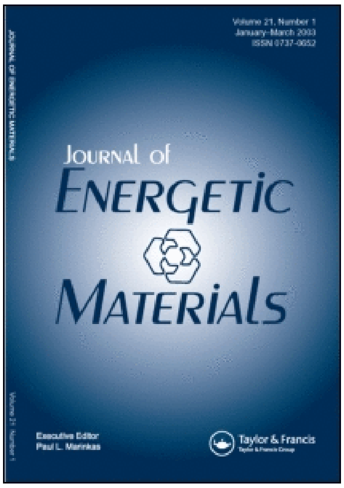

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

A transient explosive vapor generator based on capillary gas chromatography

George A. Reiner[a]; Cheryl L. Heisey[a]; Harold M. McNair[a]
[a] Department of Chemistry Virginia Polytechnic, Institute and State University, Blacksburg, VA

To cite this Article Reiner, George A. , Heisey, Cheryl L. and McNair, Harold M.(1991) 'A transient explosive vapor generator based on capillary gas chromatography', Journal of Energetic Materials, 9: 3, 173 — 189

To link to this Article: DOI: 10.1080/07370659108019863

URL: http://dx.doi.org/10.1080/07370659108019863

A TRANSIENT EXPLOSIVE VAPOR GENERATOR BASED ON CAPILLARY GAS CHROMATOGRAPHY

George A. Reiner, Cheryl L. Heisey,
and Harold. M. McNair

Department of Chemistry
Virginia Polytechnic Institute and State University
Blacksburg, VA 24061

ABSTRACT

A vapor generator is described which produces transient clouds of pure explosive vapor. This vapor generator is based upon a commercially available capillary gas chromatograph. By using a gas chromatograph, and generating transient vapor clouds, a higher purity of explosive vapor is obtainable than was previously possible. The chemical composition of the vapor generator was confirmed by both gas chromatography/mass spectrometry and by ion mobility spectrometry. Although this research only involved the generation of dinitrotoluene (DNT), trinitrotoluene (TNT) and 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) vapors, this system should be able to generate vapors of any volatile explosive. The vapor generator was successfully used in comparative testing of four commercially available explosive vapor detection systems.

Journal of Energetic Materials vol. 9, 173-190 (1991)
Published in 1991 by Dowden, Brodman & Devine, Inc.

INTRODUCTION

This laboratory was recently charged with evaluating several commercially available explosive vapor detection systems. As part of this effort, a quantitative method of generating pure explosive vapors was required. Since it has been well documented that adsorption is the primary factor responsible for the loss of trace amounts of explosives[1,2], a reliable vapor generator was needed which could test the ability of the systems to detect the vapors of explosive compounds while minimizing the effects of adsorption.

Existing explosive vapor generators fell into two basic types. The first was a temperature controlled chamber which contained a quantity of high explosive over which an inert gas passed. After equilibrium was established the exiting gas stream produced explosive vapors at the outlet.[3]

The second type of explosive vapor generator consisted of a packed GC column, a long tube which was packed with a solid support coated with an explosive. Again an inert gas flowed through the tube and over the explosive coated solid support. After equilibrium was established, explosive molecules were available for detection at the outlet of the tube.[1]

The potential problem with both types of vapor generators was that the purity of the vapor produced was only as good as the purity of the explosives used in the generators. In the first case, the high explosive contained other components such as binders and plasticizers which might have produced a response in the vapor detectors being tested. In the second case, any impurities from the coating process could cause the same problem. In addition to the purity problems, the second vapor generator required extremely high inlet pressures to produce useable flows at the outlet. Clearly neither of the available explosive vapor generators were applicable to our project.

By moving from a continuous vapor generator to a transient method, and by using a capillary gas chromatograph as the basis of the vapor generator, we were able to produce a transient explosive vapor cloud that was pure. Additionally, by using conventional capillary gas chromatography, we were able to easily monitor the purity of the explosive vapor produced at picogram levels.

