

# Vapor-generation methods for explosives-detection research

Jay W. Grate, Robert G. Ewing, David A. Atkinson

The generation of calibrated vapor samples of explosives compounds remains a challenge due to the low vapor pressures of explosives, adsorption of explosives on container and tubing walls, and the requirement to manage (typically) multiple temperature zones as the vapor is generated, diluted, and delivered. Methods that have been described to generate vapors can be classified as continuous or pulsed-flow vapor generators.

Vapor sources for continuous-flow generators are typically explosives compounds supported on a solid support, or compounds contained in a permeation or diffusion device. Sources are held at elevated isothermal temperatures.

Similar sources can be used for pulsed vapor generators; however, pulsed systems may also use injection of solutions onto heated surfaces with generation of both solvent and explosives vapors, transient peaks from a gas chromatograph, or vapors generated by programmed thermal desorption.

This article reviews vapor-generator approaches with emphasis on the method of generating the vapors and on practical aspects of vapor dilution and handling. In addition, a gas chromatograph system with two ovens that is configurable with up to four heating ropes is proposed, and could serve as a single integrated platform for explosives-vapor generation and device testing. We also discuss issues related to standards, calibration, and safety.

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## 1. Introduction

Because explosives are a significant threat, there is great interest in the development of improved explosives-detection devices and systems. Detection of vapors is important in three contexts. First, detection systems that rely on the collection of particles from residues, rather than directly detecting vapors, will often vaporize the sample as part of the detection process. For example, the widespread use of explosives-trace detectors in airports for screening is focused on swabbing residues from surfaces, placing the sampling media containing the residue into the instrument where it is heated to vaporize and to desorb the explosives as vapor molecules, followed by transport of these molecules in the gas phase to a detector [e.g., an ion-mobility spectrometry (IMS) instrument].

The second context for vapor detection is the direct detection of vapors from ambient gas sampling. This approach may be feasible where there is sufficient vapor pressure and current (or future) instrumentation has sufficient sensitivity. Direct vapor detection offers the promise of a

non-contact detection paradigm, rather than contact-based collection of solid particles or residues. Some explosives (e.g., nitroglycerin) can already be detected directly in the vapor phase with relative ease [1]. The same ease of vapor detection is true with other volatile explosives-related materials [e.g., 2,4-dinitrotoluene (2,4-DNT) in samples of trinitrotoluene (TNT)] [2–4], or taggants [e.g., 2,3-dimethyl-2,3-dinitrobutane (DMNB)] [5,6] that are deliberately added to explosives (by law in the USA) to facilitate vapor detection. Many less volatile explosive compounds are difficult to detect directly as vapors with current technology.

The third context for vapor detection involves the use of canines rather than instruments. In this context, the odor of an explosive material may be detected rather than the vapors of the explosive chemical itself [7–9]. Explosives manufactured and packaged for operational use (e.g., military, mining, and construction) are typically mixtures of a number of chemicals rather than single pure explosive compounds. This is done to make the material easier or safer to handle. The

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added chemicals may include solvents, plasticizers and/or taggants, whose vapors may be more volatile than the explosive chemical. The odor may also include contaminants and degradation products from the explosive compound. This characteristic odor is often referred to as the “explosives bouquet” [10,11]. There is a long-running scientific debate with respect to which compounds or mixtures of compounds trigger an alarm in canines used for explosives detection [12]. This concept must be kept in mind if designing a vapor-generator system that may be used for canine training or evaluation.

In development and evaluation of new detection devices and approaches, it is often necessary to generate test vapors of a known concentration under controlled conditions, and deliver them to the device under test. A vapor-generation system functions to generate explosive molecules as monomers in the gas phase from a condensed matter source, transport these molecules from the source, and present them to the detector or other device under test as a vapor. This process is significantly more challenging for explosives than volatile organic compounds (VOCs). Typical solid explosive materials have very low vapor pressures, and the kinetics of vaporization of molecules into the gas phase may be slow. Explosives compounds are often described as “sticky”, because they may interact strongly with material surfaces, and most have a tremendous tendency to adsorb on surfaces before arriving at the device under test [13,14]. Surfaces downstream in the flow system must therefore be maintained at elevated temperatures to reduce adsorption, and to prevent cold spots that condense explosive vapors. Failure to control these processes can lead to unknown or variable output concentrations. Hence, thermal control is important not only for the source, but for the entire gas-flow system and often involves multiple temperature-control zones. Finally, vapor-generation systems using explosive materials, and their waste streams, must be designed to be safe, as explosive compounds are significantly reactive, and can be subject to dangerous detonation or deflagration if caution is not exercised.

Explosives-vapor generators have been historically developed for a variety of purposes. In some cases, the generator must simply get explosives vapor (or even particulates) into the air in order to test the ability of a sampling device to capture that explosive and deliver it to a detector. The sampler could be a walk-through explosives-detection portal [15] or a small volume pre-concentrator device [16–18]. Alternatively, a generator may be required to challenge the ultimate detection limits and assess the performance of commercial detectors; in this case, the ability to generate ultra-low concentrations reliably and reproducibly is paramount. In other cases, a generator may be required to provide test vapors conveniently for new sensors under development. Accordingly, there is no “best” vapor-generator design,

and the descriptions below are not meant to identify a “winner”. Rather, we seek to set out the principles and the approaches used in the past, so that researchers are well informed for selection or development of a vapor-generator method suited to their own requirements. Typically, an explosives-vapor generator is intended to deliver either a known concentration of the explosive in a carrier gas, or a known mass of explosive molecules. The system may generate a continuous flow or deliver a pulse containing the explosive.

We review vapor-generator approaches with emphasis on the method of generating the vapors and on practical aspects of vapor dilution and handling. Further details of the flow systems – and details are very important – can be found in the primary cited literature. Some vapor-generation approaches are described in articles specifically on the generator. In other cases, articles about a detection method also describe the vapor-generation method used to enable testing of the detection method. In his review on explosives-detection approaches, Moore cited 11 publications on vapor-generation approaches, but specific vapor-generation approaches were not described [19]. In a book in 1999, Yinon described a number of the published vapor-generation approaches [20]. Explosives-vapor-detection sensors, instruments, and systems were reviewed previously and are not covered here [2,8,19–28]. Difficulties and constraints that confound explosives detection, many of which also apply to the generation of explosives vapors, were set out in an article by Steinfeld, aptly entitled “Explosives detection: a challenge for physical chemistry” [21].

