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Calibration of an Explosives Vapor Generator Based on Vapor Diffusion from a Condensed Phase

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Abstract

In the field of explosives detection there is currently a need for a calibrated source of explosives vapor. Such a source could be used to test and calibrate explosives detection systems which identify explosives via the collection of vapor or air borne particulate matter. This paper describes the principles of operation and evaluation of one such explosives vapor generator. This generator is based on the diffusion of vapor from a condensed phase (i.e. solid or liquid) in a source reservoir, and the output has been tied to a National Institute of Standards and Technology (NIST) mass standard. We discuss results of the calibration of this generator using the explosives 2,4,6-trinitrotoluene (TNT) and cyclonite (RDX). The mass output of this generator is stable over hundreds of hours of continuous operation, and is adjustable from the low picograms(pg)/sec range to at least 10 nanograms(ng)/sec. In the case of TNT, the mass output correlates well with predictions based on gas phase diffusion theory. In the case of RDX, the agreement with theory is less good. This may be attributable to a variety of factors, possibly including inaccuracies in the published data on RDX vapor pressure as a function of temperature.

Introduction

The use of explosives by terrorists worldwide continues to fuel interest in areas of research relating to explosives detection. Development of explosives vapor detectors has been especially rapid during the past few years, with a growing number of increasingly sophisicated ion mobility spectrometry- (IMS), electron capture detector-, and chemiluminescence-based systems appearing on the market. A persistent problem in this area is the lack of a standardized source of explosives vapor which can be used to test and calibrate systems of this type. Producing well-quantified and reproducible amounts of explosives vapor is difficult for several reasons. First, the vapor pressures of these compounds are extremely low in some cases. For example, TNT has a vapor pressure of a few parts per billion, and RDX has a vapor pressure of a few parts per trillion [1]. Developing a generator to produce known amounts of vapor from these compounds without also producing significant amounts of impurity vapor will therefore clearly be a challenge. Second, explosives are highly reactive compounds which tend to decompose when heated, and thus there is the possibility that the vapor produced will contain more decomposition products than undissociated explosive. Finally, the vapor produced by a generator must be transported to the detector without a significant loss of the compound, and there are obvious engineering problems associated with doing this.

In this paper, we describe an explosives vapor generator developed at Varian Associates and tested at New Mexico State University (NMSU) and Sandia National Laboratories (SNL). This generator produces vapor by heating a condensed phase explosive in a glass sample tube within a constant temperature oven, with

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the vapor output rate being controlled by the oven temperature and by diffusion of vapor up the tube. We discuss experiments dealing with the mass output calibration of this generator for both TNT and RDX at several different temperatures. Of particular interest is the fact that the mass output for both molecules has been tied to an NIST mass standard. The results of this study indicate that this generator offers a highly reproducible and quantifiable output of pure explosives vapor for these compounds.

Description of the Varian Vapor Generator

A schematic diagram of the Varian vapor generator is shown in Figure 1.

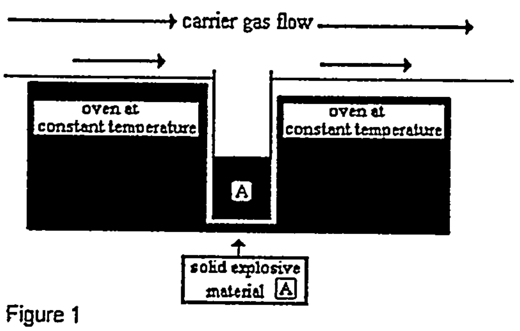

Figure 1

The explosives source reservoir is a small amount of solid explosive powder placed in the bottom of a thin glass tube. While the tube dimensions could be varied, the tubes used in this study were 10 cm long with an inner diameter of 0.47 cm. This tube is placed in a well insulated oven, the temperature of which can be varied from room temperature to at least 200 °C with an accuracy of ± 1 °C. The chosen oven temperature will result in a certain equilibrium vapor pressure for the chosen explosive, and some of the vapor will diffuse upwards to the top of the sample tube. At this point, the vapor diffusing from the tube is swept along horizontally in an inert carrier gas flow (usually nitrogen or purified air), and carried through a short glass ducting tube to exit the vapor generator. By pushing a button on a control box, the vapor flow can be directed either out the generator exit nozzle and thus into a desired detector, or through a zeolite trap where the vapor is readsorbed (and thus only clean carrier gas leaves the generator).