EXPERIMENTAL

Equipment

Two Gas Chromatographic (GC) systems were employed for this research. The first was a Hewlett Packard (HP) (Avondale, PA) model 5890 GC equipped with a capillary split/splitless injector, electron capture detector (ECD), and flame ionization detector (FID). This system used a HP Series 300 Chem Station to store chromatograms and increase flexibility in integration of chromatograms. To improve reproducibility, an HP model 7673A automatic injector was installed on this GC. A Supelco (Bellefonte, PA) Heated Gas Purifier was placed in line with the make-up gas to prevent any oxygen from entering the ECD. This chromatograph was used for the vapor generator as well as to measure purity of explosive solutions at the picogram level.

The second system was a HP 5890/5970 dynamically coupled gas chromatograph/mass spectrometer (GC/MS). This system was employed to verify the purity of solutions, and to identify contaminants at the nanogram level. The GC/MS system was also used with the IMS described below to verify the output of the vapor generator.

An ion mobility spectrometer (IMS) model "Phemto Chem-110" from PCP Inc. (West Palm Beach, Florida) was used to assist in verifying the output of the vapor generator. This unit was equipped with the model RGS-4 Recirculating Gas Supply, and the model SF-12 Air Sampler.

The following consumables were used during this research: Supeltex M-2A ferrules from Supelco were used in connecting the columns to the injectors and detectors of both GC systems; Thermogreen LB-2 septa from Supelco were used in the injection ports; Hamilton (Reno, NV) models #701 and #80377 syringes were used for manual and autosampler injections, respectively; Airco (Murray Hill, NJ) grade 5.0 Helium was used as the carrier gas for both the GC and the GC/MS, and Airco grade 5.0 Nitrogen was used as the make-up gas for the ECD.

Instrumental conditions

The conditions used for both the GC and the GC/MS are presented in table 1.

TABLE 1
Chromatographic Conditions for Both GC and GC/MS

Injector	205°C Splitless for 30 sec. (190°C for RDX)
Carrier Flow	1.3 ml/min. (5 psi head pressure) Grade 5.0 Helium
Column Oven	75°C for 1 min. Then 20°C/min to 200°C and held for 2 min.
Column	Hewlett Packard Ultra 2 (95% methyl, 5% phenyl polysiloxane) 5 m length 0.20 mm ID 0.33 µm film thickness
Detector	250°C (ECD) 195°C (FID)
Make-Up Flow	60 ml/min. Grade 5.0 Nitrogen

The mass spectrometer conditions were as follows: The transfer line from the GC to the MS was held at 195°C, the same as the vapor generator heater. The ion source pressure with carrier gas flowing was 8×10^{-5} torr. The electron energy was 70 eV, and the voltage on the electron multiplier was 2600 volts. For all mass spectra, the HP 5970 MSD was calibrated with PFTBA and used normalization factors to permit proper comparison with library spectra.

Conditions for the IMS were: air carrier flows of 200 ml/min, drift flows of 500 ml/min, and a temperature of 190°C. The carrier and drift gases were both compressed breathing air which was humidified by passing through a water filled bubbling chamber. Water vapor was necessary to provide reactant ions for the IMS.

Design and Construction of the Vapor Generator

The following modifications were made in converting the HP 5890 GC for use as a vapor generator: first, the tower assembly of the FID was removed, and the capillary flame tip of the FID assembly was replaced with the HP flame tip designed for packed column use. This flame tip had a larger aperture which permitted the capillary column to be inserted through the flame jet and extended outside of the GC by 9.5 cm. To prevent condensation of the explosives vapors on the walls of the exposed capillary column, a heater was designed for the exposed portion of the capillary column. This effluent heater is shown in figure 1.

The inner portion of the heater was 2 mm ID soft glass tubing, 9.5 cm in length. This tube was wrapped in 30 gauge chromel wire, spaced 1.5 to 3.0 mm between windings. This wire-wrapped tube was placed inside a 4.0 mm ID glass tube, 9.2 cm in length. After this assembly was completed, the ends of the inner tube were flared to hold the heater in place. The wire heater was then connected to the 25.2 volt leads of a 25.2/117 volt step down transformer, fed by a 120 V Variac. The Variac was adjusted to obtain a temperature of 195°C inside the tube, when measured by an Omega (Stamford, CT) model HH-81 digital thermometer.