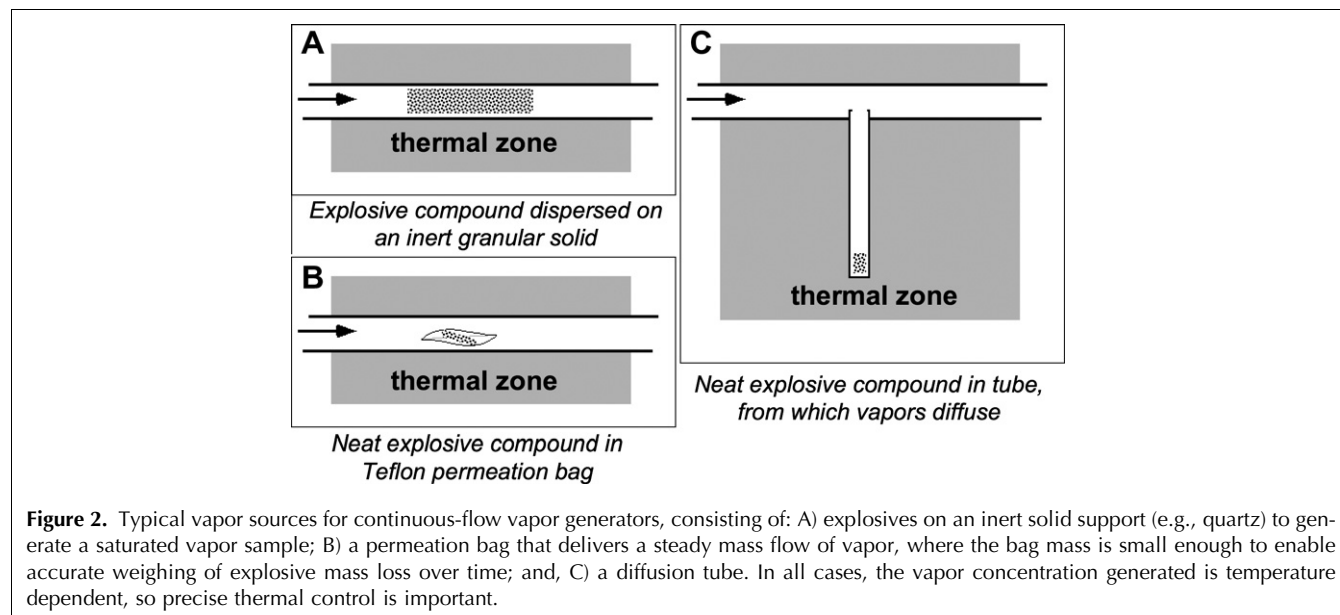
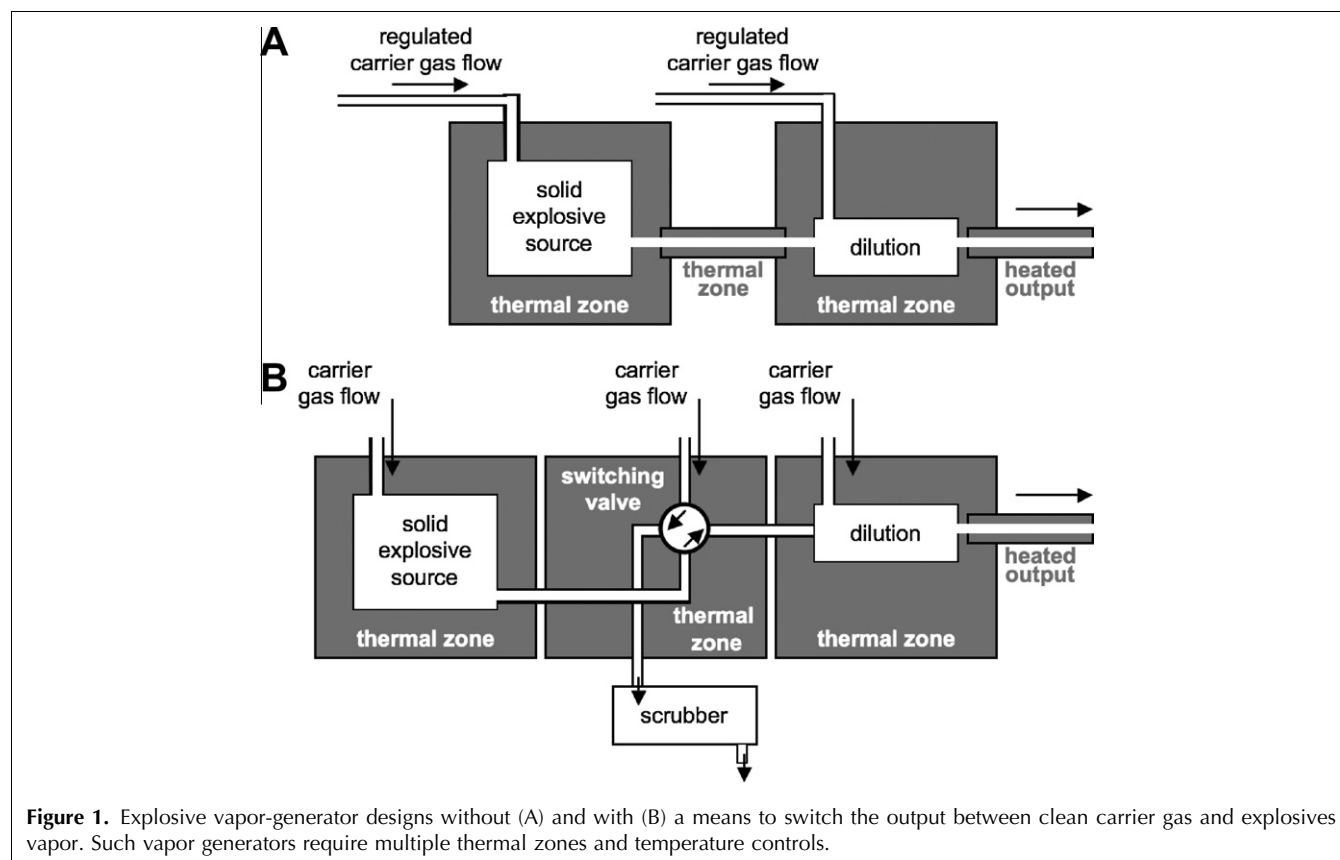
The vapor pressures of explosive compounds are of obvious relevance to vapor generation and detection. However, the vapor pressures are beyond the scope of this article; they are covered separately in a companion review submitted to this journal [29] and in another recent review [30].

Some of the vapor generators to be described below were used in the determination of explosive vapor pressures by collecting the vapors from a continuous isothermal saturated vapor stream for a known period of time and analyzing the generated mass by gas chromatography (GC) [29]. Vapor-pressure equations can be used to predict what saturated vapor concentration will be obtained from an explosive held at a given temperature as the vapor source.

## 2. Continuous-flow vapor generators

### 2.1. Neat and supported solid sources

Most continuous-flow generators are based on the passage of carrier gas over a solid sample of the explosive chemical. {Here we refer to neat explosive chemicals, as opposed to explosive-material formulations [e.g., plastic explosives (e.g., Semtex and C-4) that contain one or



more explosive chemicals, plasticizers, binders, fillers and solvents remaining from the manufacturing process}}.

Fig. 1 shows the components of typical vapor-generation systems. Examples of the explosive sources are shown in Fig. 2. The explosive source may be neat explosive chemical; however the use of explosive chem-

icals dispersed on non-volatile solid supports (e.g., silica) is generally preferred (Fig. 2A). The latter approach provides more surface area for vaporization while also being far safer because of the reduced explosive hazard. The use of a neat source was described as early as 1976 [31] and as recently as 2010 [32].

In 1986, Dionne et al. used thermostatted sources of several explosives, including solid TNT, 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), and [3-nitrooxy-2,2-bis(nitrooxymethyl)propyl] nitrate (PETN) to generate vapors for the determination of explosives-vapor pressures and equations describing their temperature dependence [33]. (The acronym RDX is derived from Research Department Explosive rather than its proper chemical name, and the more commonly used chemical name is cyclotrimethylenetrinitramine. The more commonly used chemical name for PETN, and the source of its acronym, is pentaerythritol tetranitrate).

