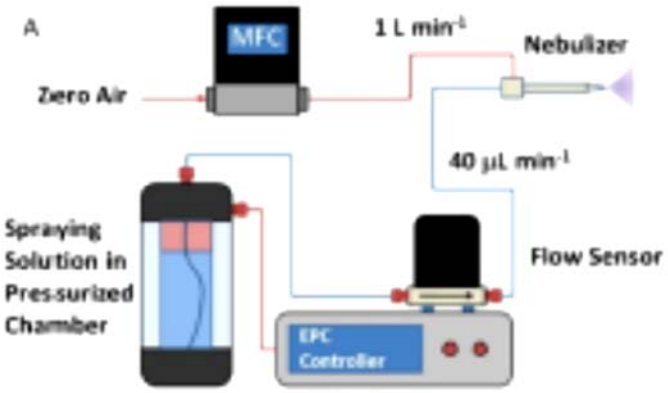

Figure 2. Diagram of PMLDS-nebulizer system flow path, including liquid flow meter and control box used to set liquid flow rate from the reservoir. Additionally, the airflow rate into the nebulizer is controlled by a mass flow controller (MFC), from Giordano et. al. [6].

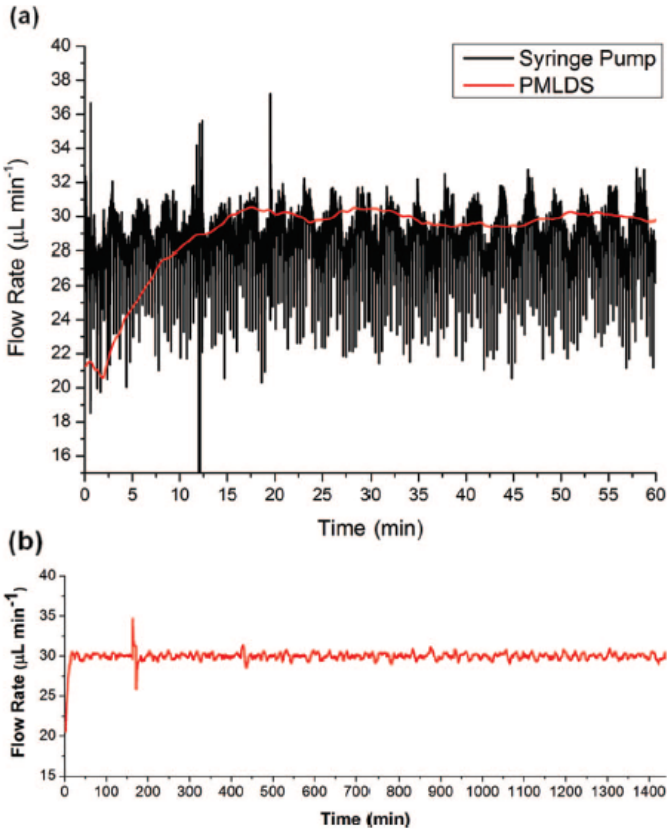

Figure 3. Plot of measured flow rate for (a) commercial syringe pump (black trace) and PMLDS (red trace) over 1 hour, and (b) PMLDS over 24 hours, from Field et. al. **[7]**.

For delivery of the vapor generated by the PMLDS-nebulizer, a Trace Explosive Sensor Testbed (TESTbed) was designed [2]. The TESTbed couples the PMLDS-nebulizer with a dual-line manifold system that allows for rapid switching between clean and analyte vapor streams, and has the capability to deliver trace vapor streams in the presence of interferents for improved testing

under more realistic situations. The entire system was fabricated in such a way to prevent or minimize analyte loss due to adsorption to the interior surfaces of the flow path. The bottom portion of the dual-line manifold is dedicated to clean, analyte-free air, while the upper portion carries the analyte vapor (Figure 4). The whole manifold unit is then surrounded by a recirculating box oven for controlled heating. The upper and lower portions of the manifold are coupled using a three-way ball valve (Figure 4C) that allows for rapid switching between the two sides. The vapor exits the manifold through six identical sample ports consisting of passivated stainless steel which is jacketed by copper to improve thermal conductivity.

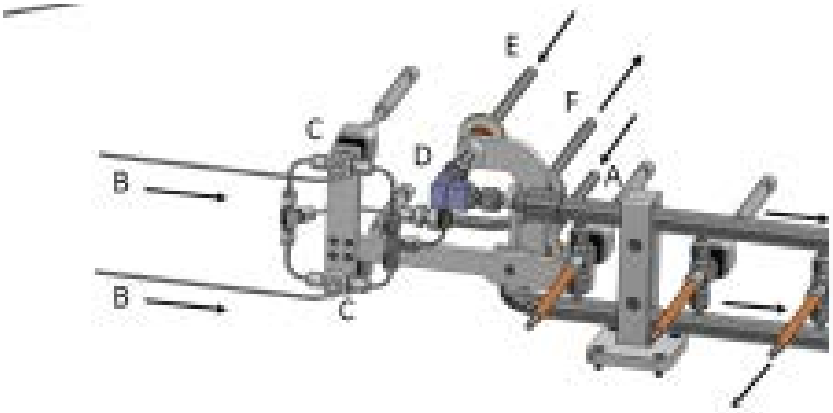

Figure 4. Diagram depicting vapor entry to a dual-line TESTbed manifold where (A) indicates clean air entry, (B) analyte vapor entry, (C) three-way ball valve that directs vapor either to (D) vortex mixer or to (F) the bypass line, and (E) diluent air entry, from Collins et. al. [2].

Diluent air, free of all organic contaminates as well as water vapor and particulates, is provided to the TESTbed using two zero air generators (one for each side of the manifold). Additionally, a Miller Nelson Temperature Humidity Control System (Miller-Nelson Instruments) controls diluent air temperature and humidity prior to entry to the manifold. Humidity matching between the two sides of the manifold is critical as the analyte side introduces additional water into the vapor stream due to the nebulization of aqueous solutions. In turn, TESTbed software was designed to provide automated feedback control for balancing the output of the humidity control systems for both lines. Finally, a vortex mixer (Figure 4D) is used to mix the diluent and analyte vapor streams, resulting in rapid and efficient mixing prior to entrance into the manifold. This comprehensive vapor generation and delivery system has been demonstrated to deliver vapor streams from seven different explosive analytes across a wide dynamic range, from ppq_v to ppm_v. Challenges associated with analyte adsorption, low volatility, and thermal lability were addressed,

as were the requirements for pulseless, continuous, and steady vapor generation in the absence of organic solvents [2].

Following the success of the TESTbed, a third generation vapor generation and delivery unit was developed by the Naval Research Laboratory. The newest design retains the benefits of the TESTbed, but greatly reduces the footprint of the unit, incorporate in only a single vapor output port. The Trace Vapor Generator for Explosives and Narcotics (TV-Gen) utilizes two separate but identical PLMDS-nebulizers for the analyte and clean manifold sides, thus eliminating the need for multiple clean air generation systems and no longer requiring humidity matching. Additionally, the manifold into which the nebulizer sprays the micro-droplets had its diameter, increased to allow for the nebulizer to spray directly into the center of the tube. Additionally, carrier gas is introduced coaxially around the tip of the nebulizer. These modifications eliminate the need for the vortex mixer and allow the micro-droplets additional time to interact with the carrier gas. Detailed TV-Gen design elements as well as validation of the TV-Gen unit is described herein.

III. SYSTEM COMPONENTS

A. *Overview*

The TV-Gen consists of four main components: the control box (Figure 5), the oven (Figure 6), the manifold (Figure 7), and sample introduction (Figure 5B). The sample is introduced from the control box (Figure 5B), whereupon it is nebulized and sent through the manifold to a vapor output port protruding from the oven (see Figure 8 for the flow path). The manifold is contained within the oven and has two isolated flow paths for clean and analyte vapor streams. The control box contains all of the hardware necessary for the operation of two nebulizers: one for the clean side of the manifold, and one for the analyte side. The design of each component will be detailed in the following sections, as will the analytical evaluations and quantitation of resultant vapor streams.

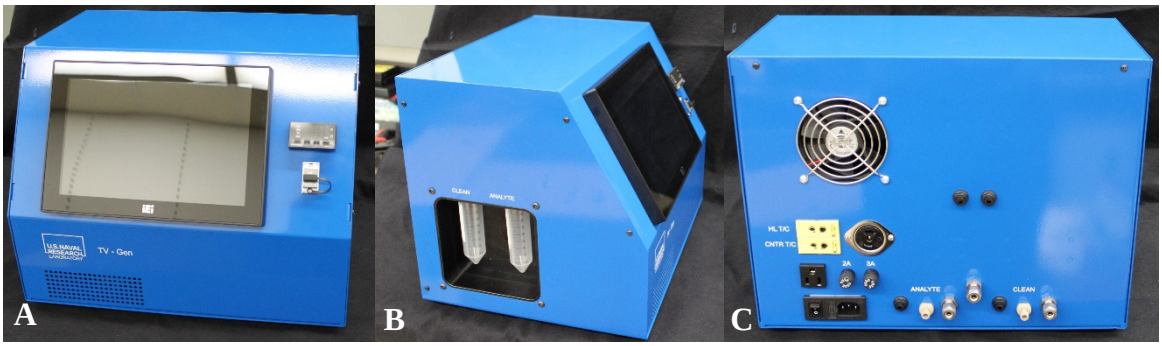

Figure 5. TV-Gen control box and sample introduction; (A) Front view of control box with user interface, (B) Side view of control box with sample introduction, (C) Back view of control box.

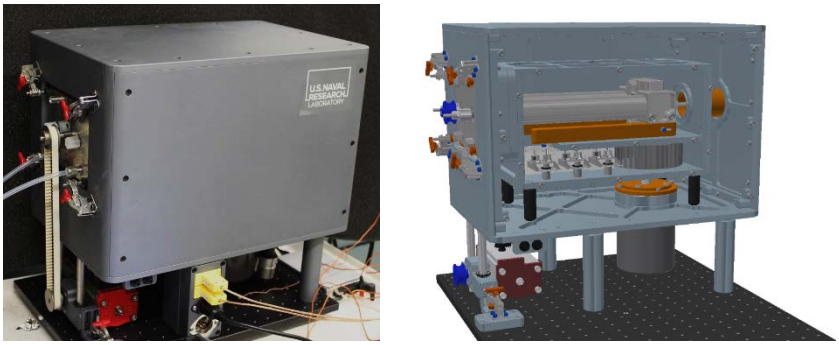

Figure 6. TV-Gen oven with manifold; (A) External view of oven, (B) Oven with shell and core wall removed exposing in-place manifold.