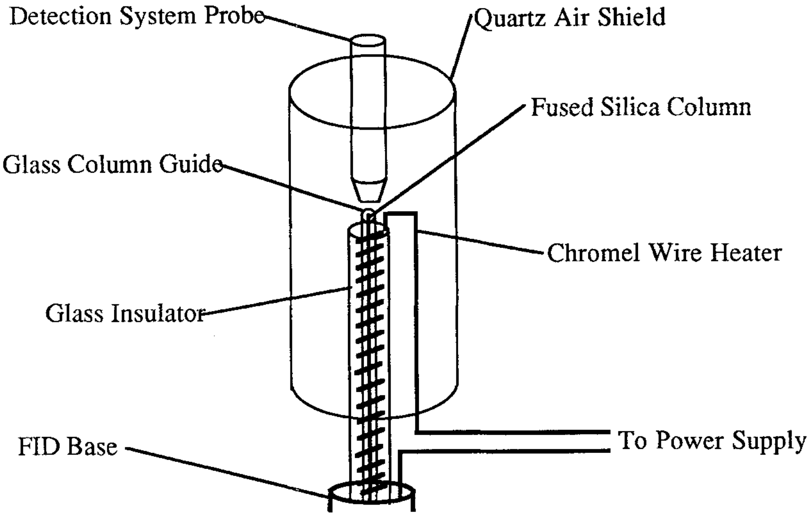

FIGURE 1
Diagram of Effluent Heater System.

The probes of the detection systems were placed one to two millimeters from the end of the capillary column which was set flush with the end of the inner glass portion of the heater. To prevent air currents from interfering with detection of the explosive vapors, a piece of glass tubing, 3 cm in diameter was placed around the heater about 3 to 4 cm above the FID base as an air shield. Thus the exit of the capillary column became the source of explosive vapors.

Calibration of Vapor Generator

The calibration of the vapor generator was carried out by the injection of known standards of highly pure explosive solutions into the GC with the capillary column connected to the ECD. Replicate analysis of the solutions to be used in testing were performed to evaluate the reproducibility of the vapor generator. An assumption was made that adsorption in the GC system was negligible. Although this assumption means that an absolute calibration was not performed, calibrating in this manner made the entire study relative to the HP 5890 ECD and permitted comparisons between detection systems. This assumption was probably valid at concentrations greater than 100 pg/µl since highly deactivated injector inserts and columns were used. Data is being collected to show that this assumption is valid.[4]

Preparation of Solutions

The solutions used in calibrating the vapor generator were the same solutions used in subsequent testing of the detection systems. These solutions were prepared as follows.

All explosives used for the preparation of solutions were provided in recrystallized form by the Naval EOD technology center (Indian Head, MD). The solvent used for all solutions was Fisher (Pittsburgh, PA) Optima grade 2-propanol. Weighing of explosives was performed on a Mettler (Hightown, NJ) model H33AR analytical balance. Quantitative transfer of stock solutions were performed with Brinkman Instruments (Westbury, NY) Eppendorf model 4710 digital pipettes.

Prior to using any glassware, it was rinsed with five aliquots of the solvent. The last aliquot was analyzed by GC/ECD to ensure that no residual explosive was present on the walls of the glassware. The rinsing was repeated if necessary.

Stock solutions of explosives were prepared at nominal concentrations of 100 ng/μl by weighing the appropriate amount of explosive, transferring to a 100 ml volumetric flask, and dissolving in 100 ml of solvent.

Dilute solutions were prepared by serial dilution and in auto injector vials by using the digital pipets to transfer both stock solution and solvent. In order to minimize the effects of adsorption, the glassware employed for dilute solutions was equilibrated with the explosive by equilibrating with a solution of the same concentration which was then discarded and re-made.

Testing Procedure

With the GC at initial conditions, the background signal of the ECD was required to be under 25.0 (arbitrary units) as read from the front panel of the GC.

A manual injection (2 μl) of the stock solution containing the explosive under investigation was then injected. This step primed the interior surfaces of the GC with the explosive if necessary. After injecting the stock solution manually, the auto injector was used to inject a known mass of explosive as a solution in 1 to 5 μl of 2-propanol. The results of these chromatograms were used to verify that the vapor generator was performing in a reproducible manner.