In 1976, Pella described the use of explosives dispersed on a Chromosorb support [34].

In 1992, Kenna et al. discussed vapor emission from dispersed sources in detail, and examined RDX-vapor emission from coated beads and coated screens [35]. Generator outputs were monitored with an IMS instrument. These approaches use solid sources to generate explosive vapors without additional solvent vapors, assuming the solid source contained a pure compound to begin with.

Given an adequate amount and surface area of dispersed material at a sufficient temperature, and within certain flow limitations, the explosive molecules will equilibrate to a saturated concentration in the gas phase. However, if these conditions are not met, a continuous-flow generator may deliver a sub-saturated concentration.

It is also possible to start with a neat or supported solid source using an approach that deliberately sets up defined diffusive limitations in order to generate a sub-saturated concentration. Permeation tubes and diffusion tubes, better known for use with neat liquid sources [36], operate by these principles (Figs. 2B and 2C). We describe below examples of this design for explosives-vapor generation.

## 2.2. Generators based on supported solid sources for continuous flow

The 1976 report by Pella from the National Institute of Standards and Technology (NIST, formerly known as the National Bureau of Standards), describing the generation of vapors from TNT, 2,4-DNT, 2,4-dinitrotoluene (2,6-DNT), and ethylene glycol dinitrate (EGDN), provided a thorough account that illustrated key aspects of vapor generation from explosives on solid supports [34]. In this approach, a saturated vapor sample in equilibrium with the solid is generated and then diluted downstream. The sources were created by dispersing the explosive materials from solutions onto Chromosorb supports; these sources were then contained in spiral glass columns with silanized internal surfaces. The glass columns were maintained in a constant temperature bath with control to  $\pm 0.05^\circ\text{C}$ . A gas-flow system inside an oven at elevated temperature mixed all or part of the

output from the source column with additional carrier gas for dilution. The flow path from the source to the oven was heated with a heating tape. This system is similar in concept to that in Fig. 1A. The gas-flow system could dilute the output from the source column by a factor of up to about 200 times; even larger dilutions could be obtained by mixing only a fraction of the source output into the dilution gas. This dynamic gas-blending system could deliver gas concentrations as low as 0.05 ppb<sub>v</sub>. Variations of the source temperature, the fraction of the source output flow used, and the flow rate of the dilution gas determined the final output concentration. Using adsorbent-collection tubes and a GC system with an electron-capture detector (ECD) for analysis, the authors studied output concentrations as a function of source flow rate to determine if saturation was achieved. In addition, they reported equilibrium-vapor concentrations as a function of source temperature for the four explosive compounds considered.

In 1978, Carter et al. from the Sandia National Laboratories and Lucero from the Aerospace Corporation also described a generator using explosives dispersed on a solid support [37]. The source material was packed in a tapered aluminum insert inside a beryllium-copper temperature-controlled block. Aluminum inserts with different explosive sources could be interchanged. The authors noted that a temperature variation of just  $1^\circ\text{C}$  can change the vapor pressures of some explosives by up to 19%. These authors diluted the source flow using a turbulent mixing approach, injecting the source flow through a 180- $\mu\text{m}$  diameter jet into dilution air within a 19 mm diameter by 420 mm length nickel tube serving as the mixing chamber. The nickel-tube walls were porous, and the dilution gas was delivered into the tube from the exterior through the wall; this approach was designed to minimize the adsorption of the explosive molecules on the inner nickel-tube surfaces. The diluted explosive vapor was delivered at the output fully mixed and at ambient temperature. To switch the final output, a four-port two-position valve was located between the source and the mixing chamber, such that either the source vapor or clean carrier gas could be injected into the mixing chamber. A switching valve between source vapor and dilution gas is shown schematically in Fig. 1B. Explosive vapors that were not injected were captured on a charcoal scrubber. The switching valve was housed in an oven at a temperature  $20^\circ\text{C}$  above the source temperature. This report focused on the novel design approaches just described without reporting the specific explosive compounds used to generate vapors or providing analytical results on its efficacy.

In 2001, Houser et al. described a vapor generator for nitroaromatic compounds to support the development of hydrogen-bond acidic polymers as selective layers for explosives detection using surface acoustic wave (SAW) devices [38]. Hydrogen-bond acidic polymers for

chemical sensing and preconcentration have been reviewed [39,40].

Houser and colleagues set up four copper columns in parallel in a thermostatted water bath, where two columns contained the sources of TNT and 2,4-DNT, a third contained sand without explosives, and a fourth was empty. A manual valve was used to select the source (or blank) column, the output was diluted downstream with humidified air, and the blank air or the explosive-containing sample was delivered at room temperature to the sensor(s) under test. The source columns contained NESTT materials [41], which consist of the explosive material dispersed on sand. The NESTT acronym stands for Non-Hazardous Explosives for Security Testing and Training [42]. These materials are available commercially, and are intended for training canines or testing instruments. SAW sensors were tested by first delivering clean air passed through one of the blank columns to establish a baseline followed by carrier gas containing vapor from one of the source columns. This paper was focused primarily on the polymers and sensors.

In 2003, Rana et al. produced a similar vapor generator to that described by Pella, dispersing TNT on solid supports that were packed into temperature-controlled spiral glass columns [43]. These authors investigated three support materials:

- (1) alumina spheres of 5–8 mm diameter;
- (2) alumina chips prepared by crushing smaller alumina spheres; and,
- (3) crushed molecular sieves of the same size.

TNT vapors from each source at different flow rates and temperatures were collected on charcoal and analyzed by high-performance liquid chromatography (HPLC). These authors found that smaller size solid supports were preferred, as expected, and that the molecular sieve support gave more consistent output concentrations than activated alumina. These authors developed their generator to facilitate testing and calibration of polymer-coated SAW devices for explosives detection [44].

### **2.3. Generators based on sources with diffusion limitations for continuous flow**

In 1993, Lucero and collaborators from the Federal Aviation Administration (FAA) Technical Center described a vapor generator based on the permeation of vapors from a neat explosives sample contained within a thin-walled Teflon bag (see Fig. 2B) [45]. These bags were prepared by heat sealing the edges of Teflon films, and varying the size and the film thickness as required to obtain desired permeation rates. The bags were contained in a thermal chamber at 75°C, consisting of a porous metal tube surrounded by a solid metal tube; heated carrier gas was delivered to the annular space between the tubes and flowed through the porous wall into the inner tube, thus minimizing vapor adsorption on

the inner tube walls. The output from this vapor-generation chamber was delivered into a tubular membrane at 150°C and out to a scrubber cartridge. Diffusion of vapor molecules through the tubular membrane into a dilution carrier gas produced a highly dilute flow of explosive vapor. This generator approach used two stages of diffusive limitation – the permeation bag and the tubular membrane – to generate a constant mass flow into the dilution carrier gas. The concentration then depended on the diluted mass flow divided by the dilution gas volumetric flow; the former is constant for a given permeation bag, explosive, or tubular membrane, while the dilution gas flow can be varied over a large range. The final output to the device under test could be switched between clean carrier gas and explosive sample using a valve. This approach was unique in using permeation constraints, delivering exceptionally low levels of explosives for instrument testing, and achieving high levels of dilution while being conservative with the use of carrier gases.