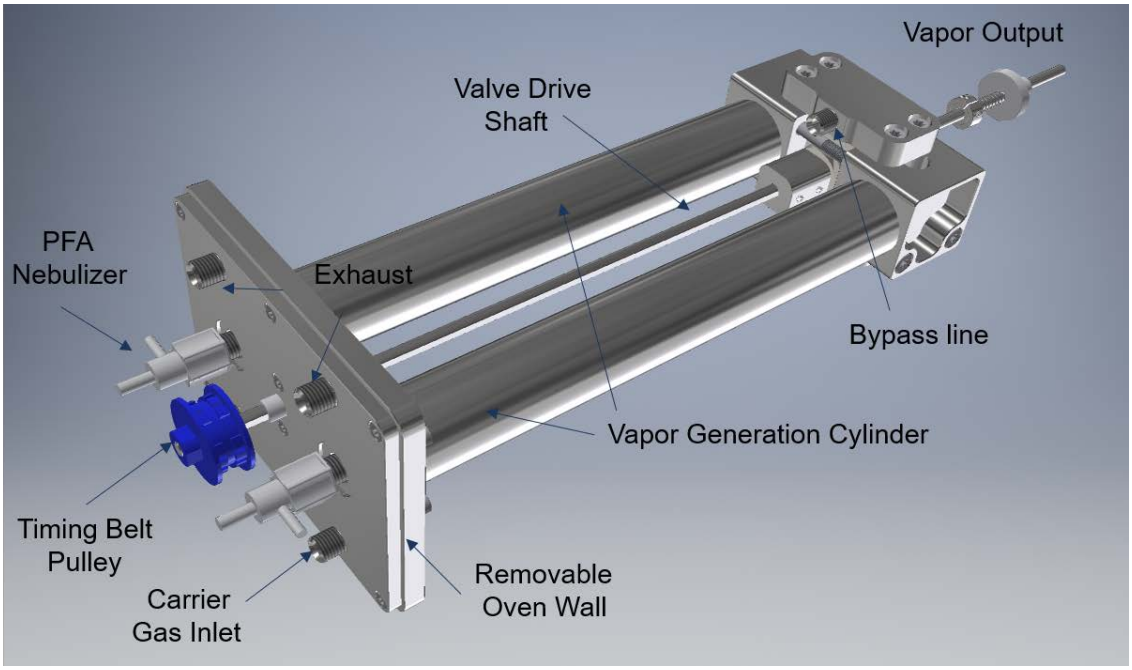

Figure 7. Manifold for sample introduction into dual vapor generation cylinders housed in the TV-Gen oven.

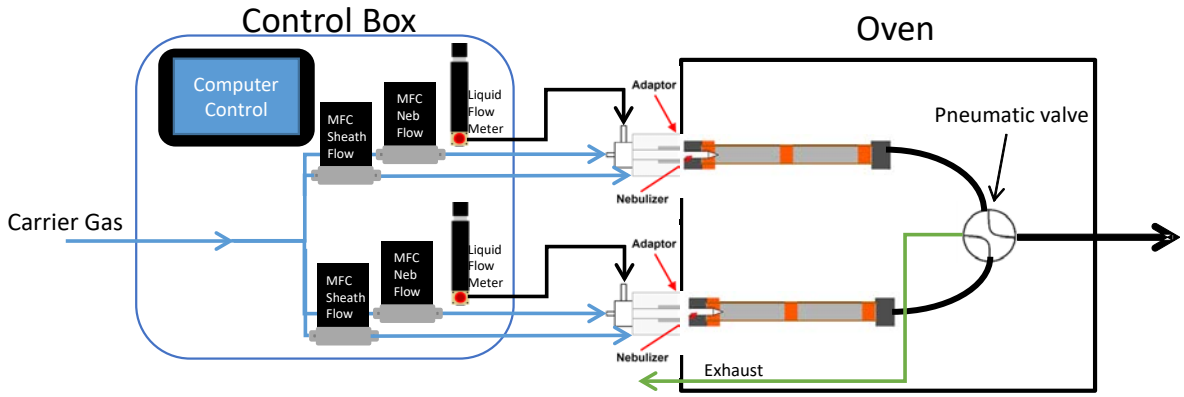

Figure 8. TV-Gen flow path from control box to oven/manifold.

B. Sample Introduction and Vapor Output

The TV-Gen design was based on the original, larger TESTbed, though several improvements / changes were made to improve its performance. In moving from the TESTbed to the TV-Gen, many of the costly commercial off-the-shelf components used to supply diluent air and add humidity to the analyte side and clean side of the manifold were no longer necessary due to changes in sample introduction methods. In the TV-Gen, the sample aerosol is generated within completely separate, individual vapor generation cylinders, each associated with their own PFA nebulizers (Figure 7) and using identical nebulization processes. By flowing aqueous solutions through the clean and analyte nebulizers under the same conditions, the humidity is automatically matched on both sides, eliminating the necessity for humidity matching required for the TESTbed.

The nebulizers are crucial to the continuous and reproducible supply of analyte vapor, and have been shown to be capable of producing stable vapor streams for a variety of trace explosives (concentrations as low as ppq_v). Explosives are nebulized as aqueous solutions at relatively low temperatures, preventing thermal decomposition of thermally-liable analytes, such as PETN. Liquid flow meters allow for precise control of the flow of the aqueous solution. Additionally, the use of water as a solvent avoids the introduction of organic solvents into the vapor stream, which is both unrealistic to real-world scenarios and potentially harmful to sensors or materials being tested. The nebulizers themselves are the same as those used on the TESTbed and are further described elsewhere [8, 2, 6].

The sample introduction from the nebulizer to the TV-Gen manifold has been altered significantly from the TESTbed model. In the TV-Gen, there is a ring of eight holes through which sheath gas (also referred to as diluent air) is evenly distributed (Figure 9) around each nebulizer. This method of introducing the nebulized vapor with the surrounding sheath gas yields more efficient vapor transport than the system used on the TESTbed. In the TESTbed, vapor from the nebulizer flowing at 1 L min^{-1} is diluted in make-up air in a vortex mixer some distance from the nebulizer. Whereas, in the TV-Gen, the sheath flow (or make-up air in the TESTbed) immediately surrounds the nebulized vapor at the point of nebulization. The benefit of this design is two-fold. First, the need for the vortex mixer is eliminated, and second, the nebulized droplets are able to completely vaporize prior to interaction with the manifold surface.

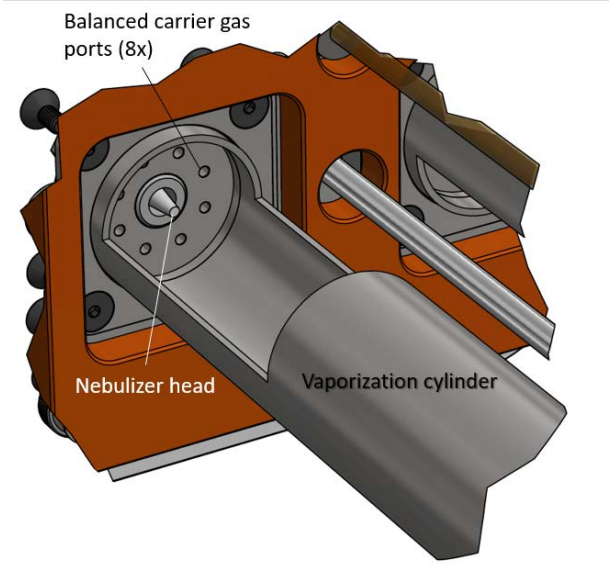

Figure 9. Diagram of eight sheath flow gas ports organized concentrically around nebulizer at head of vapor generation cylinders.

C. Manifold and Oven

The TV-Gen manifold and oven (Figure 6) design include a two-sided manifold within a custom convection oven. The manifold system was designed according to the flow diagram described in Figure 8 and enables users to exchange and disassemble manifolds with minimal time and effort. The back wall of the manifold becomes the back oven wall, which allows for simple manifold exchange. To aid in disassembly, o-rings and screws were chosen over permanent welds. In order to simplify cleaning requirements and minimize loss of analyte to adsorption, all wetted surfaces inside the manifold were SilcoNert 2000 – coated (Silcotek).

The back wall of the manifold also incorporates an air balancing system and consists of two halves containing channels for the sheath gas (Figure 10). The channels allow the sheath gas to be slightly warmed while keeping the back of the manifold cooler to the touch.

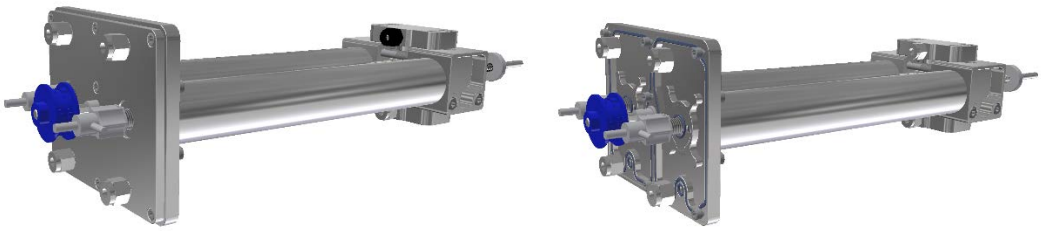

Figure 10. Vapor generation cylinders attached to the back wall of the manifold, showing (a) both halves of the wall, and (b) only the inner most portion of the back wall, exposing the sheath air flow path.

The two vapor generation cylinders making up the manifold meet at a Swagelok 4-port 2-way crossover valve (Figure 11). This valve directs vapors from each cylinder to either the exhaust line or the vapor output port at the face of the TV-Gen. It is actuated by a drive shaft which protrudes through the back wall of the manifold (seen in Figure 7), avoiding any internal valve drive connections prior to changing out the manifold.

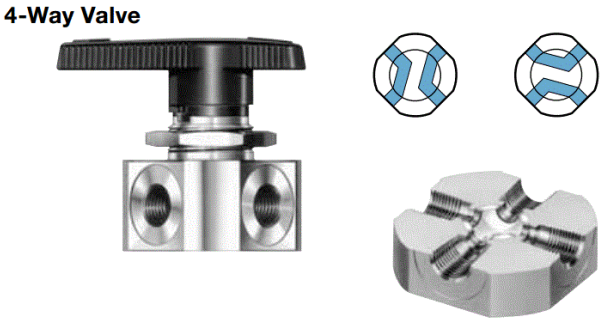

Figure 11. Swagelok 4-way crossover valve between the two vapor generation cylinders, exhaust line, and vapor supply port.

The oven containing the manifold (Figure 6) is housed within custom inner and outer anodized alumium walls separated by a two inch gap filled with ceramic insulation. The inner oven walls are connected to the outer shell by four PEEK (polyether ether ketone) standoffs and an Ultem ring which seals the inner core up against the back of the manifold.

D. Control Box and User Interface

The control box (Figure 5) was designed to house the flow controllers, a PID controller to regulate oven temperature, a pneumatic switch to actuate the manifold valve, power supplies, electronic pressure controllers, and conical tube reservoirs for the analyte solution and clean solvent (water). A supply of clean compressed air (60-80 psi) for the sheath gas and nebulizer airflows is supplied to the control box via a 1/4" Swagelok compression fitting. The control box holds two 50 mL conical tube vials containing the clean and analyte solutions, as can be seen in Figure 5B and Figure 12. Liquid from the vials is carried to the nebulizer via 1/16" PEEK tubing.

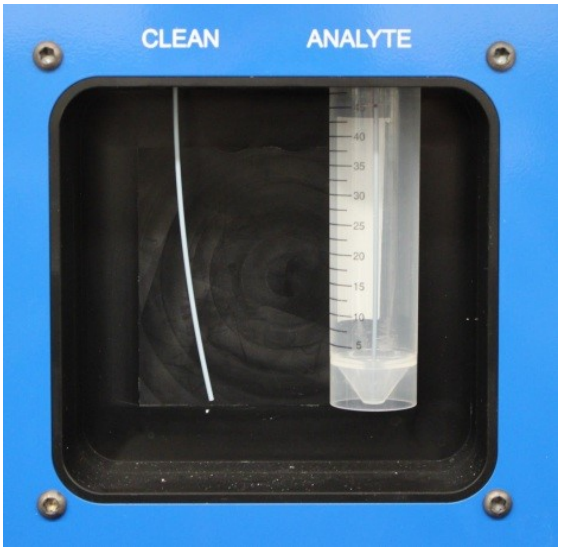

Figure 12. Side of TV-Gen control box that holds reservoir vials for clean (vial not shown) and analyte (vial shown) solutions. Clean side shows 1/16" PEEK tubing used to deliver solution.