The mass output of explosive vapor per unit time is thus controlled both by the oven temperature, which establishes the explosive vapor pressure, and by the tube dimensions, which control the rate of vapor diffusion to the top of the tube. Although the rate of carrier gas flow across the top of the tube will affect the concentration of explosives vapor in the carrier gas that exits the system, it does not affect the rate of explosives mass output. From gas phase diffusion theory, the mass output of such a vapor generator is predicted to be

(1) output = ADn_0/L,

where the output is in units of mass (typically ng in this case)/sec, n_0 is the equilibrium vapor concentration of the explosive at the chosen oven temperature in units of mass/cm^3, D is the gas phase diffusion coefficient of the explosive molecule in units of cm^2/sec, A is the cross sectional area of the sample tube in cm^2, and L is the tube length in cm [2]. The values of A and L are known, while n_0 can be obtained from published equations or tables of vapor pressure data [3]. The value of D is not known precisely and this prevents an exact prediction of the generator mass output, but for cyclic compounds such as TNT and RDX the value of D is typically 0.05-0.1 cm^2/sec. Thus once the output has been measured for a given set of experimental conditions, equation (1) can be used to back out a value of D, and a D value that falls within the expected range serves to at least partially validate both the model and the observed results. Another noteworthy feature of equation (1) is that it predicts an exponential increase in generator mass output with oven temperature, due to the exponential increase in n_0.

Experimental

A detailed description of the experiments performed in this work will be provided elsewhere [4]. In brief, the experiments performed at NMSU involved running the vapor generator continuously over dozens or hundreds of hours, with the sample tube being removed from the vapor generator periodically to measure the sample mass loss on a Perkin-Elmer AD-6 microbalance. This balance has a sensitivity of ±

0.1 microgram, and calibration with a 10 milligram NIST standard mass provided the desired traceability to a NIST mass standard. The carrier gas was nitrogen with a flow rate of 100 cm^3/min. Experiments at SNL utilized an ion mobility spectrometer (IMS) detector to calibrate the vapor generator independently by comparing the IMS signal from the generator to the IMS signal for direct injections of known explosives masses from standard solutions. These experiments will also be described in detail elsewhere [4].

Results

Figure 2 shows mass loss data as a function of time for TNT at four different generator oven temperatures from 79 to 150 °C.

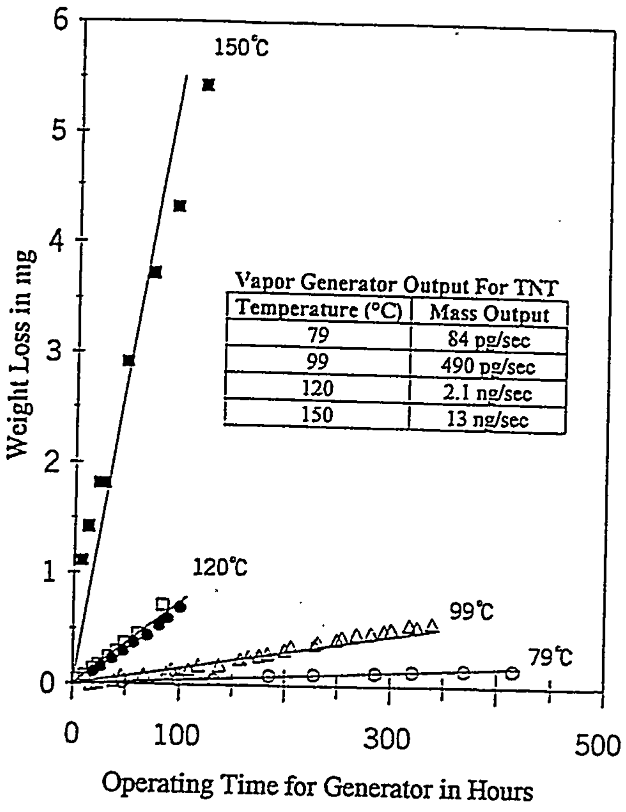

Figure 2

The plotted data at each temperature are clearly very linear, and the slopes of these lines yield the mass output per unit time. The inset lists the average mass output rates at these temperatures, which range from 84 pg/sec at 79 °C to 13 ng/sec at 150 °C. The linearity of these plots over hundreds of hours confirms the stability of the vapor generator output, and the approximately exponential increase of output with temperature is in accord with theoretical predictions. Plots of this type for RDX are quite similar but show somewhat more experimental scatter. The mass output values for RDX vary from 50 pg/sec at 110 °C to 2.4 ng/sec at 150 °C. Several experimental runs were performed at both of these temperatures and at 129 °C, and the relative standard deviation in the measured output at each temperature is approximately 25-30 %.

Figure 3 shows plots of log(output rate) versus 1/T for both TNT and RDX.