Using RDX as an example, a permeation bag with a 1 L/min carrier flow rate generated an RDX concentration approximately 1500 times lower concentration than the saturated vapor pressure at 75°C. At a dilution carrier gas-flow rate of 1 L/min, the generator output of RDX was stated to be  $2 \times 10^{-3}$  ppt<sub>v</sub> or  $2 \times 10^{-14}$  g/min, although the analytical measurements validating these values were not provided. The mass-flow rate of the permeation bag could be calibrated by periodic determination of weight loss over a period of weeks (i.e. gravimetrically).

Permeation devices develop a gradient across the permeation membrane from the constant high concentration on the “inside” to the diluted concentration on the outside; maintaining this gradient across the thickness of the membrane is essential to obtaining and maintaining a known stable mass-flow rate of the compound of interest. Accordingly, a permeation-based system effectively has to be generating vapor all the time, regardless of whether the final output is directed to the instrument output or to waste, or even whether the generator is being used at all, in order to maintain this gradient.

A diffusion-tube method was described by Eiceman et al. in 1997 [46]. Solid samples of neat TNT, RDX, or PETN were loaded into the bottom of a nuclear magnetic resonance (NMR) tube serving as a diffusion tube with a precision bore of defined internal diameter and length (see Fig. 2C). Vapors diffusing out of this tube were swept away into a carrier gas, creating a gradient up the length of the tube from the source solid to the tube outlet. The mass-flow rate of vapor depended on the temperature, vapor pressure and molecular diffusivity of the explosive, as well as the dimensions of the diffusion tube. The system was configured such that all wetted surfaces were glass and the diffusion tube could be

readily removed for periodic mass determinations. The overall system had four thermally-controlled zones, including a heated vapor outlet. The diffusion tube temperature was 79–150°C to vary the generated vapor mass-flow rate. This study was extremely thorough in determining the generator performance. Mass-flow rates were determined gravimetrically by periodic weighing of the source, tracing the microbalance measurements to NIST standards. Output concentrations for TNT were also measured using IMS. The chemical purity of the generated vapors was determined by mass spectrometry (MS). Gravimetric determinations and IMS determinations for TNT at 79°C were in excellent agreement and were compared with outputs expected based on calculations. Mass-flow rates could be adjusted from several ng/s down to a few pg/s by the source temperature, and were stable over several hundred hours of continuous operation. The final output could be switched using a module added to the output stage.

#### **2.4. Generators based on vaporization of liquid solutions for continuous flow**

In a departure from methods based on the evaporation of stationary solid explosive samples, Verkouteren and Gillen at NIST, working with Taylor at Microfab Technologies, developed an approach using inkjet technology [47]. A solution of known explosive concentration is dispensed at a known rate onto a heated ceramic surface, vaporizing both the solvent and the explosive molecules into a carrier-gas flow. This approach is designed to generate explosive vapors on demand as a continuous-flow method or to generate pulses. A linear array of six inkjet devices was mounted in a head with a carrier-gas distribution system designed to mix with the vaporized molecules. Flow rates of 1–10 L/min were described. By varying injection solution concentration, inkjet rates, the number of nozzles used, and the flow rate, the system could vary concentrations over six orders of magnitude with a lower concentration generation capability of 290 fg/L. Vapors were generated from TNT, RDX, and PETN, and detected by IMS. This novel approach has the advantages of simplicity, wide dynamic range, on-demand vapor generation, and suitability for portable configurations. Its primary disadvantage is the generation at the same time of solvent vapors that are not separated from the explosive vapors. Further reports have described additional aspects of this approach [48,49].

### **3. Pulsed or transient flow vapor generators**

#### **3.1. Pulsed versus continuous generators**

A pulsed-flow generator delivers a known mass of explosive material, or a known volume of a known concentration of explosive vapor, for a short period of

time. A number of the continuous vapor generators are capable of switching the output between a clean carrier gas and the explosive vapor concentration, and back again, and hence can function as pulsed vapor generators. However, a variety of generators have been developed that are not capable of sustained continuous flow of a controlled explosive-vapor concentration, but can deliver a pulse of explosive vapor for a short period of time. This pulse may be derived from a saturated vapor source, or represent the vaporization of an injected solution of known volume containing a known concentration of the explosive, or the vaporization of a known quantity of solid that was originally deposited from a known volume of a known concentration solution. Pulsed vapor sources provide explosive vapor only when needed; they do not generate a continuous waste stream and are less likely to lead to the accumulation of explosives material in undesired locations or quantities.

#### **3.2. Pulsed generators with saturated vapor from supported solid sources**

In 1992, McGann et al. described a heated syringe as a pulsed vapor generator that delivered a known volume of vapor saturated at a known temperature [50,51]. The explosive source consisted of RDX or C-4 deposited on mineral wool and placed within the syringe barrel. The entire syringe barrel and tip were maintained at a constant temperature. Using an ECD in constant current mode for detection, the authors evaluated the time required to saturate the vapor within the syringe barrel (about 6 min for RDX) and the linearity of the detected response with injected syringe volume (very linear). In related work with RDX, TNT, and PETN, a back-to-back dual-syringe system was designed to withdraw upstream carrier gas while injecting explosive vapors to prevent gas-flow changes at the detector from causing a flow-induced response [51].

In 1993, Davies et al. from the Idaho National Engineering Laboratory described a pulsed vapor generator, whose design was adapted from those of continuous-flow vapor generators [52,53]. A thermostatted, coiled column containing explosives material deposited onto solid quartz beads served as the source. However, an automated flow-control system with pressure transducers, solenoid valves, and flow control meters was developed to deliver pulses of known flow rate and pulse width from this source, thus delivering a known mass of explosive. Precise pulses of 5-s duration were investigated and demonstrated, with elapsed time between pulses of a few minutes. The initial reports on this generator focused on the calibration of the output using sample collection tubes and an IMS detection system. It was found that saturated vapors from TNT matched predictions based on vapor-pressure equations, but generated RDX concentrations gave poor agreement. Details of heated zones in the generator were suggested as a possible contributor

to higher than expected RDX outputs. A report in 2007 described the explosive vapor reservoir in additional detail [54]. An outlet tip was designed using a porous stainless-steel tube inside a solid stainless-steel tube; carrier gas was delivered into the annulus and through the porous tubing to mix with the vapor stream in a technique reminiscent of prior work reported by Carter [37]. This vapor generator has found use by others in, as just one example, the development of chemical micro-sensors for explosives detection [55].

### 3.3. Transient chromatographic peak as a pulsed source

In 1991, McNair et al. described an explosives-vapor generator that produced a transient pulse of explosive compound from the outlet of a GC system [56], in contrast to previous methods based on the equilibration of explosives vapors with solid sources, as discussed in the section on continuous generators above. The GC system was modified so that the capillary column (95% methyl, 5% phenyl polysiloxane stationary phase) could be extended outside of the oven, such that the column end served as the vapor outlet. A custom sleeve was created to heat this outlet to 195°C. The system was equipped with a capillary split/splitless injector. The explosive sources consisted of dilute solution standards in 2-propanol that were injected into the GC system using splitless injection and an autoinjector for consistency. This method delivers a known mass of explosive. In addition to producing a transient vapor pulse, the GC method provided two advantages: the explosive was separated from the solvent, exiting the column at a different time; and the explosive was purified on the column. Thus, the detectors to be evaluated could be tested against pure explosives free of solvent and contaminants. It was assumed that there was no loss of explosive in the column, so that the output mass was based on the injected concentration and volume.