The TV-Gen is controlled using a touch screen computer running a custom graphical user interface (GUI) designed in-house. The software allows the user to control all vapor generation parameters, including the sheath gas and liquid nebulizer flow rates, in addition to controlling the manifold valve. The program displays the last hour of data from the nebulizer flow rate and sheath flow, while continuously saving all data in daily log files. Upon turning on the TV-Gen, the user is presented with a screen that displays all of the flow rates for the TV-Gen (Figure 13). The top left of the control screen displays the liquid flow rate (μL min^{-1}), the nebulizer carrier gas flow rate (mL min^{-1}) and the sheath flow rate (L min^{-1}). Dropdown boxes allow for entry of the liquid flow rate (30-100 μL min^{-1}) and sheath flow rate (0-20 L min^{-1}), as well as the oven temperature set point (0-130 °C). Both nebulizers, clean and analyte, utilize the same set point values for liquid

and sheath flow rates. Toggle buttons are present to control the status of both the air flow and nebulizer liquid flow, as well as to switch the output between the two manifold pathways. Both the air flow and nebulizer flow switches are displayed in green if the flows are on and white if turned off. The pathway switch is green if the clean pathway is connected to the output and red if the analyte pathway is connected.

A full explanation of the system control is included in the TV-Gen User Manual (see Appendix A).

Figure 13. TV-Gen control box GUI (screenshot).

IV. ANALYTICAL EVALUATION

A. Humidity measurements with airflow

The humidity and flow rate capabilities of the TV-Gen were validated by running a matrix of trials with the nebulizer flow rate set to 20, 30, 40, 50, and 60 µL/min, and the total airflow rates controlled between 2-20 L min^{-1}. The oven was heated to 130 °C and the humidity measured by attaching a length of PTFE tubing to the Swagelok tee at a distance far enough removed from the sample port that the air is at room temperature. The back exhaust port was capped off, allowing the full flow of the TV-Gen to exit out the front port. The majority of airflow was exhausted to the room while the sample chamber holding the humidity sensor (Sensirion SHT1, custom electronics package) was set to sample at a flow rate of 500 mL min^{-1} from the tee.

Absolute humidity levels from 1-30 g m^{-3} were achievable depending on the liquid flow rate and total airflow (Figure 14). Figure 14 includes data from both the left and right sides of the manifold, demonstrating excellent overlap between the two. The dash lines represent ideal humidity levels calculated based on liquid flow rate (g) divided by the total air flow (m^3) measured from both sides of the manifold. At low total air flow rates, less than 4 L min^{-1}, humidity levels greater than 17 g m^{-3} were generated at liquid flow rates of 40 mL min^{-1} or higher, producing condensation at room temperature. Should the TV-Gen be used in the testing of water-sensitive materials, care must be taken when approaching such high humidity levels.

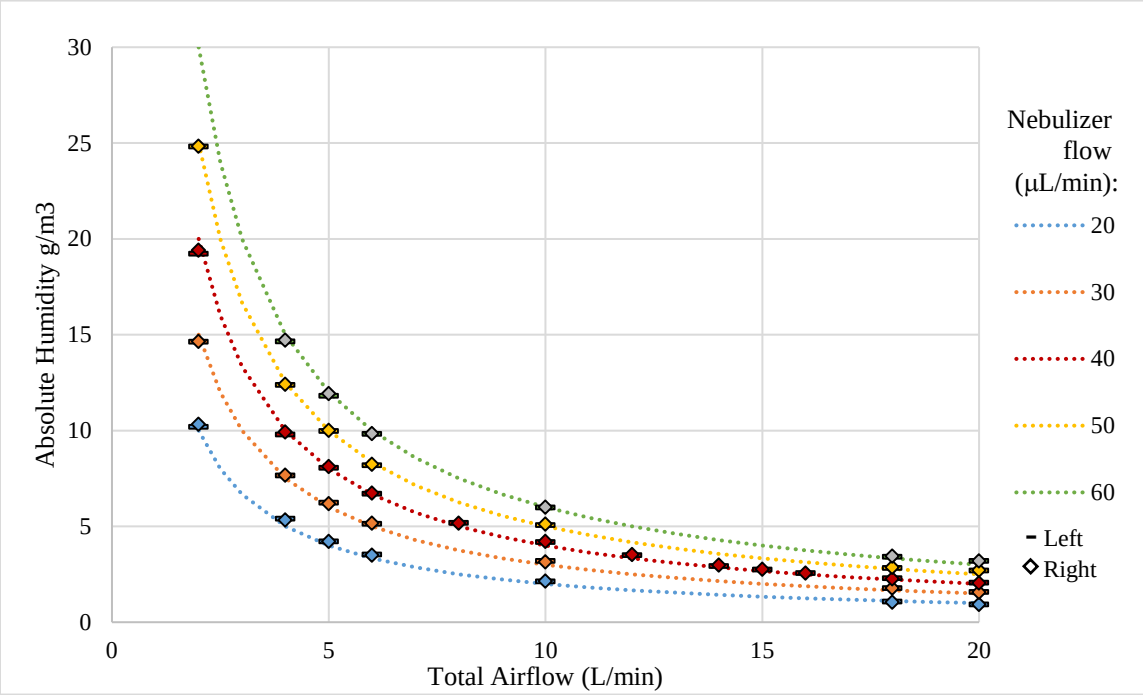

Figure 14. Plot of TV-Gen humidity (g/m^3) versus nebulizer flow and total air flow rates. Dash lines give the ideal humidity based on airflow and liquid spray from the nebulizer, while the measured humidity is plotted for the left (dash) and right (diamond) sides of the manifold.

B. Evaluation of Vapor Generation Performance

The performance of the TV-Gen to generate continuous and adjustable vapor streams was analytically evaluated for the generation of a number of explosive vapors, included in Table 1. Evaluation parameters included efficiency (experimentally-determined versus theoretical vapor concentration as a function of solution concentration) and linear dynamic range (demonstrated using air flow dilution). Finally, the scale and duration of any carryover from analyte solution to

clean water was assessed. All explosive materials, with the exception of the TATP, were purchased in solution as analytical standards from AccuStandard. Aqueous solutions were prepared by starting with the analytical standards, evaporating off the solvent, and reconstituting in water to the appropriate concentration. Alternatively, TATP bulk sample was placed in a stainless steel dynamic headspace vapor generator that was coupled to the airline associated with the nebulizer system. In this configuration, TATP vapor was presented through the nebulizer, with humidity arising from the nebulized water.

Table 1. List of explosive analytes used in vapor generation experiments. References indicating the published instrumental detection methods used for vapor validation are included.

Name of Explosive	*Abbreviation*	*Published detection methods*
2,4,6-trinitrotoluene	TNT	[6]
Hexahydro-1,3,5-trinitro-1,3,5-triazine	RDX	[6]
Pentaerythritol tetranitrate	PETN	[9]
Nitromethane	NM	Unpub.
Nitroglycerine	NG	Unpub.
Ethylene glycol dinitrate	EGDN	Unpub.
Triacetone triperoxide	TATP	[10]

All vapor samples, with the exception of TATP (to be discussed below), were generated using the microflow nebulizer. Aqueous explosive solutions were delivered to the nebulizer at 40 μL min^{-1}. The resulting vapor streams were then carried to the TV-Gen at 1 L min^{-1}. Diluent airflow was incorporated into the vapor stream and was adjusted as a means for manipulating the final vapor concentration delivered. The TV-Gen oven was heated between 70 and 100 °C and the transfer line temperature at the vapor output port was held at either 100 or 130 °C, with both of these variables dependent upon the analyte (see TV-Gen parameters for each analyte in Table 2).

Table 2. TV-Gen parameters for each analyte.

Analyte	*solution flow rate (mL min-1)*	*nebulizer air flow rate (L min-1)*	*TV-Gen oven temp (C°)*	*Solution concentrations tested (ng mL^{-1})*	*Total flow rates tested (L min-1)*	*Transfer line and sample output temp (C°)*
TNT	40	1	100	0.1, 0.01, 0.001	5, 10, 15, 20	130
RDX	40	1	100	0.1, 0.01, 0.001	5, 10, 15, 20	130
PETN	40	1	70	0.1	5, 10, 15, 20	n/a*
NM	40	1	70	304	5, 10, 15, 20	100
NG	40	1	70	1	5, 10, 15, 20	100
EDGN	40	1	70	1	5, 10, 15, 20	100
TATP	n/a**	n/a**	100	bulk	0.25, 3.25, 6.25	130

**Vapor samples were collected onto Tenax sample tubes as opposed to through the heated transfer line*
***Total flow rate equals the sum of nebulizer and carrier gas flow rates*

For online detection and quantification of explosive vapors generated through the TV-Gen, the vapor output port was connected directly to the GC/MS (7890A GC/5975C MSD; Agilent Technologies) by a heated transfer line (225 °C; Clayborn Lab). The GC contains a 15 m RTX-5MS column (0.25 mm x 250 nm; Restek Co.). For all analytes other than PETN, vapor was concentrated before the head of the GC column in a cooled programmable temperature vaporizing (PTV) inlet from Gerstel Inc. The Gerstel online cold injection system (CIS; CIS G4) housed a liner of either deactivated baffled glass or packed with Tenax-TA (Gerstel Inc.) which was cooled for analyte trapping. CIS-GC/MS methods were optimized separately for each analyte and are summarized in Table 3. Detailed descriptions of the methods can be found elsewhere (see Table 1 for references).

Table 3. Trapping, separation, and analysis parameters for all analytes.

Analyte	*TDS collection*	*CIS flow rate (mL min^{-1})*	*CIS liner type*	*CIS absorb temp (°C)*	*CIS desorb ramp*	*GC flow rate (mL min^{-1})*	*GC over parameters*	*MS (CI or EI) or ECD*	*SIM ions (m/z)*
TNT	n/a	175	deactivated baffled	10	5 °C s^{-1} to 100 °C, then 12 °C s^{-1} to 250 °C	5	100 °C, hold 0.5 min, 50 °C min^{-1} to 250 °C, hold 0.25 min	CI (negative mode)	227, 210, 197
RDX	n/a	175	deactivated baffled	10	5 °C s^{-1} to 100 °C °, then 12 °C s^{-1} to 250 °C	5	100 °C, hold 0.5 min, 50 °C min^{-1} to 250 °C, hold 0.25 min	CI (negative mode)	129, 120, 46
PETN	Collection: 30 min at 100 mL min^{-1}; Oven: 180 °C min^{-1} to 175 °C, hold 5 min	500	deactivated baffled	0	10 °C s^{-1} to 175 °C, hold 5.75 min, 10 °C s^{-1} to 250 °C	5	80 C°, 20 °C min^{-1} to 175 °C, hold 0.5 min	ECD	n/a
NM	n/a	10	Tenax-TA	10	16 °C s^{-1} to 150 °C, 12 °C s^{-1} to 250 °C	1.4	35 °C for 1 min, 50 °C min^{-1} to 100 °C	CI (negative mode)	60, 46
NG	n/a	25	Tenax-TA	25	5 °C s^{-1} to 100 °C, 12 °C s^{-1} to 250 °C	5	45 °C for 0.5 min, 50 °C min^{-1} to 135 °C, 40 °C min^{-1} to 165 °C	CI (negative mode)	289, 62
EDGN	n/a	25	Tenax-TA	25	5 °C s^{-1} to 100 °C, 12 °C s^{-1} to 250 °C °	5	45 °C for 0.5 min, 50 °C min^{-1} to 135 °C, 40 °C min^{-1} to 165 °C	CI (negative mode)	62, 46
TATP	n/a	24.2	Tenax-TA	20	12 °C s^{-1} to 235 °C, hold 2 min	3	45 °C, 25 °C min^{-1} to 135 °C	CI (negative mode)	107, 56

PETN vapor was collected from the TV-Gen sample port onto thermal desorption tubes filled with Tenax-TA sorbent (Gerstel Inc.). A vacuum pump (DIVAC 1.4 HV3; Oerlikon Leybold Vacuum; Switzerland) with a multi-flow controller (M100 Smart Trak 2; Sierra Instruments; Monterey, CA)

was used to control the flow rate to the tube at 100 mL min^{-1}. Following collection, the tube was removed and thermally desorbed in the Gerstel Thermal Desorption System (TDS). The TDS was mounted atop a Gerstel CIS, as described above, for refocusing and subsequent desorption to an Agilent 7890A GC with a μ–Electron Capture Detector (ECD). Further method details are given in Table 3 and [9].