To test an explosive vapor detection system, the fused silica capillary was removed from the ECD and placed in the FID exit port of the oven. The capillary was adjusted with its end flush with the end of the fused silica heater clamped in place immediately above the FID. When the detection system was stable, the explosive solution was injected into the GC. The GC program was started and the detection system was moved into place and secured by 30 sec. prior to the elution time of the explosive. The detection system was then monitored for a response at the elution time of the explosive. Only alarm (positive) and clear (negative) responses were noted since the signal strengths given by the detection systems were in arbitrary units, and thus not comparable between detection systems. Once the response of the detection system had been recorded, the detection system was left in place over the heater for 2 min. in order to clean out any residual explosive from the system. After heating the probe tips, the units sampled room temperature air until they gave clear signals. These precautions were performed to ensure that no contamination occurred from one test to another.

RESULTS AND DISCUSSION

Confirmation of Vapor Generator Output

The output of the vapor generator was confirmed by two methods. The first was quadrupole mass spectrometry (MS) using electron impact (EI) ionization. The second was ion mobility spectrometry (IMS), using the instrument in the negative ion polarity mode.

The mass spectra of DNT, TNT and RDX obtained from the EI/MS are shown in figures 2 through 4 below. It should be noted that since explosives are by definition unstable, the standard 70 eV ionization current provides too much energy to permit detection of the explosive's molecular ion. However, in all three cases, the electron impact spectra produced compared favorably with library spectra from the NBS mass spectral library, revision E.

The second method of verification, IMS, involved the comparison of actual explosive vapor from the vapor generator to headspace vapor of the crystalline explosives. Since the ion mobility spectrometer generally has several reactant ions, two peaks were present in the RDX spectrum. This was not a major concern as long as the spectra generated from the vapor generator matched the vapors from the headspace of the explosive. The drift times for the explosives are presented in Table 2.

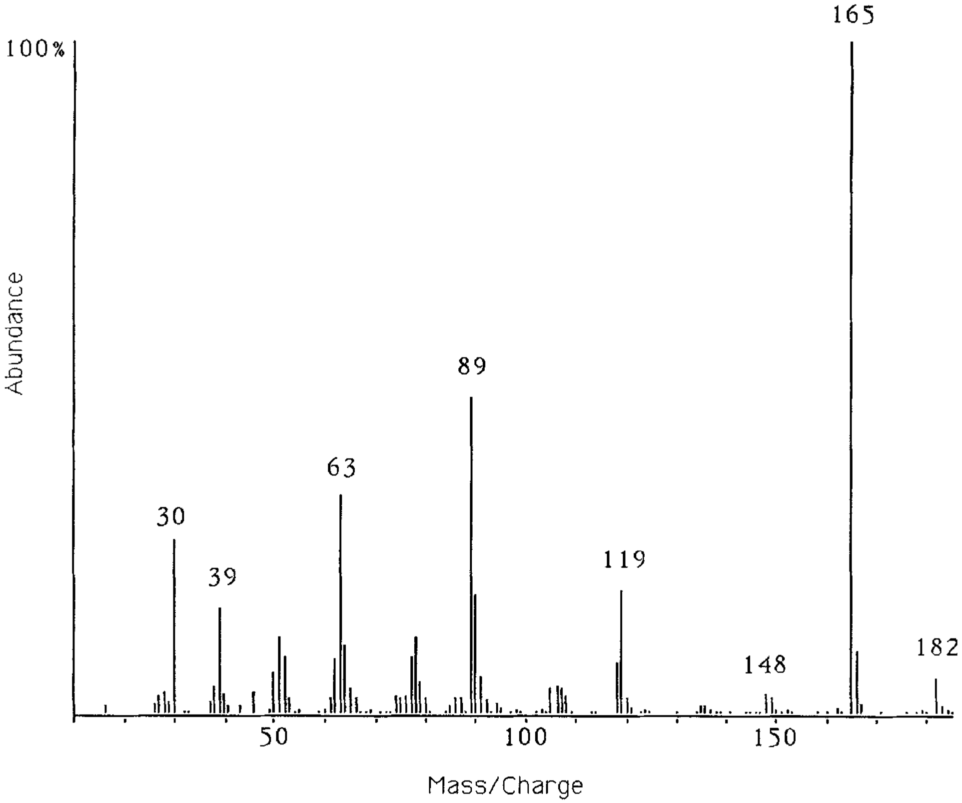

FIGURE 2
EI Mass Spectrum of DNT.