The output of the vapor generator was evaluated using an ECD detector, a mass spectrometer, and an ion-mobility spectrometer. Generation of DNT, TNT, and RDX was demonstrated. It was confirmed that the generator delivered the same vapors as those present in the headspace of the pure explosives compounds. The transient nature of the explosives-vapor generator helped to avoid saturation of the commercial detectors under evaluation.

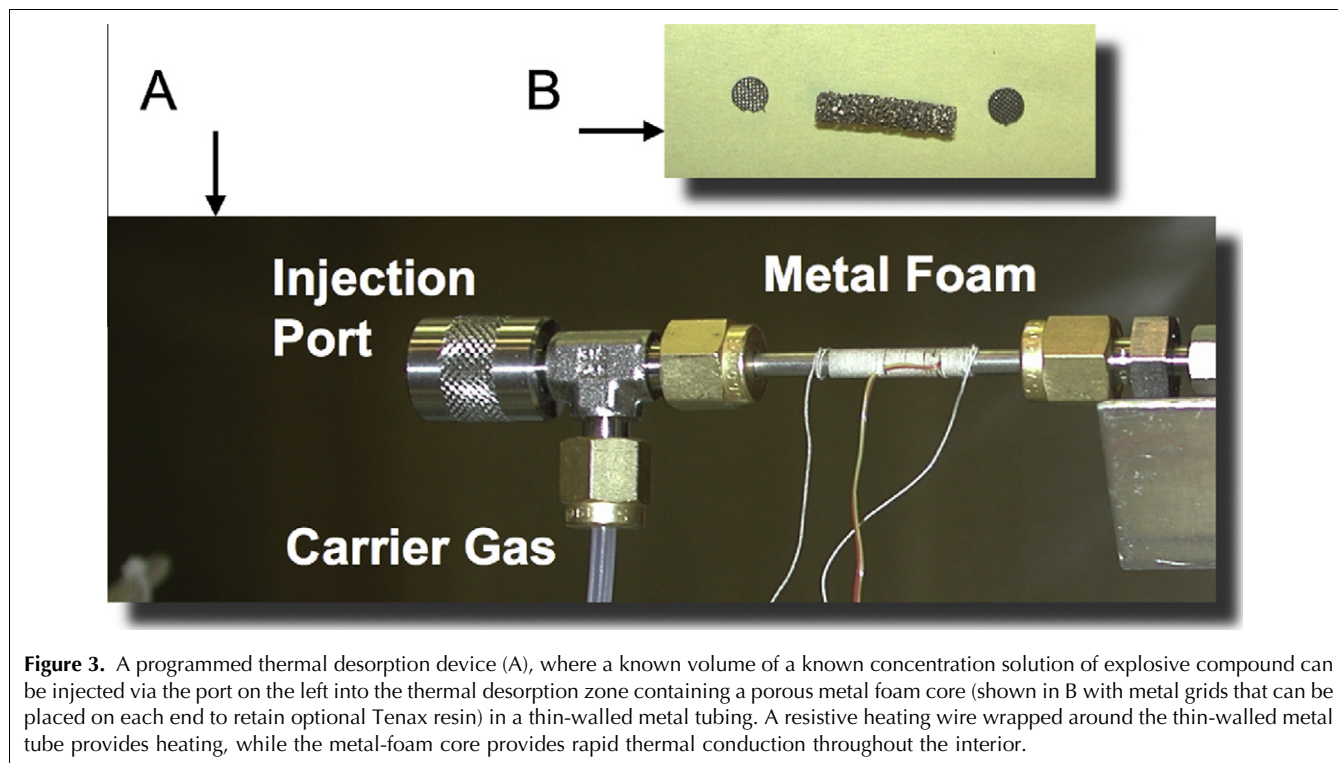
### 3.4. Vapor generation by thermal desorption

Bromberg et al. adapted the sampling component of a chromatographic explosives-analysis system for use in generating vapors for trace-detection portal evaluation [57]. The sampling component consisted of a coiled ribbon of resistively-heated material within a cylinder. In normal analytical use, explosives from a flowing sample would deposit on the unheated ribbon; subsequently, the ribbon was heated to desorb greater than 90% of the

captured explosives in less than 2 s. For use as a vapor generator, a known mass of explosive material was deposited on the ribbon by injecting a solution from a syringe. The collector ribbon was then mounted in a holder and heated, with vapors in a carrier gas exiting the device through a heated nozzle. It was assumed that, after vapor generation, the explosive would be present as both vapor and condensed particulates. This device could be mounted in different locations within a portal to measure detection response of the portal. In addition, these authors described fabric or paper samples containing adsorbed explosives as standards to test portals. Explosives EGDN, nitroglycerin (NG), DNT, TNT, PETN, and RDX were discussed.

Poziomek et al. designed a thermal desorption-based generator specifically for delivering pulsed masses of vapor to solid adsorbent surfaces as part of the sampling interface of an IMS instrument [58]. As depicted in a vertical format, from the top, the generator consisted of an inlet tube for carrier gas, a chamber containing a flow-through quartz-fiber filter with a resistive nichrome-wire heater above it, and an exit to a short transfer tube that delivered the vapor through the hinged lid of a collector containing the IMS sample holder. The explosive source was prepared for each experiment by depositing a dilute solution onto the quartz-fiber filter; this filter was placed in the holder and the apparatus just described was assembled. Resistive heating with carrier-gas flow vaporized the explosive and transferred it downstream, where a portion was captured by a planar adsorbent material in the sample holder (e.g., filter paper, cloth, or Teflon membranes). The apparatus was cleaned with solvent after each use. Curiously, the authors were not concerned about quantitative delivery of vapor from the generator to the adsorbent in the collector, and careful analysis of solvent rinses showed that explosive accumulated on inside surfaces of the fittings, transfer tube, and collector. Empirically, it was found that, for a given explosive mass deposited onto the source filter, a consistent IMS response was observed; the response increased with the amount of deposited mass in a non-linear fashion.

Grate and colleagues previously described a programmed thermal desorption method used with small-volume vapor preconcentration devices [59–61]. These preconcentrators contained porous polymer or carbon adsorbents; in one design, the adsorbents are dispersed in a cylinder of metal foam contained inside a thin-walled metal tube [60]. Resistive wire wrapped around the outside provided heat; the metal foam on the interior facilitated heat transfer from the exterior heating wire to the interior of the adsorptive bed, improving temperature uniformity within the adsorptive core. In conjunction with chemical-sensor research, a programmed thermal desorption method was demonstrated for controlled vapor release, where vapors with different



**Figure 3.** A programmed thermal desorption device (A), where a known volume of a known concentration solution of explosive compound can be injected via the port on the left into the thermal desorption zone containing a porous metal foam core (shown in B with metal grids that can be placed on each end to retain optional Tenax resin) in a thin-walled metal tubing. A resistive heating wire wrapped around the thin-walled metal tube provides heating, while the metal-foam core provides rapid thermal conduction throughout the interior.

desorption temperature could be partially separated [60,61].