2,4,6-Trinitrotoluene (TNT) and Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)

Liquid solutions of RDX and TNT in water from 0.1 to 0.001 μg mL^{-1} were spayed at a constant flow rate of 10 L min^{-1}. The resulting vapor concentrations were stable for more than five hours (RSD < 5 %) after reaching equilibrium (Figure 15). The approximate time to equilibrium for TNT was 15 minutes and 45 minutes for RDX. The performance was linear within the range of concentrations tested (Figure 16). The vapor stream achieved from the 0.1 μg mL^{-1} liquid solution was further diluted proportionally to the total volume of air using total flow rates ranging from 5 to 20 L min^{-1}. The vapor concentration also scaled linearly with 1 / total airflow rate (Figure 17). The measured vapor concentration was compared to the theoretical vapor concentration to determine efficiency. Efficiency was >82% for all TNT concentrations and >85% for RDX, with efficiency decreasing with increased total flowrate (Table 4).

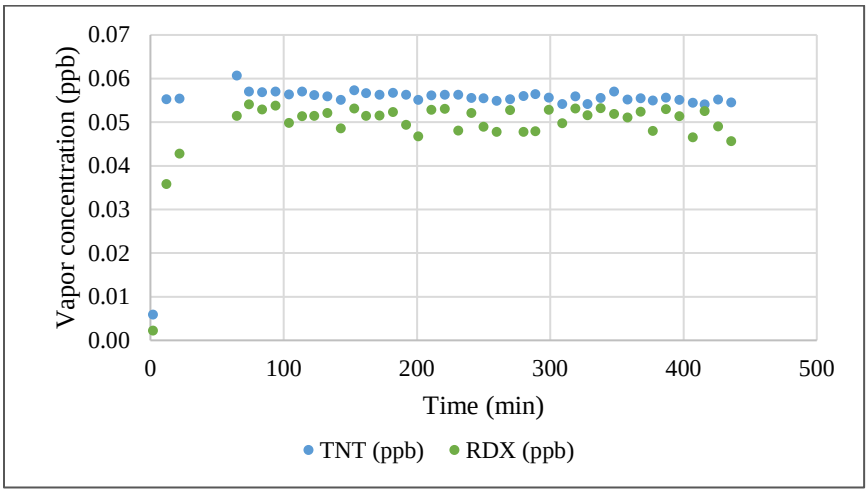

Figure 15. TNT and RDX vapor concentration produced by the TV-Gen from 0.1 μg mL^{-1} aqueous solutions and a total flow rate of 10 L min^{-1} over time.

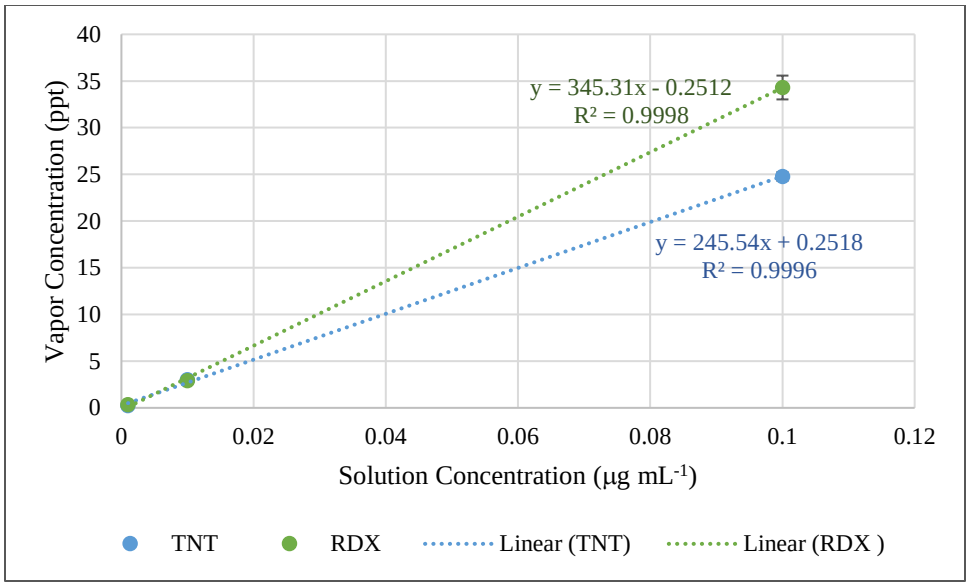

Figure 16. TNT and RDX vapor concentration produced by the TV-Gen using solutions of concentrations ranging from 0.1 ng/µL to 0.001 ng/µL with a total flow rate of 10 L min^{-1}. Note. Error bars represent one standard deviation from average, and some error bars are contained within the symbol.

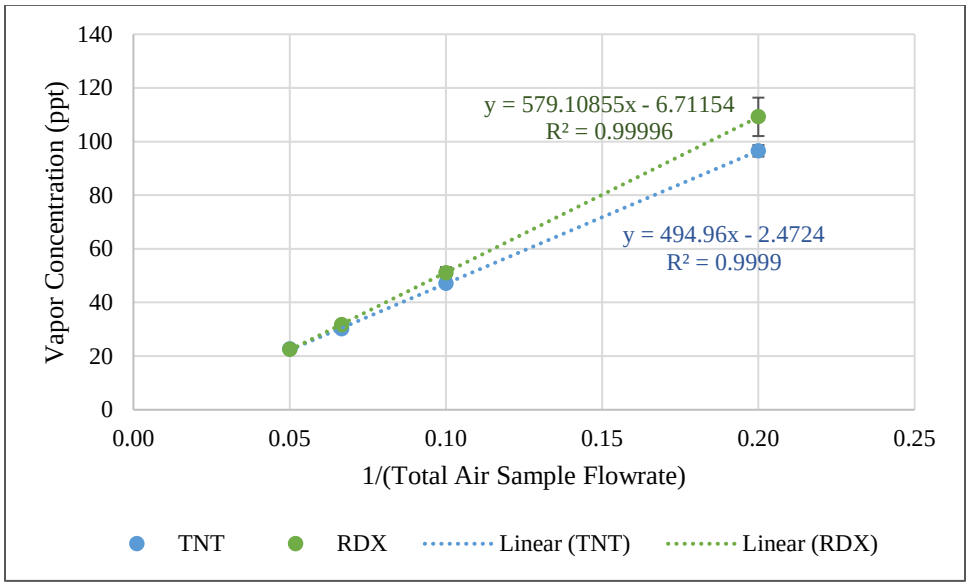

Figure 17. TNT and RDX vapor concentration produced by the TV-Gen using varying diluent air flowrates (ranging from 5 to 20 L/min total flow) through the TV-Gen, showing the correlation between the dilution factor of the total air flowrate versus the resulting concentration. Note. Error bars represent one standard deviation from average, and some error bars are contained within the symbol.

Table 4. Measured efficiency of TNT and RDX vapor analyses as determined by comparing nominal and measured vapor concentrations.

TNT/RDX solution concentration (mg L^{-1})	*TV-Gen flow rate (L min^{-1})*	*TNT Nominal conc. (ppt)*	*TNT Measured conc. (ppt)*	*TNT Efficiency %*	*RDX Nominal conc. (ppt)*	*RDX Measured conc. (ppt)*	*RDX Efficiency %*
0.1	5	108	97	89	110	109	99
0.1	10	54	47	87	55	51	92
0.1	15	36	30	84	37	32	86
0.1	20	27	23	82	28	23	85
0.01	10	5.4	3.0	56	5.5	2.9	53
0.001	10	0.54	0.23	43	0.55	0.35	64

Pentaerythritol tetranitrate (PETN)

The PETN tests were performed using the same parameters as the TNT and RDX tests, with a 0.1 µg mL^{-1} aqueous solution of PETN and 40 µL min^{-1} liquid flow. Sampling was performed by collecting vapors onto Tenax sorbent tubes for 30 minutes at 100 mL min^{-1} air flow, and analyzed using a GC-ECD instrument set up with a Gerstel TDS sorbent tube sampler [9]. The resulting concentration of PETN vapor was linear according to the total air dilution (Figure 18). It took less than one hour to reach the equilibrium concentration, which was shown to be steady beyond 3 hours (Figure 19). The standard deviations of the resulting PETN vapor concentrations were higher than TNT or RDX (relative standard deviations between 5% and 15%), with the increase in deviation due to variability associated with each individual Tenax sampling tube. The efficiency ranged from 48% at 20 L min^{-1} and 78% at 5 L min^{-1}. The measured concentrations in comparison to theoretical concentrations and resulting efficiencies for PETN and the other remaining analytes are included in Table 5.

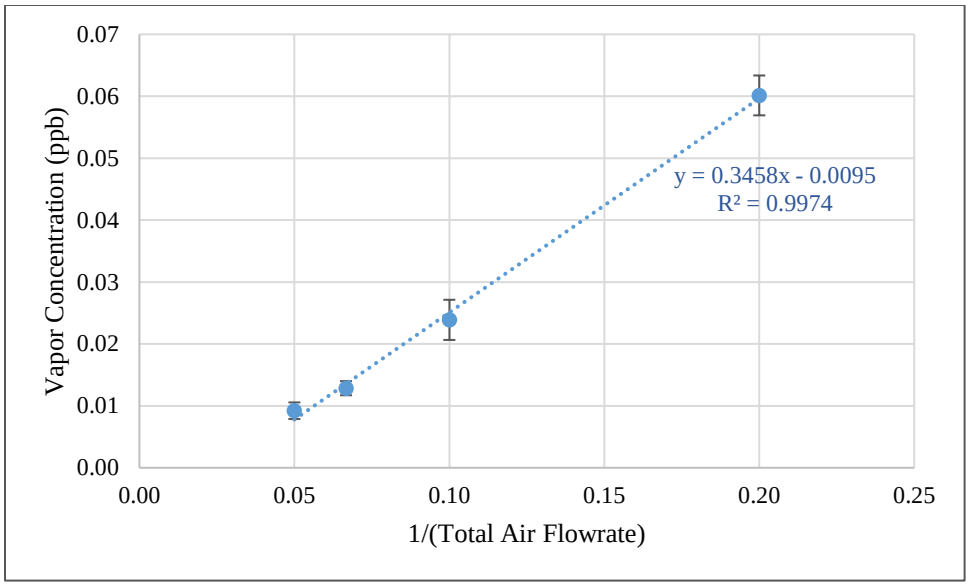

Figure 18. PETN vapor concentration produced by the TV-Gen using varying diluent air flowrates (ranging from 5 to 20 L min^{-1} total flow) through the TV-Gen, showing the correlation between the dilution factor of the total air flowrate verses the resulting concentration. Note. Error bars represent one standard deviation from average, and some error bars are contained within the symbol.