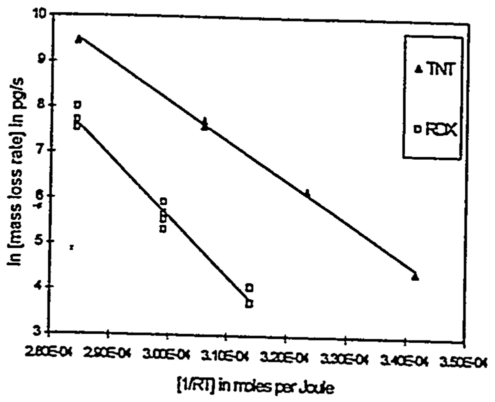

Figure 3

The approximately linear nature of these plots provides a more direct demonstration of the exponential increase of the output rate with temperature for both molecules. Note that the mass output values for TNT are 1-2 orders of magnitude above those for RDX due to the much higher vapor pressure of TNT.

Figure 4 shows data obtained at SNL in performing an IMS calibration of the vapor generator output for TNT at 79°C.

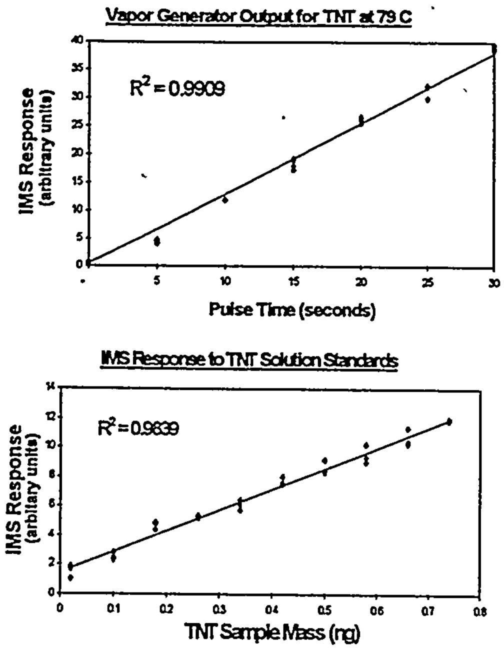

Figure 4

The upper plot shows the IMS response to timed doses of TNT from the vapor generator, while the lower plot shows the IMS response to known TNT masses from standard solutions. Taking the ratio of the two slopes yields an estimate of the mass output that is completely independent of that derived from the mass loss plot in Figure 2. The value obtained in this case is 85 pg/sec, and the nearly perfect agreement with the mass loss estimate is a further confirmation of the accuracy of these results. These IMS studies also showed that the generator output consisted of pure TNT vapor entrained in the carrier gas, with no identifiable impurities or decomposition products.

As discussed above, the measured mass output values can be used to estimate the diffusion coefficient D for each molecule, and thus further test the validity of the gas phase diffuion model. For TNT at 79 °C, tabulated vapor pressure data combined with our results yield a D value of 0.07-0.1 cm^2/sec. This falls precisely within the expected range and it can therefore be concluded that the model accurately describes the physics behind the vapor generation process for this molecule. Estimates of D for TNT based on data at the other oven temperatures are similar. In the case of RDX, our measured outputs combined with n_0 values derived from the Dionne equations [3] yield D values close to 1.0 cm^2/sec. This seems unreasonably high and might lead one to suspect that there is a problem with the results. However, a recent unpublished study [5] suggests that the vapor pressure of RDX may be considerably higher than values derived from the Dionne equation would indicate. Using an equation from this more recent study we obtain a D value of ~ 0.2 cm^2/sec, which is much more reasonable.

Conclusions

The results of this study indicate that the Varian vapor generator provides a quantifiable and reproducible source of explosives vapor for both TNT and RDX, and the mass output for each explosive can be tied to an NIST mass standard through carefully performed mass loss measurements. This generator could thus be used to test or calibrate explosives detectors which detect vapor of these two compounds. Use of this generator with other types of explosives such as dinitrotoluene (DNT) may also be possible, but has yet to be demonstrated. Initial experiments with pentaerythritol tetranitrate (PETN) indicate that molecular decomposition may be a severe problem with that compound.

Acknowledgments

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References

[1] See for example J. Yinon and S. Zitrin, in "The Analysis of Explosives", Pergamon Press, Oxford, 1981, p. 243.

[2] This equation has been derived in an unpublished manuscript on the vapor generator by James T. Arnold of Varian Asociates, 3075 Hansen Way, Palo Alto, CA, 94304.

[3] The most commonly cited source of vapor pressure data for TNT and RDX is the so-called

Dionne equation for each molecule. B. C. Dionne, D. P. Rounbehler, E. K. Achter, J. R. Hobbs, and D. H. Fine, Journal of Energetic Materials 4, 447 (1986).

[4] G. A. Eiceman, D. Preston, G. Tiano, J. Rodriquez, and J. E. Parmeter, manuscript in preparation.

[5] R. Stimac, private communication. Work performed at PCP, Inc., 2155 Indian Road, West Palm Beach, FL, 33409-3287.