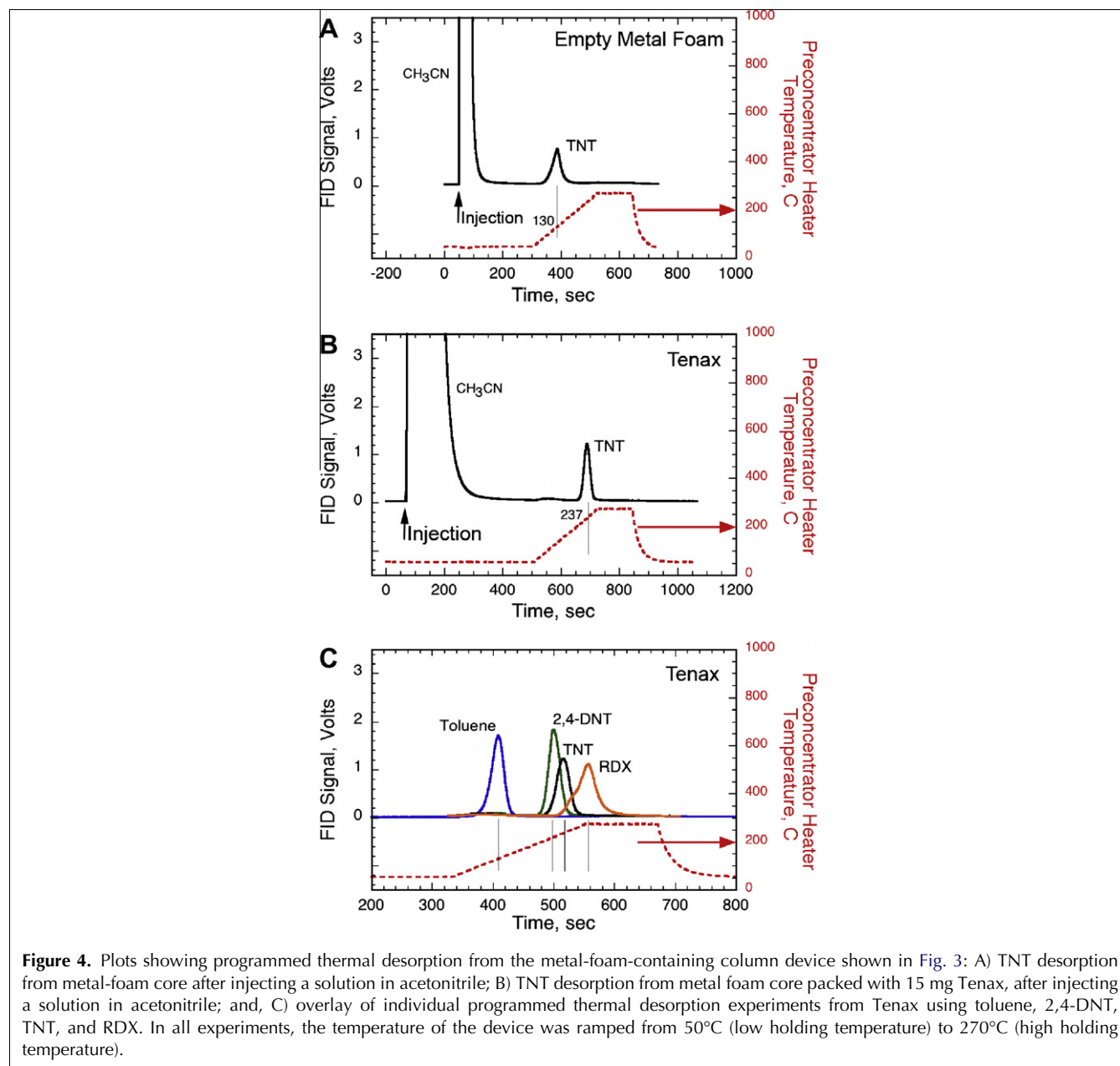
Recently, this technology has been adapted to generate pulses containing a known mass of explosive, as shown in Fig. 3. A tee-fitting upstream from the device, fitted with an injection port and a carrier-gas supply, enables the injection of explosives-containing solutions on the metal-foam core; solvent evaporation (typically acetonitrile or ethanol) leaves an explosive residue of known mass in the device. The metal-foam core can be empty or can be packed with Tenax adsorbent. Plots of thermal desorption of explosives are shown in Fig. 4, using quantities detectable by flame-ionization detection to illustrate the principle. Vapor samples from 2,4-DNT, TNT, and RDX were generated by this method, with the output peaks detected as the temperature ramped through 100°C, 130°C and 180°C, respectively, when desorbing from bare metal foam. From Tenax, approximate desorption temperatures were observed of 220°C, 240°C, and 270–280°C for 2,4-DNT, TNT and RDX, respectively. This approach provides a simple method to deliver a known mass of explosive, but details on generating trace levels by this method remain to be demonstrated and published. In the simplest configuration, this approach has the disadvantage that it delivers both solvent vapors and explosive vapors; however, they are temporally separated. A method to separate the temporally separated vapors spatially using a Deans valve is suggested below.

#### 4. Generators for canine testing and training

The testing and the training of canines for explosives detection have also motivated the development of vapor generators and vapor standards. The requirements for testing canines differ significantly from those for testing instrumental detection systems and sensors. While most detection testing is focused on the vapors of the explosive chemicals, canine testing must focus on the vapors the dogs detect [7,8]. A training aid for dogs must therefore deliver all the components of the odor of an explosive; the source and delivery system must not fractionate the sample in time, or fail to deliver some fraction of the vapor mixture that a real explosive contains.

Non-hazardous vapor sources referred to as NESTT, popular for use in canine training, are generators based on explosives on solid supports, as described above [8,41]. Training aids for more volatile explosives have also been created by adsorbing vapors onto gauze or cotton balls [62]. Dynamic flow vapor-generation systems have been developed for canine training and testing [41,63–65]; furthermore, they have been used to elucidate which odorant chemicals the dogs key in on when sniffing out explosives [66–68]. Canine generators are based on thermostatted sources of odorant vapors (e.g., military-grade TNT or C-4) and serial dilution of the vapors downstream. Vapors delivered by the generator have been evaluated by both IMS and GC-MS. As one example, a study in the development of this vapor gen-





erator demonstrated that it delivered cyclohexanone from C-4 (a solvent used during the manufacturing process) while the RDX explosive was undetectable except in the source reservoir itself [64].

Lovestead and Bruno recently identified the trace chemicals in the headspace of solid explosive materials [e.g., Semtex (containing PETN and RDX) and C-4 (containing RDX)] using a cryoadsorption method; again, the chemicals detected in the headspace were solvents, plasticizers, and intentional taggants (e.g., DMNB), rather than the explosive compounds themselves [9].

## 5. Generator calibration and standards

Calibrated vapor generators are needed because the properties of explosives, particularly their low vapor pressures, make it difficult to create standard vapor samples. One of the early papers on vapor generators [34] came from NIST, and a more recent generator paper from the same institution also mentioned the lack of standards. Moore discussed the lack of standards, reference materials, and calibration protocols [19], noting the “urgent need for standard testing protocols”, and, furthermore, to “compare methods on an equal footing, it

would be more desirable to have some sort of standards available, or to arrange interlaboratory comparison(s) . . . using the same materials or samples." [19]. In 2009, MacCrehan described NIST standard reference materials (SRM 2905 Trace Particulate Explosives) consisting of explosives dispersed on C18-silica [69]. Two concentrations each of C-4 and TNT comprised the final four SRMs.