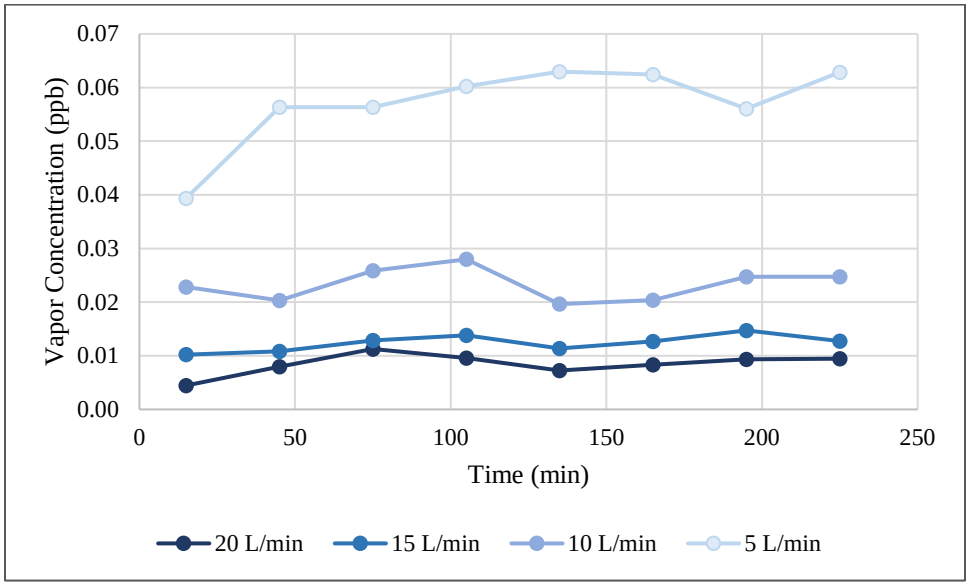

Figure 19. PETN vapor concentration generated over time at 5, 10, 15, and 20 L min^{-1}.

Table 5. Measured efficiencies of analyte vapor generation and analyses as determined by comparing nominal and measured vapor concentrations.

Analyte	*Solution concentration ($\mu g\ mL^{-1}$)*	*TV-Gen flow rate ($L\ min^{-1}$)*	*Nominal conc. (ppt)*	*Measured conc. (ppt)*	*Efficiency %*
PETN	0.1	5	77	60	78
PETN	0.1	10	39	24	62
PETN	0.1	15	26	13	50
PETN	0.1	20	19	9.2	48
NM	304	5	1140	562	49
NM	304	10	518	250	48
NM	304	15	380	188	49
NM	304	20	285	145	51
EGDN	1	10	751	636	85
EGDN	1	15	501	436	87
EGDN	1	20	376	327	87
NG	1	10	503	316	63
NG	1	15	335	205	61
NG	1	20	252	139	55

Nitromethane (NM)

Nitromethane (NM) has a significantly different chemical structure and characteristics than the previously discussed nitroaromatic compounds, and thus a much higher, 304 $\mu g\ mL^{-1}$, aqueous concentration of nitromethane was required for vapor generation in order to approach real-world vapor concentrations. Like the compounds previously tested, the vapor concentration was correlated with increasing diluent airflow (Figure 20). The sampling efficiency for NM was lower due to its high volatility, reducing the trapping efficiency of the online-CIS system. The overall efficiency was approximately 50% for all flowrates (Table 5), with the sample concentration within 1% RSD (Figure 21).

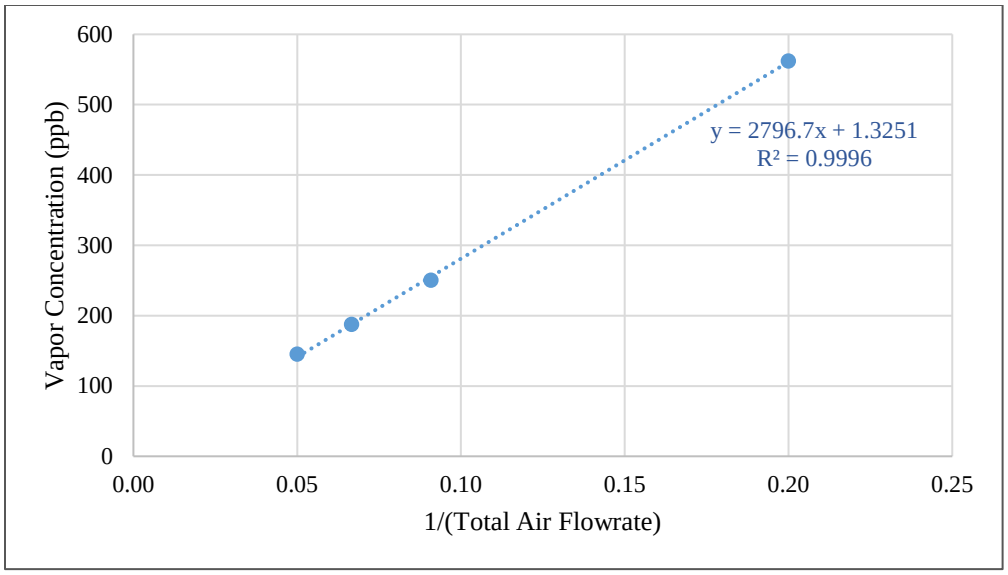

Figure 20. NM vapor concentration produced by the TV-Gen using varying diluent air flowrates (ranging from 5 to 20 L min-1 total flow) through the TV-Gen, showing the correlation between the dilution factor of the total air flowrate verses the resulting concentration. Note. Error bars are contained within the symbols and represent one standard deviation from average.

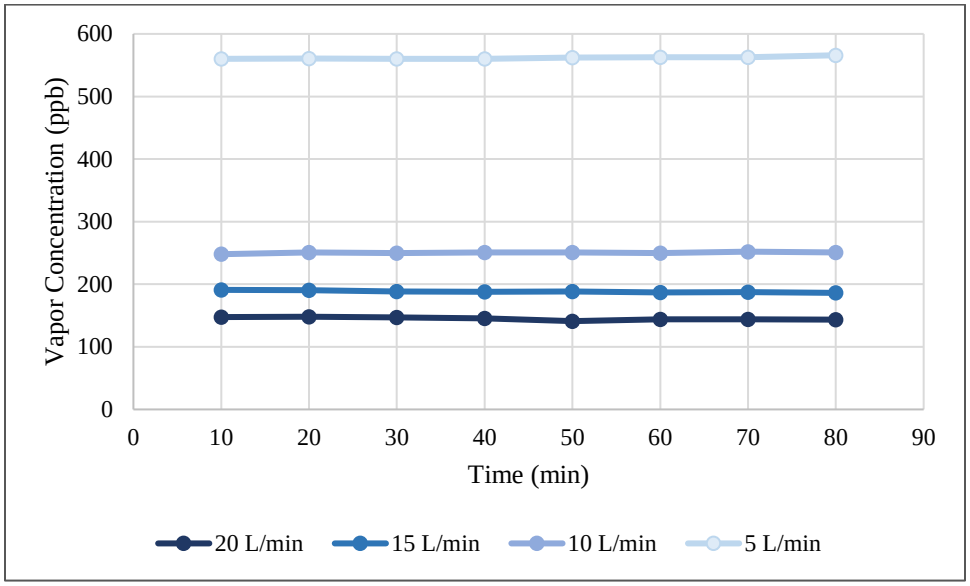

Figure 21. NM vapor concentration generated over time at 5, 10, 15, and 20 L min^{-1}.

Nitroglycerine (NG) and Ethylene glycol dinitrate (EGDN)

For both EGDN and NG, vapor was generated using a 1 µg mL^{-1} aqueous solution of both compounds. NG has a lower sampling efficiency due to its increased thermal sensitivity compared to EGDN. A detectable amount of decomposition was seen due to the required heating of the sampling apparatus. For both compounds, the resulting vapor concentration was directly correlated to the diluent airflow within the range of 10-20 L min^{-1} total flow from the TV-Gen (Figure 22)

with efficiencies of approximately 86% for EGDN and 60% for NG (Table 5). However, at the lowest flowrate of 5 L min^{-1}, both compounds experienced a significant decrease in sampling efficiency and were not linear with the other data points (Figure 22). This is likely due to the fact that EGDN and NG are both prone to adsorbing to surfaces as well as being thermally labile. As flowrate decreases, the dwell time of the vapor inside of the TV-Gen increases, thus increasing the likelihood for both adsorption and decomposition to occur in the process. It takes approximately 30 minutes for the EGDN to reach equilibrium concentration at the detector, whereas NG takes approximately 1 hour at 20 L min^{-1}. Once at equilibrium the vapor concentrations remained steady within 1 % for EGDN and 5 % for NG (Figure 23).

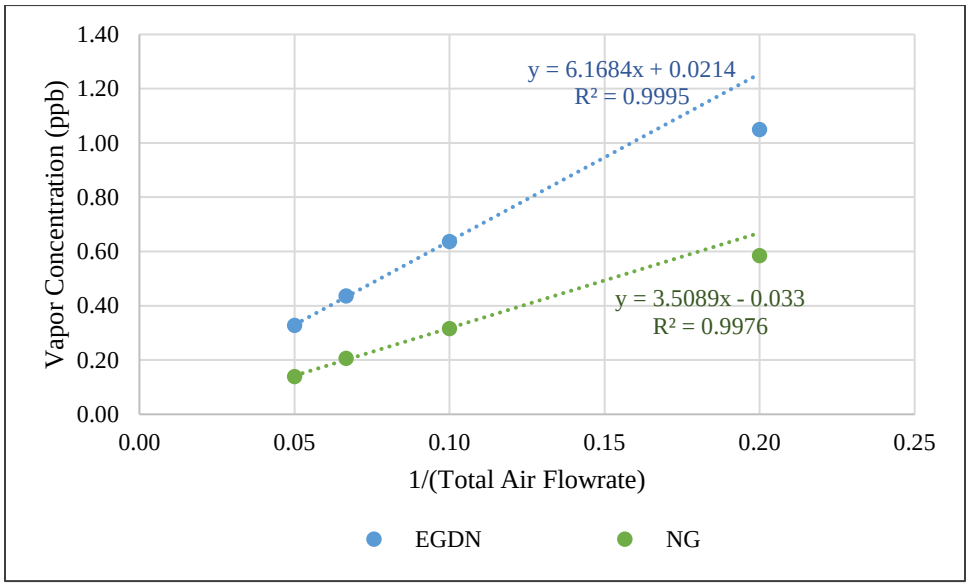

Figure 22. EDGN and NG vapor concentration produced by the TV-Gen using varying diluent air flowrates (ranging from 5 to 20 L min-1 total flow) through the TV-Gen, showing the correlation between the dilution factor of the total air flowrate verses the resulting concentration. Note. Error bars are contained within the symbols and represent one standard deviation from average. Additional note. Best fit line disregards the final data point.

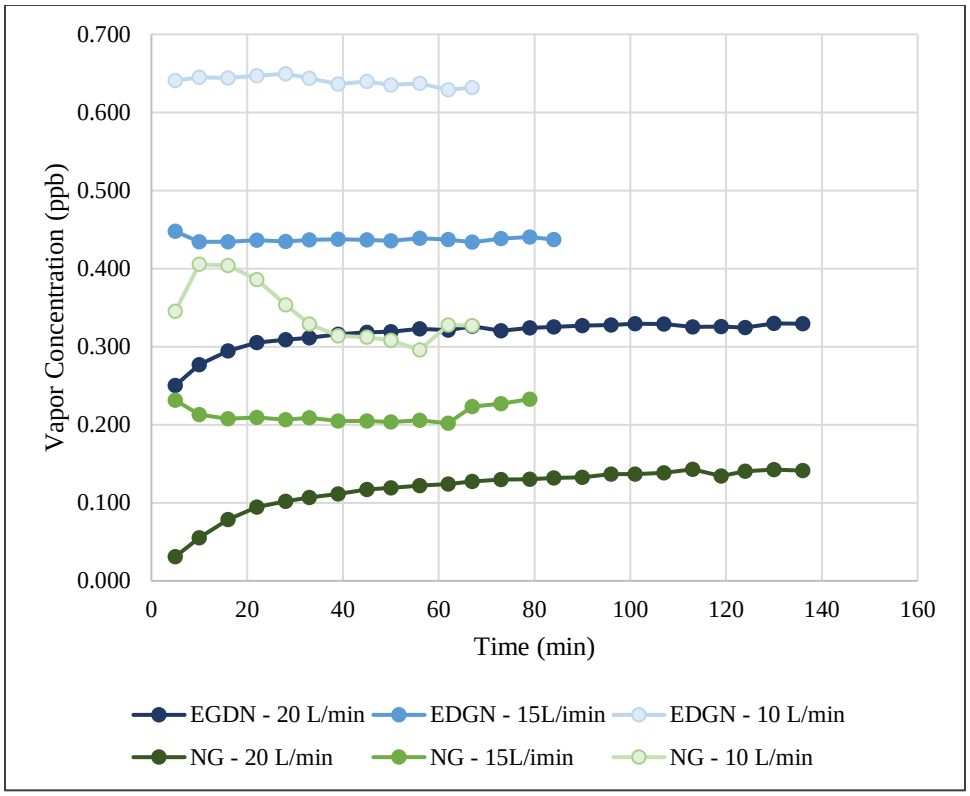

Figure 23. EGDN and NG vapor concentrations generated over time at 10, 15, and 20 L min^{-1}.