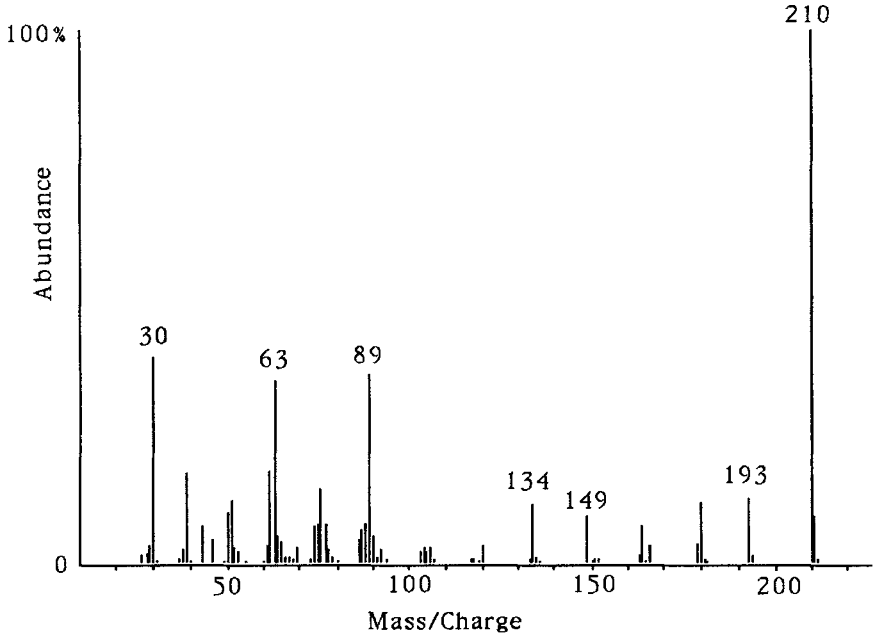

FIGURE 3
EI Mass Spectrum of TNT.