Verifying and calibrating the output of an explosives-vapor generator is an issue in itself. It is not a trivial matter just to connect a commercial detector and measure the output. Careful analytical measurements are required, and it is possible to generate vapors at concentrations that are not directly detectable with current instrumentation. In some studies, outputs from saturated sources are simply assumed to be at the concentration predicted by a vapor-pressure equation. If collection tubes or cold traps are used to accumulate sample for measurement, the results provide only an average output over time, and may miss the real-time dynamics of vapor-generator output. For permeation-bag and diffusion-tube sources [45,46], the measured weight loss provides data on the source mass-flow rate averaged over time. Currently, the most sensitive methods for measuring output concentrations and compositions are GC with an ECD detector, IMS, and MS. Although IMS detectors are well known for explosives detection, issues arise with regard to the sample-introduction method, the limited dynamic range of the detector, and the ease with which this detector can become saturated.

The reviewed literature on vapor generators has described the use of adsorbent collection tubes or cold traps with subsequent GC analysis [31,33,34], or HPLC analysis [43,46]. IMS approaches for output analysis have included collection tubes [52], vapors accumulated on a preconcentration sampler that is part of the IMS instrument [47], and generator outputs interfaced directly to the IMS instrument [35,46,52]. An IMS instrument has also been coupled to a tandem mass spectrometer [46]. Recently, Spitzer et al. [32] described a generator with output analysis by GC-ECD and GC-MS.

Output analysis of vapor generators is required to address several questions on generator function and performance. If a saturated vapor source is used, is it truly saturated, and does the output concentration match that predicted by vapor-pressure equations? What is the maximum flow rate at a given temperature where the source will sustain saturation? Is the output from a diluted source as expected, or could there be losses somewhere in the system (e.g., by adsorption in a cold spot)? Is the source releasing compounds other than the explosive (e.g., solvents left over from source deposition)? Are there contaminants left over from explosive compound synthesis or degradation products from the explosive itself appearing in the output? Is the source a

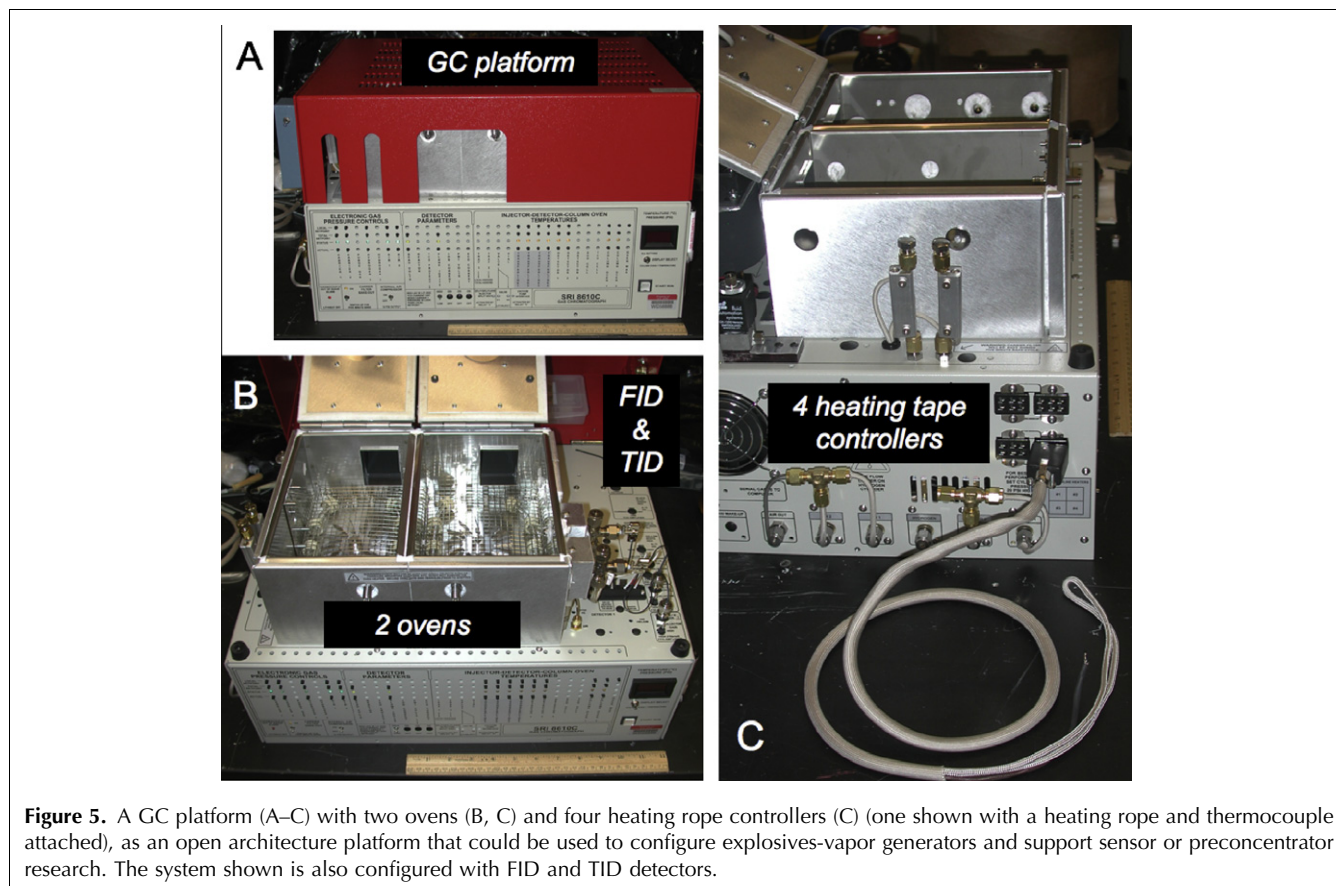
commercial explosive formulation prepared for detonation applications, and what other vapors does it release? Finally, is the generator releasing particles from the solid explosives source, or particulates condensed from generated vapors, instead of monomeric explosives-vapor molecules?

Few vapor-generator developments have had the time or resources to address all these questions. Typically, the generator is developed to support an intended application (e.g., sensor development, adsorbent materials evaluation, or detector testing); generators are moved into the intended application as soon as possible.