Triacetone triperoxide (TATP)

Qualitative analysis of TATP was carried out on vapor produced with the TV-Gen. While TATP is a solid at room temperature, it readily sublimes producing an appreciably saturated vapor concentration (63 ppm); [1]). For this reason, and due to its poor solubility in water, TATP vapor was produced by placing the bulk explosive (~800 mg) in a dynamic headspace chamber, as described in [10, 12]. In this instance, the TATP vapor replaced the air source of the nebulizer at a flow rate of 1L min^{-1} and the humidity was provided by nebulizing water in the TATP vapor. TATP was successfully detected in this manner using the previously developed analytical method [10].

Analyte Carryover

The persistence of residual analyte vapor, or carryover, when switching from the analyte line to the clean line within the TV-Gen was assessed. A mixture of 0.1 µg mL^{-1} DNT, TNT, and RDX solutions in water was delivered through the TV-Gen for 2 hours while using a 10 L min^{-1} total air flow. The TV-Gen was then switched to the clean side, which was purged for 5 minutes to ensure no vapor was present in the internal valve and the outlet port. Prior to sampling from the clean

side, the entirety of the instrumental sampling apparatus was baked and purged. This procedure was followed as it was previously shown that some carryover existed due to contamination of the instrumental sampling apparatus during a run. Finally, the sampling apparatus was reconnected and any analyte vapor remaining in the clean vapor stream was measured. Approximately 20 minutes was required after switching vapor streams to ensure that the analyte signal fell below the detectable limit for all compounds, while more volatile compounds such as TNT were no longer detected after just 5 minutes. It is believed that much of this carryover is actually due to the analytical detection system and not the TV-Gen, as there was anecdotal evidence from investigations with a separate detector wherein the carryover was mitigated in a much more rapid fashion.

Validation of Replicate Units

A second, identical TV-Gen unit was evaluated against the first to confirm reproducibility and reliable vapor generation across units. The evaluations were carried out using three analyte vapors, TNT, RDX, and PETN. The performance was consistent between the units with an average net difference of 13% between the RDX and TNT vapor concentrations. The vapor concentrations generated for PETN were nearly identical. Figure 24 illustrates the changing vapor concentrations with total airflow as well as the stability of the vapor concentration at a particular set of conditions over time, as given by the small error bars.

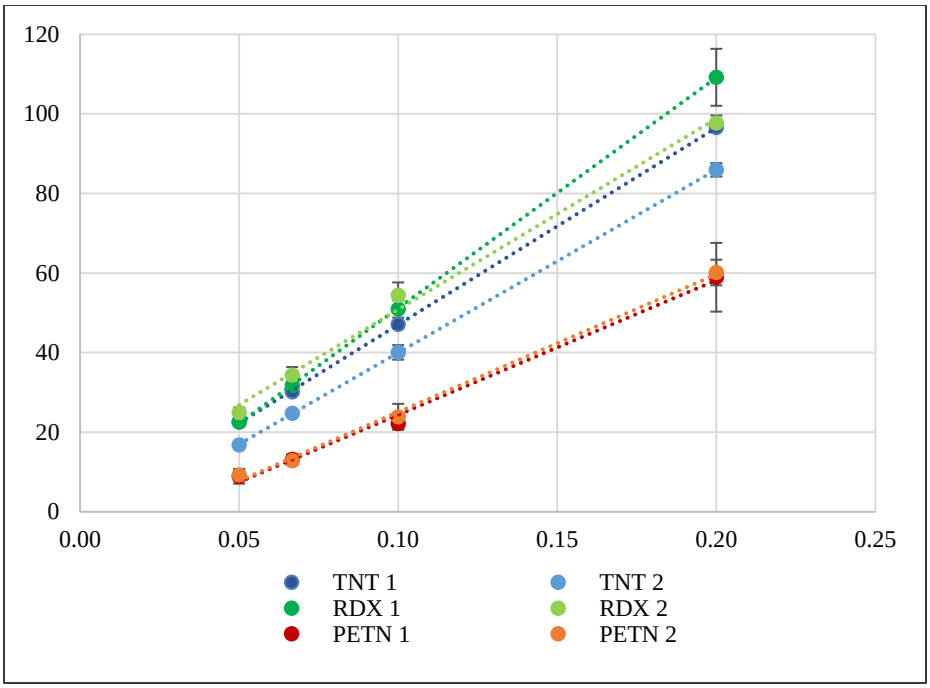

Figure 24. TNT, RDX, and PETN vapor concentration produced by two identical TV-Gen instruments. Diluent air flowrates from 5 to 20 L min-1 total flow. Note. Error bars are contained within the symbols and represent one standard deviation from average.

V. CONCLUSIONS

The TV-Gen was designed as a portable, compact system capable of reproducibly and accurately generating trace vapors (ppq_v to ppm_v) of troublesome, low vapor pressure compounds such as explosives. Key features of the TV-Gen include the ability to generate vapors from thermally labile explosives, rapid switching between clean and analyte manifolds, a linear dynamic range of more than three orders of magnitude, and nebulization of explosives in water preventing interference from organic solvents. Additionally, the placement of the dual manifold in a custom oven in addition to the passivation of the entirety of the vapor flow path ensures more efficient transport of low vapor pressure explosives. Finally, the system has the potential for simple introduction of interference gases to an explosives vapor stream via an additional inlet vapor port.

VI. ACKNOWLEDGEMENTS

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VIII. APPENDIX A – Operations Manual (v1.0)

A.1. Purpose and Description of TV-Gen

The Trace Vapor Generator for Explosives and Narcotics (TV-Gen) is a testbed, which has been developed to provide the Department of Homeland Security Science and Technology Directorate (DHS) with independent validation and verification (IV&V) of the new materials and sensors under development for explosives and narcotics detection. The Chemistry Division of the Naval Research Laboratory (NRL) has designed and constructed this testbed for the evaluation of a broad range of detection systems, materials and sensors. The testbed consists of a vapor generation system reliant upon the nebulization of solution-based analytes for a wide variety of explosives and potential interferents, an oven to promote efficient transport, and a control box that provides dedicated computer control with logging capabilities.

Operation of the TV-Gen is contained in the following Sections of this document:

- Section 2 discusses the setup and method for replacement of the manifold inside the main oven.
- Section 3 details the touch screen computer interface.
- Section 4 describes in detail the method for analyte introduction into the manifold using a nebulizer.
- Section 5 describes methods for routine operation.
- Section 6 details FAQ and operational issues.

A.2. Setup and Installation

A.2.1. Setup

The TV-Gen consists of three main parts: the Control Box, Oven and Manifold. The TV-Gen also uses the follow supplied accessories:

Table A-1. List of accessories supplied with the TV-Gen.

1	Power cord (NEMA 5-15)
For the manifold	
2	25-30 µL/min self-aspirating nebulizer
2	1/4 inch PFA nut
1	Timing belt
For connecting between the Oven and the Control Box	
2	Type K thermocouple cable
1	Fan Power cord (NEMA 5-15)
1	Oven power cord (NEMA ML2-15)
2	4 mm flexible nylon tubing (for pneumatic actuator, 4 feet)
2	1/4 inch PFA tubing (for sheath flow, 4 feet)

The manifold is contained within the oven (see section A.2.2) and has two isolated flow paths for clean and analyte vapor streams. The control box for the TV-Gen contains all the hardware necessary to operate the two nebulizers connected to the manifold. The nebulizer for the left side of the oven connects to the clean side while the nebulizer connected to the right side is the analyte side.

Figure A-1. Rear and Left side of TV-Gen Control Box showing setup locations.

The two inputs for the box are power (via a standard C13 plug) and a supply of clean compressed air (60-80 psi) which is connected to the 1/4" Swagelok port located between the clean and analyte outputs (AIR IN). The oven actuator valve is connected to two 4 mm push fit connectors (VALVE OUT).

Each nebulizer is connected via three different style/size connectors. The liquid portion of the nebulizer is connected via 1/16" tubing with an IDEX 1/4-28 flat-bottom threaded fitting. The nebulizer airline connects to the 4 mm push-fit connector. Sheath flow is provided via a 1/4" Swagelok fitting. 50 mL centrifuge tubes are placed on the left side of the control box for each of the clean and analyte solutions to spray.

The oven is connected to the control box via 4 cables to provide power and monitor oven temperature. Oven power is provided by the round turn-lock plug and fan power is provided via the NEMA-15 plug. Temperature is monitored by the two K-type thermocouple jacks, the upper one being the high-limit thermocouple (HL T/C) and the lower one being the control thermocouple (CTRL T/C). The oven valve is a pneumatic actuated valve where the air is provided by the upper two 4 mm push-fit connectors.

Figure A-2 shows the power and temperature connections on the oven, the upper one being the high-limit thermocouple (H) and the lower one being the control thermocouple (C). Below that is a C14 connector for the fan power. Lastly, at the bottom, there is a ML2-15 connector for the oven power. The top left shows the oven side of the two 4 mm push-fit connectors for the pneumatic actuator to control the manifold valve.

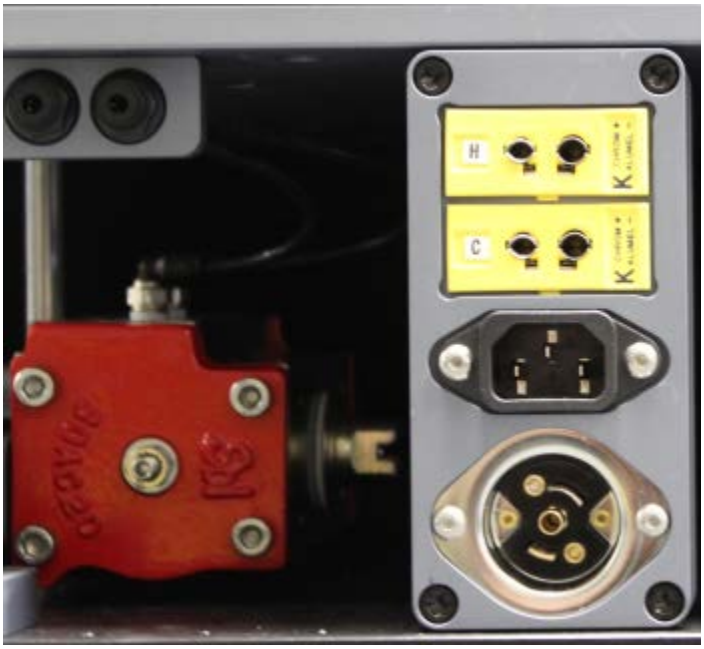

Figure A-2. Oven Power and Temperature Connections (right) and the two 4 mm push-fit connectors (top left) for the valve actuator.

Figure A-3 shows the left side of the oven where the manifold is positioned, as well as the six 1/4" Swagelok ports. The top two ports are exhaust ports for the two sides of the manifold. The left port is a “full” exhaust port, which connects to the manifold side currently not selected for output through the front sample port. The top right port is the “split” exhaust port, which is connected to the front sample port for the manifold side currently selected for gas sampling. Vapor from that side of the manifold will freely flow out both the “split” exhaust port and the front sample port unless restricted or moderated using external flow control mechanisms.