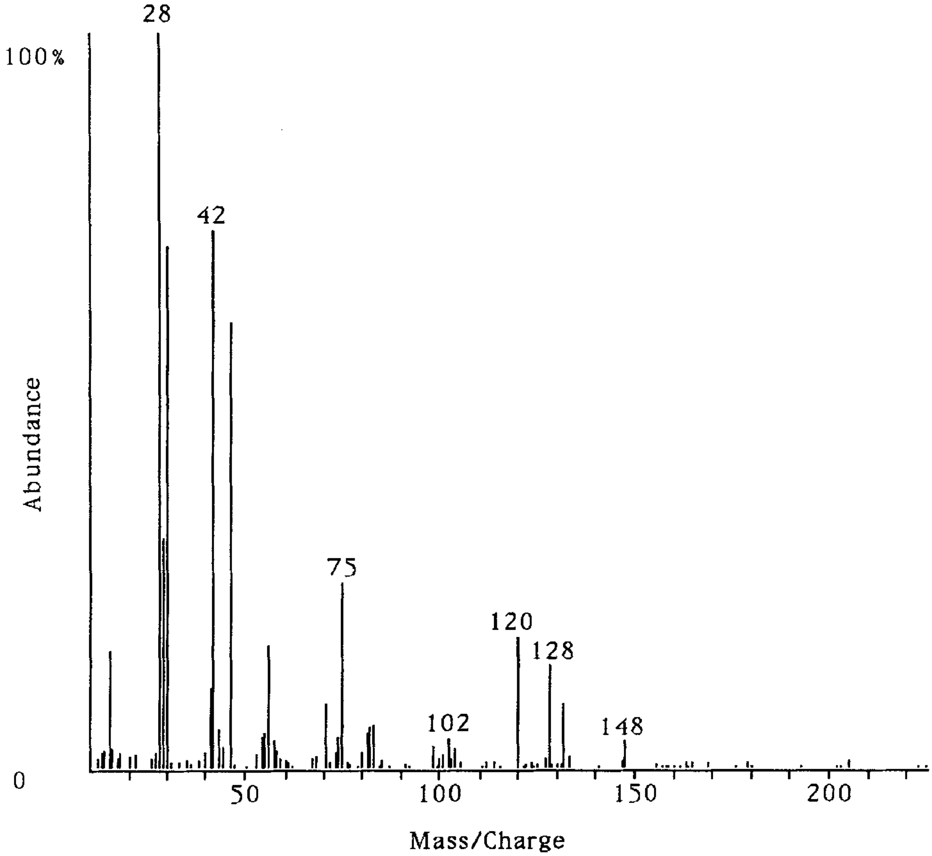

FIGURE 4
EI Mass Spectrum of RDX.

TABLE 2
IMS Drift times of nitrotoluenes in msec.

Explosive	Drift Times Vap. Gen.	Headspace
DNT	13.89	13.89
TNT	15.07	15.04
RDX	15.94, 16.56	15.92,16.58

The variation in these drift times is well within the reproducibility of the IMS system. The GC/MS and the IMS both show that the vapor generator produced explosive vapor equivalent to the headspace vapor of the explosive. Decomposition products would have shown different EI mass spectra and would also have exhibited different ion mobility drift times.

Vapor Generator Design

The vapor generator described above differs greatly from those previously employed because it uses a gas chromatograph to purify the vapor. By producing vapors in this manner, all volatile impurities will be separated and elute at different times, thus eliminating any false alarms. A direct result of producing vapors in this manner is that the explosives elute from the vapor generator as a peak which is transient in nature. Precisions of retention times for the three explosives tested were better than 1% relative.

Because the commercial detection system operated differently, each employing its own concentration system, it was necessary to test the abilities of each detection system to capture, analyze, and respond to explosive vapors. The transient nature of the explosive vapor generated by the GC system is well suited to this type of testing. Since the vapor cloud of explosive is present for less than a minute, there is neither enough time nor enough explosive to saturate a detection system's concentrator and permit explosive to pass through to the detector. With continuous stream vapor generators, this priming of the detection system's inner surfaces is possible

CONCLUSION

The vapor generator described in this paper is capable of producing explosive vapors which are equivalent in chemical composition to the vapors in the headspace of an explosive compound. The transient nature of the vapor produced permits explosive vapor detection systems to be tested in a manner which evaluates the abilities of the systems to capture, analyze and respond to specific levels of explosive vapors. This vapor generator minimizes the both primming effects, and the loss of explosives due to adsorption.

SUMMARY

The vapor generator described above produces purified explosive vapor by employing a capillary gas chromatographic column to first separate any impurities from explosive compounds. After the separation, the explosive compounds elute from the chromatograph as a transient cloud of vapor. This vapor is then available for detection by explosive vapor detection systems. By using the vapor generator to

the detection systems can be made.

ACKNOWLEDGEMENTS

This work was supported by the Naval Surface Warfare Center, Dahlgren, VA contract # N60921-83-A165 B042. The authors would like to thank Mr. Louis Wasserzug of the Naval EOD Technology Center, Indian Head, MD, Mr. Frank J. Conrad of Sandia National Laboratories, Albuquerque, NM, and their associates for assistance and input into this research. The strong technical support and useful discussions of the VPI & SU chromatographic research group under Dr. Harold M. McNair are greatly appreciated

REFERENCES

1 Hannum, David W., "Characteristics of Select Glass Tube Preconcentrators Used With an Ion Mobility Spectrometer", Sandia Report #SAND89-0242•UC-15, April (1989).

2 Kenna, B. T., and Conrad, F. J., "Studies of the Adsorption/Desorption Behavior of Explosive-Like Molecules", Sandia Report #SAND86-0141•UC-501, October (1989).

3 Dionne, B. C., et. al., J. Energetic Matl., 4, (1986), p447.

4 Reiner, George A. and McNair, H. M., "Adsorptive Effects in Trace Analysis of Explosives by Capillary GC, ECD", 1990 Pittsburgh Conference, Paper #1110.