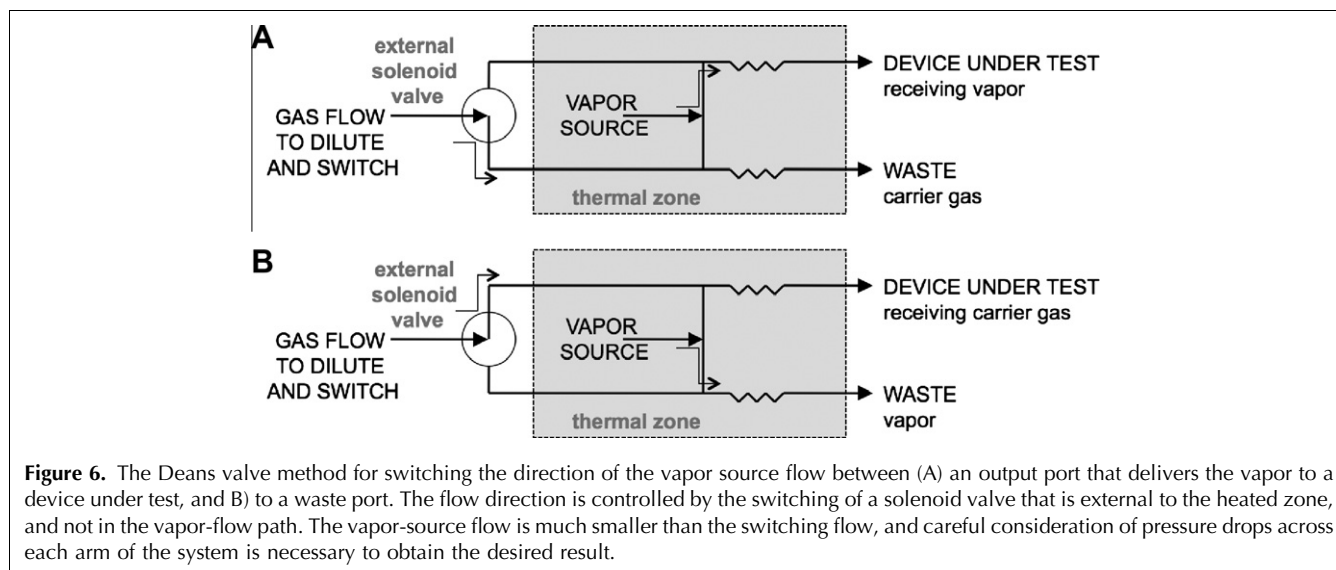
## 6. Platform concept

From the review of vapor generators, and as shown in Fig. 1, it is clear that thermal controls are critical to vapor-generator development, and that multiple thermal zones may be required in most designs. Setting up each of several thermal zones can lead to a cumbersome apparatus with multiple individual controllers. An additional common factor to vapor generators is the need to switch the flow direction of a gas stream containing explosive vapors (e.g., to change the output from clean carrier gas to explosive vapor and back). The use of mechanical valves to switch the flow paths of explosives containing gas streams can raise a number of concerns, due to the possibility of interactions of explosives with the valve materials or explosives adsorption within the valves. Valves for use in heated zones may be subject to temperature limitations of the valve itself.

We have developed a platform concept that may simplify these aspects of vapor-generator design. A commercial GC system can provide thermal control for one or more ovens. In addition, some chromatographs have additional thermal controllers for heated transfer lines consisting of a heating tape or rope placed along a section of tubing inside an insulating sheath, and packaged with a thermocouple. We have configured a commercial GC system with two adjacent column ovens [70] specially ordered with four temperature controllers for heated transfer lines. These four controllers can be used to heat and to control transfer lines or anything else one wishes to wrap with a heating tape or rope. This platform is shown in Fig. 5. This system provides a single integrated platform with six independent thermal controls. The two adjacent ovens with lids on the top provide an open architecture for assembling a vapor-generation system and for supporting experimentation on devices (e.g., preconcentrators, sensors, or detectors). The system can also be configured with GC detectors for use as needed to monitor vapor outputs or to use in conjunction with devices under test. The vapor source could be located in one of the ovens, externally in a separate region with a high-precision temperature con-



**Figure 5.** A GC platform (A–C) with two ovens (B, C) and four heating rope controllers (C) (one shown with a heating rope and thermocouple attached), as an open architecture platform that could be used to configure explosives-vapor generators and support sensor or preconcentrator research. The system shown is also configured with FID and TID detectors.



**Figure 6.** The Deans valve method for switching the direction of the vapor source flow between (A) an output port that delivers the vapor to a device under test, and B) to a waste port. The flow direction is controlled by the switching of a solenoid valve that is external to the heated zone, and not in the vapor-flow path. The vapor-source flow is much smaller than the switching flow, and careful consideration of pressure drops across each arm of the system is necessary to obtain the desired result.

troller (e.g., a water bath), or provided by an injection method.

To provide a switching mechanism without a mechanical valve in a heated zone, a Deans valve was incorporated. The Deans valve uses a configuration of

tee junctions, as shown in Fig. 6, and a switchable externally supplied flow, to direct the path of an input gas stream (indicated at “vapor source” in Fig. 6) in one of two directions. The Deans valve was originally developed for valveless switching in GC [71] and recently

has found renewed application in two-dimensional GC [72]. A single 3-port solenoid valve external to the oven directs the switching flow of clean carrier gas to one side or the other of the flow circuit of the Deans valve. This flow splits at the first tee junction it encounters; the portion of the flow toward the vapor source tee junction directs the vapor source flow out. In this approach, there are no mechanically-actuated valves in the oven, nor are there such valves in the flow path of the explosive vapor stream or pulse. A commercial, off-the-shelf part (Agilent, Santa Clara, CA, USA) is currently available to provide an integrated microfluidic circuit instead of constructing the system with discrete tee junctions and tubing sections. An additional advantage of the Deans valve approach is that it simultaneously provides dilution of the vapor source.

These concepts could be used for configuring a continuous-flow generator or some form of pulsed generator. If one used the thermal desorption method indicated in Figs. 3 and 4, then the switching mechanism can be used to direct the solvent vapors from the injected explosives solution to waste. Then, upon heating to desorb the explosive, the Deans valve could be switched to deliver these molecules to the device under test. In this way, one can use the simple injection of a solution of explosive to deliver a known mass of explosive, without exposing the device under test to the solvent.

## 7. Safety

It should go without saying that working with explosive materials may present safety hazards due to energetic detonation as well as substance toxicity. The present authors are not explosives safety engineers, so the following discussion is provided to raise awareness of issues for researchers to consider, and not to define the boundaries between safe and hazardous conditions.

The detonation hazard of an explosive is reduced in a dilute solution, or when dispersed on a supporting solid. Government agencies in the United States have percentage limits for the content of an explosive in a solution, below which the solution is treated as a flammable hazard rather than an explosive hazard. Explosive compounds for analytical research can be obtained as dilute standard solutions in sealed glass ampoules. Explosive compounds dispersed on solid supports are also available as the NESTT materials described above.

For vapor generators, the use of explosives dispersed on solid supports is generally preferred to the use of neat materials. This form reduces the possibility of supporting and sustaining a detonation while increasing the surface area for vaporization. If neat materials are used, or if solutions are present that might evaporate and leave a significant quantity of explosive residue, it is pertinent to consider critical diameters. Assuming a spherical particle,

the critical diameter is the minimum size that can propagate a detonation wave. Values for critical diameters vary considerably in the literature [73–77]. Nevertheless, as a pair of reference points, we note that the critical diameters for TNT and RDX have been reported to be approximately 2 mm and 0.5 mm, respectively [77]. Assuming densities of 1.58 g/cm<sup>3</sup> and 1.70 g/cm<sup>3</sup> that are provided in the same publication, these diameters correspond to masses of approximately 6.6 mg for TNT and 0.11 mg of RDX. These numbers are offered to illustrate how little explosive is required to sustain a detonation, not to define safe quantities. Short of detonation, an explosive compound may rapidly produce an order of magnitude more molecules of gas than the original number of molecules in an explosive solid, leading to rapid pressure increases in closed or flow-restricted systems. The ease of initiating a detonation is a further consideration. Some of the peroxide explosives are noted to be particularly sensitive to impulses that can initiate detonation.

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