The middle two connectors are for the nebulizers which spray water/analyte into the manifold. The bottom two connectors are for the sheath flow into the manifold. The left two ports are designated for “clean” and the right two ports are designated for “analyte”.

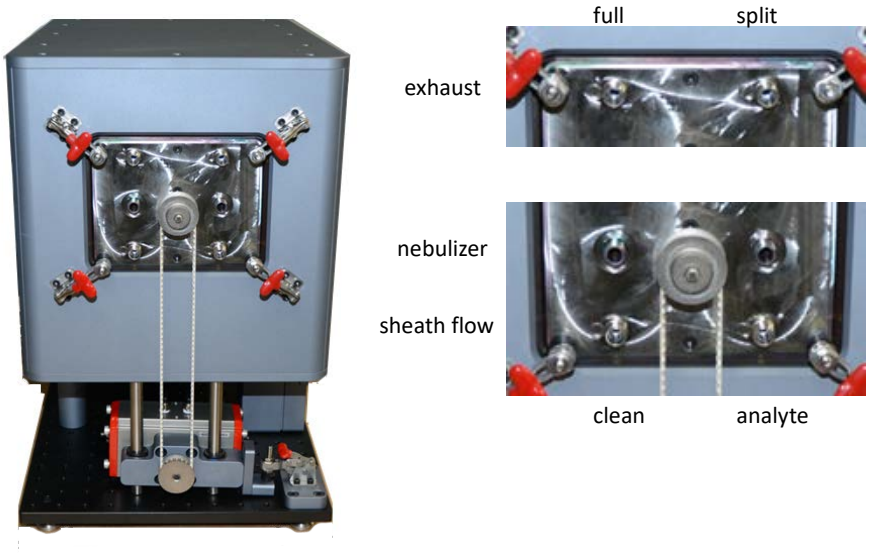

Figure A-3. Oven Manifold Connections showing inlets for nebulizers (center row) and sheath flow (bottom row) and exhaust ports (top row).

A.2.2. Manifold Installation

To remove the manifold:

1) Disconnect any attachments to the sampling port of the manifold
2) Remove the tubing and nebulizers from the manifold
3) Lift the red handle on the base to loosen and remove the timing belt
4) Lift the four red handles securing the manifold in the oven.
5) Carefully slide the manifold out of the oven

To reinsert the manifold

1) Place the manifold so that the split exhaust port is on the bottom (see Figure A-4)
2) Carefully slide the manifold into the oven.
3) Tighten the four red handles to secure the manifold in place
4) Align the timing belt shaft so that the flat notch is facing down (see Figure A-5)
5) Replace the timing belt around the center shaft, and the lower actuator box
6) Tighten the lower red handle; to secure the actuator.

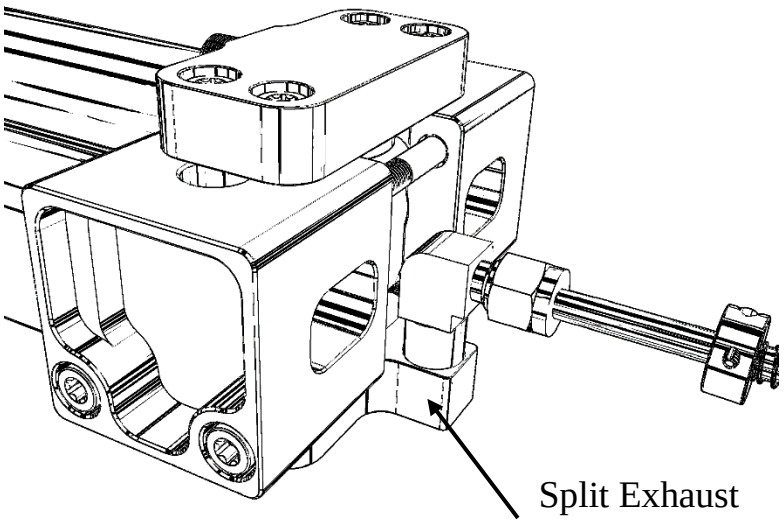

Figure A-4. TV-Gen Manifold, showing the correct orientation for placement into the oven with the split port on the bottom.

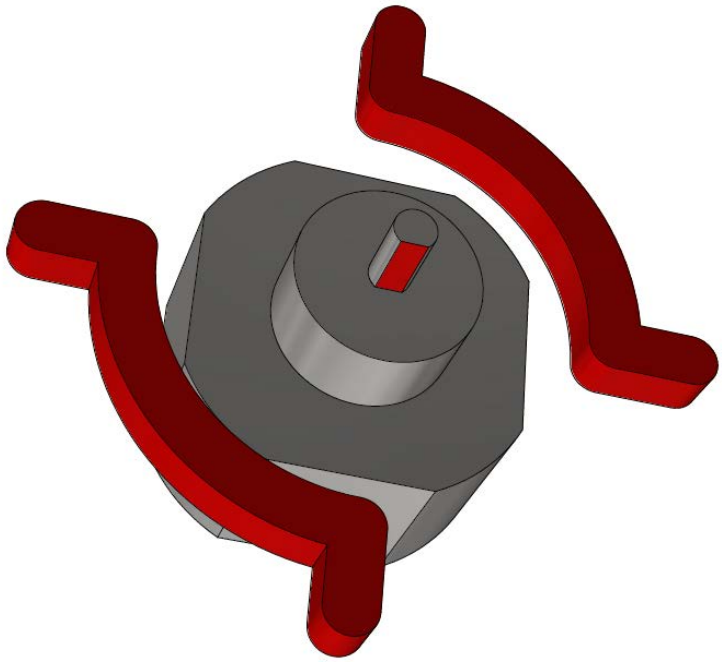

Figure A-5. TV-Gen Manifold valve path when the notch (center red) is down, indicating the correct installation orientation. The left manifold will be connected to the front/back exhaust port and the right manifold will be connected to the back exhaust port.

A.3 Touch Screen Computer Interface

The following section will familiarize the user with the touch screen computer interface utilized for TV-Gen control. The various functions of the testbed will be explained by describing the control of each available function by the computer. Limits associated with temperature and flow rate will be delineated when appropriate.

A.3.1. Main Control Screen

Upon logging into the TV-Gen, the user is presented with a screen that displays all of the flowrates of the testbed (Figure A-6).

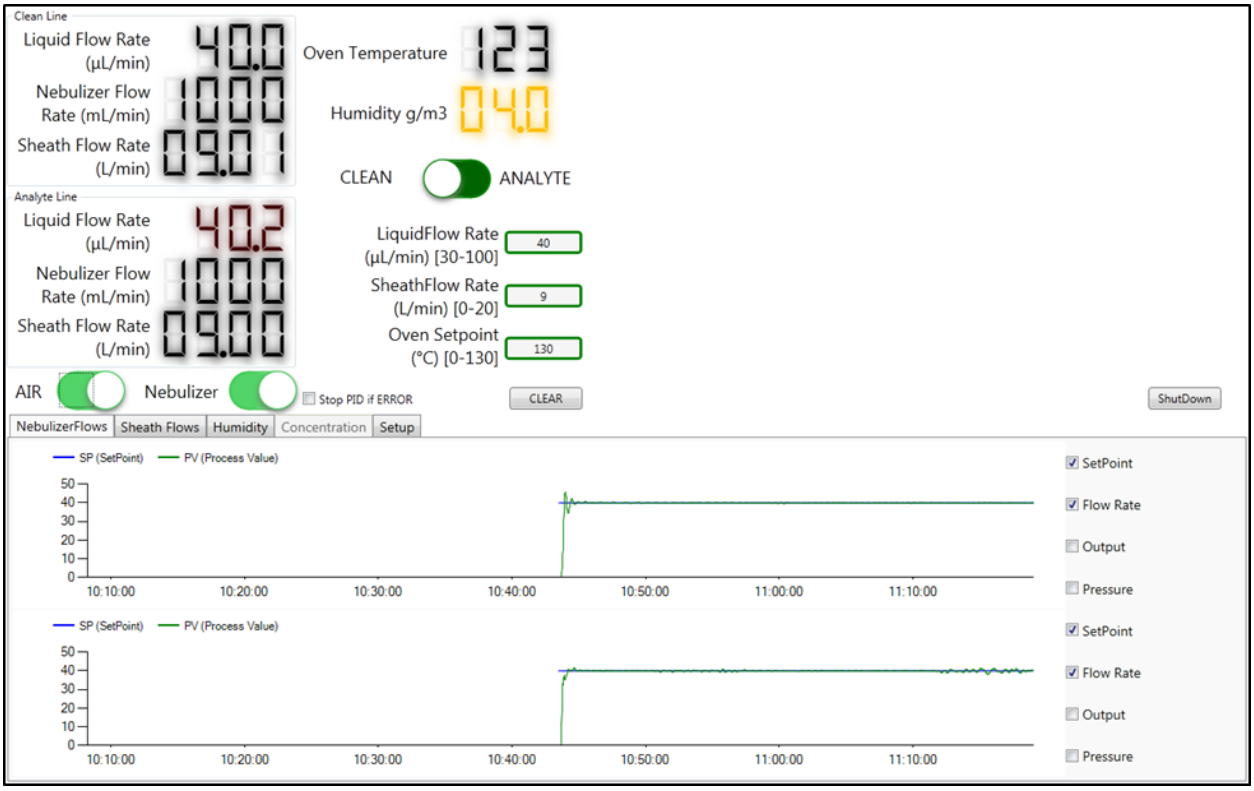

Figure A-6. Screenshot of TV-Gen Control Box GUI.

A.3.2. Data Display and Logging

The system displays a short history of all the current values, as well as a data log that runs continuously from the beginning of operations. Pressing the CLEAR button above the data display will clear old data currently being displayed while continuing to display new data from that point.

A.3.3. Flow Rate Displays

The top left of the control screen displays the Liquid Flow Rate (µL/min), the Nebulizer carrier gas flow rate (mL/min) and the Sheath Flow rate (L/min). The display is color coded based on the status of the controllers with black numbers indicating proper operation and red when outside of

proper operation. For the liquid flow rate, the display is black when the flow rate is at the desired set point (+/- 0.5 µL/min) and the last 10 values are stable (with a STD <0.5). For the carrier and sheath flows the display is black when the airflow is < 10mL/min (carrier flow) or 0.075 L/min (sheath flow) from the set point. For the carrier gas and sheath flow rates the colors are gray if there is no connection, indicating a communication error or dark gray when the air flows are off.

A.3.4. Flow Rate and Temperature Setpoints

Dropdown boxes allow for entry of the Liquid flow rate (30-100 mL/min) and Sheath Flow (0-20 L/min), as well as the oven temperature setpoint (0-130 °C). Both nebulizers, clean and analyte, utilize the same setpoint values for liquid and sheath flow rates. Touching the setpoint control will open a number pad to enter a new value. Touching the setpoint number again (or hitting the **ENTER** button) will close the popup and accept the new value. The entered value will be coerced into the acceptable range, while entering a non-numeric entry will keep the control open, and not accept the entry. The **CLR** button will clear the current entry, and allow for a new value to be entered. The **CANCEL** button will return the last good value to the control.

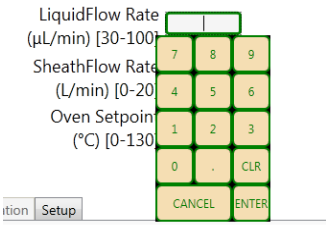

Figure A-7. Numeric touchpad of the TV-Gen interface, showing the number, clear (CLR), CANCEL and ENTER buttons.

A.3.5. Flow and Valve Toggle Switches

Toggle buttons are present to control the status of both the air flow and nebulizer liquid flow, as well as to switch the testbed's output between the two manifold pathways (Figure A-8). Both the air flow and nebulizer flow switches will display as green if the flows are on and white if turned off. The pathway switch will be green if the clean pathway (Figure A-8, upper right) is connected to the output and red if the analyte pathway is connected (Figure A-8, lower right). All three switches toggle between the two possible states by touching the button.

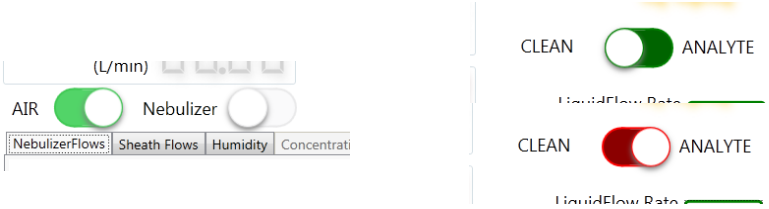

Figure A-8. The toggle switches showing the ON state for the air, OFF state for the nebulizer (left). Examples (right) of both states for the manifold CLEAN (green) and ANALYTE (red).

A.3.6. Data Charts

The charts at the bottom of the screen show a 90 minute history for each side of the manifold. The tabbed pages will show Nebulizer Flows, Sheath Flows and approximate Humidity, which assumes the sheath flow is dry air, and any water is from the nebulized solution.

A.3.7. Setup

The setup tab (Figure A-9) shows the current values from the proportional-integral-derivative (PID) loop controlling each nebulizer, the PID parameters and the Y-Axis Scales for each of the charts.

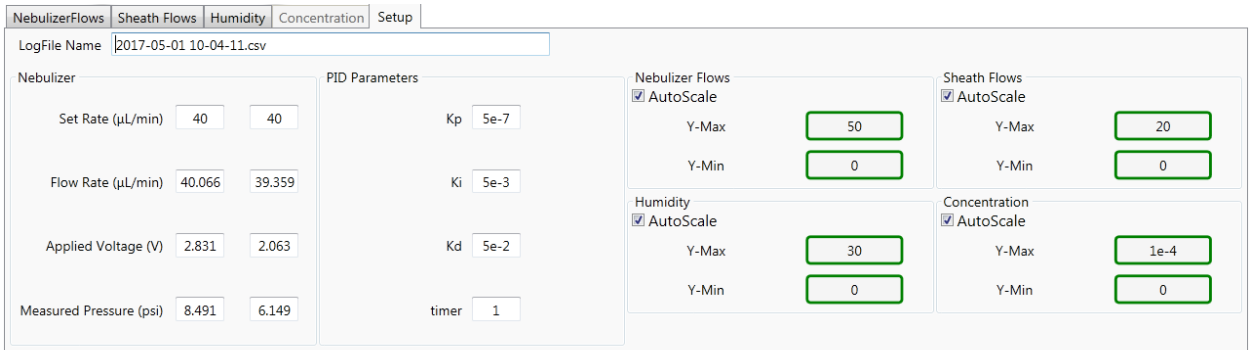

Figure A-9. Setup tab showing nebulizer PID loop values, PID parameters, and Y-Axis scales for each chart tab.

The left group box shows the current values for the components of each of the nebulizers, the desired setpoint, the current flow rate from the liquid flow meter, the applied voltage to the electronic pressure controller (EPC) and the measured pressure from the EPC.

The next group box show the PID parameters for the control loop, for reference purposes only.

The four right group boxes allow for setting the Y-Axis scales of each of the Charts on the other tabs.

A.3.8. Shutdown

Shutting down the systems will return the settings to their initial default values and close the software. The manifold will switch to Analyte Introduction into Manifold

A.4. Analyte Introduction into Manifold

The following section outlines in greater detail the method utilized by the TV-Gen to introduce analyte into the manifold: a pressure modulated liquid delivery system / nebulizer.

The nebulizer-based vapor generation system has been designed for continuous sample introduction. Sample solution is maintained in a 50 mL tube held on the side of the control box which is then pressurized between 0 and 15 psi. Figure A.4-1 shows the 1/16" PEEK tubing used to deliver the solution from the 50 mL tubes, and care must be taken not to damage, or contaminate this tubing. A pneumatic flow controller drives the flow of the sample solution through the nebulizer. A mass-flow controller delivers air flow through the nebulizer. The nebulizer is coupled to the sample-inlet manifold using a 1/4" PFA nut.

With the Nebulizer switch in the off or “no-flow” state, the user shall

1) Place the analyte solution into the left side of the control box, and screw the 50mL tube in securely, taking care not to over tighten.

2) Using the GUI: confirm the Liquid Flow rate
3) Press the Nebulizer Switch to initiate the system.

When changing the solutions, always turn off nebulization to prevent the control loop from overcompensating for the lack of flow.

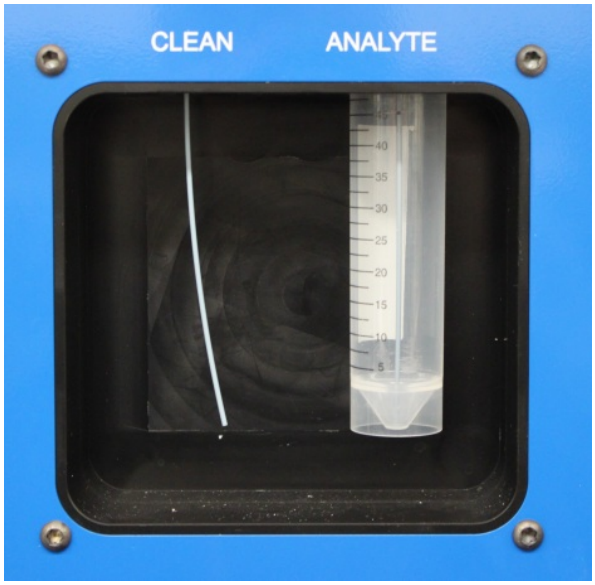

Figure A-10. Left side of TV-Gen control box, showing 1/16" PEEK tubing and 50 mL tubes for delivering analyte solutions.

Solutions for the generation of analyte vapor are made by pipetting a predetermined amount of analyte standard in solution (generally acetonitrile or methanol) and allowing the solvent to evaporate off before re-dissolving in water. The standard flowrate used for explosives compounds such as TNT, RDX, and PETN is 40µL/min; by adjusting the solution concentration and sheath flow rate the required vapor concentrations for testing can be achieved, limited by the vapor pressure of the target analyte.

A.5. Routine Operation

A.5.1. Basic Operations

a) Turn control box on; make sure air source is at 60-80 psi; wait for the display to come on and all the flow rates are showing valid values (see A.3.3)
b) Set oven to desired temperature (see A.3.4)
c) Set sheath flow rate to desired flow (see A.3.4) and turn air on (see A.3.5)
d) Prepare analyte solution, place tubes containing clean water and analyte solution into side of the control box (see A.4)
e) Wait for oven to achieve stable, uniform temperature (see A.5.2)
f) Set desired nebulizer flow rate (see 3.4); turn on nebulizer (see A.3.5) and wait until system is stable (see A.5.3)
g) Run experiment: use CLEAN/ANALYTE toggle switch (see A.3.5) to control the output between the clean and analyte vapor streams

A.5.2. Oven

The oven can be operated at a constant temperature continuously if desired without the need to reduce the temperature between uses, if operations are going to be performed on a regular basis. For intermittent use, it is recommended that the oven is powered off when not in use. Allow the oven to come to temperature and stabilize for at least 1 hour before use, to allow all internal components to reach their desired temperature.

A.5.3. Spraying

Allow 30-60 minutes upon commencement of spraying, depending on the analyte, in order for the concentration to stabilize. Extreme changes in sheath flow rate could cause destabilization of the liquid flow rate. The user should keep an eye on this parameter, or move in steps at the high and low sheath flow rates, as the pressure required to maintain the flow may exceed the limits of the EPC at 0-15 psi. If lower rates are required, a lower flow, self-aspirating nebulizer would be necessary. The delivered nebulizers are in the 25-30 µL/min self-aspiration range, and would need to be adjusted up or down depending on the desired rates.

A.5.4. Validation

A validation procedure using the more highly volatile 2,4-dinitrotoluene (2,4-DNT) should be performed in order to ensure all components of the TV-Gen are functioning correctly. A 10 mg/L solution nebulized at 40 µL/min of 2,4-DNT will produce a nominal vapor concentration of 2.6 ppb when operated at a total air flow of 20 L/min and 10.7 ppb when operated at 5 L/min. Depending on analytical capabilities, the nebulizer solution concentration can be increased by an order-of-magnitude. For qualitative purposes, expect the vapor concentration when operating at 5 L/min to be approximately 4X that when operating at 20 L/min. For quantitative purposes, total vapor efficiencies should be in excess of 90% for DNT.

The TV-Gen system has been validated for TNT, RDX, and PETN. For TNT and RDX, validation tests were run at an oven temperature of 90 °C, while PETN was run at a temperature of 70 °C. Validation tests were done using a 40 µL/min flowrate of 0.1 mg/L solutions at each of 5, 10, 15,

and 20 L/min total flow through the TV-Gen. Demonstrative results are shown in the table below (Table A-2). While the efficiencies are dependent on the operational values and the method for validation, expected TNT and RDX efficiencies are above 80%, while PETN efficiencies range from around 50-80% due to losses occurring in the sampling procedure used for validation. To ensure accurate quantitative results, validation runs should be done with the operational conditions being used for testing.

Table A-2. Demonstrative results from validation runs using TNT, RDX, and PETN.

TV-Gen Flow (L/min)	TNT			RDX			PETN		
	Nominal conc. (ppt)	Measured conc. (ppt)	Efficiency %	Nominal conc. (ppt)	Measured conc. (ppt)	Efficiency %	Nominal conc. (ppt)	Measured conc. (ppt)	Efficiency %
5	108	97	89	110	109	99	77	60	78
10	54	47	87	55	51	92	39	24	62
15	36	30	84	37	32	86	26	13	50
20	27	23	82	28	23	85	19	9.2	48

A.5.5. Cleaning

Cleaning of the dual manifold system may be necessary, depending on research needs. Maintaining the oven at 130 °C overnight typically results in near complete clear down of analyte in the manifold. This process can be assisted by introducing a 50/50 mixture of ethanol and water through the nebulizer system. The presence of organic solvent promotes desorption of analyte from the surface of the manifold. Finally, upon removal of the manifold from the oven, pure solvent can be used to rinse the inner surfaces.

Highly basic or highly acidic solutions (e.g. 1M NaOH or 1M HCl) should never be used to rinse the manifold as they may damage the SilcoNert coating.

Should clogging occur at the tip of the nebulizer, place the nebulizer in a beaker of ethanol and sonicate for approximately 1 hour. The likelihood of clogging increases if operating with liquid solutions that approach the analyte's maximum solubility in water or when the vapor concentration is near the vapor pressure of the analyte.

A.6. FAQ/Issues

Issue	Solutions
Nebulizer stops flowing with a large change in the sheath flow	Change the sheath flow in increments to allow the system to equilibrate between steps
Nebulizer flow rate not high enough to reach desired level / pressure required for nebulizer, nearing maximum of 15psi	1) Check that tube is properly installed and providing a proper seal 2) Swap nebulizer with one for higher self-aspiration range 3) Check for clog in nebulizer 4) Make sure valve is properly aligned
Nebulizer flow rate not low enough to reach desired level	1) Swap nebulizer with one for lower self-aspiration range 2) Increase sheath flow rate
Actuator valve not turning manifold	1) Check that the inlet air pressure is between 60 and 80 psi 2) Check that the black 4 mm tubing is fully inserted into the fittings on both the control box and the oven 3) Check that the timing belt is tightened and the lower level is secure
System responding slowly after running for extended period of time	Shutdown and restart program (icon on desktop)