Trace Headspace Sampling for Quantitative Analysis of Explosives with Cryoadsorption on Short Alumina Porous Layer Open Tubular Columns

Tara M. Lovestead and Thomas J. Bruno*

Thermophysical Properties Division, National Institute of Standards and Technology, 325 Broadway, Boulder, Colorado 80305

Quantitative headspace (HS) measurements have been performed on the practical industrial and military plastic bonded explosives (PBX) tagged-C-4, Semtex-1A, Semtex-H, detonating cord (detcord), and sheet explosive (Detaflex). The measurements were made by a modified purge and trap technique developed in our laboratory on the basis of cryoadsorption on short alumina-coated porous layer open tubular (PLOT) columns. Trace compounds (of both high and low volatility) were identified and quantitated as a function of HS collection temperature. The data are presented in the form of van't Hoff equations. The linear relationship of the recovered mass as a function of inverse collection temperature reveals the predictive capabilities of the methodology employed here. Knowledge of the compounds that can be detected, along with the expected concentrations to be collected, can aid in detection of explosive materials. Additionally, these data can aid in the standardization, calibration, and certification of energetic material detection devices and can aid in the training of canines for explosive detection.

Energetic Materials. A reliable approach to detect and quantify trace volatile compounds or even compounds of low volatility is imperative for developing devices that will noninvasively "sniff out" energetic (explosive) materials. Energetic materials can be classified (on the basis of their resistance to detonation) as either high or low explosives.[1] High explosives can be further classified as either primary (mercury fulminate, lead azide, diazodinitrophenol, tetrazene, and lead styphnate) or secondary explosives.[1] High explosives in military formulations include TNT (2,4,6-trinitrotoluene, CAS No. 118-96-7), RDX (cyclotrimethylenetrinitramine, CAS No. 121-82-4), HMX (cyclotetramethylenetetranitramine, CAS No. 2691-41-0), and PETN (pentaerythritol tetranitrate, CAS No. 78-11-5). For additional background information, some representative properties of TNT, RDX, HMX, and PETN are provided in the Supporting Information, Tables S-1–S-4.[1–4]

Secondary explosives are also often mixed with plasticizers, motor oil, and binders (materials added to make all of the components cohere and to resist moisture). These mixtures are referred to as plastic bonded explosives (PBXs).[5] Additionally, detection taggants are often added intentionally to facilitate identification. For example, 2-nitrotoluene (2-NT), 4-nitrotoluene (4-NT), 2,3-dimethyl-2,3-dinitrobutane (DMNB), and ethylene glycol dinitrate (EGDN) are detection taggants added to PBXs.[6,7] These taggants have higher vapor pressures than the explosive itself; thus, they may facilitate detection of the explosive material.

Some common PBXs are composition C-4 (often used as a block demolition charge), Semtex-1A, Semtex-H, and sheet explosive.[6,8] Semtex explosives were developed in the Czech Republic (formerly Czechoslovakia) to fill a need for safe handling and to be easy to shape, stable, water-resistant, and powerful explosives. We note, inter alia, that Semtex-H was used in the bombing of Pan Am flight 103 over Lockerbie, Scotland. Sheet explosives are thin, flexible rubberized explosive materials that can be cut to shape for precise dimensions. Another important energetic material that is sometimes considered a PBX is detonating cord (detcord), which is used to link multiple charges for simultaneous detonation. Detcord is a flexible cord of woven textile with a protected explosive core of PETN. It may or may not have a waxed finish.

Detecting Energetic/Explosive Materials. There are several methods that detect explosives (PBXs alone or in improvised explosive devices, IEDs): sampling vapors (e.g., canines or solid phase microextraction, SPME), analyzing surface swipes, or by

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* Corresponding author. Tel: 303-497-5158. Fax: 303-497-5927. E-mail: bruno@boulder.nist.gov.

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use of ground penetrating radar.[5,9−17] There are also several "electronic noses" for explosive material or landmine detection.[18,19]

While the vapor detection methods are attractive techniques because they have the potential for being sensitive, selective, and noninvasive (ultimately, stand-off detection), there are many challenges to detecting explosive materials in the vapor phase. Most high explosives have extremely low vapor pressures, rendering vapor detection of the high explosive compound itself exceedingly difficult.[15] Also, the more volatile or more easily vaporized components in PBXs or IEDs might have legitimate and/or nonexplosive commercial use. Additional challenges include the frequent introduction of nonstandard or novel explosive materials, weapons concealment, and nonstandard or novel weapons delivery systems.

To develop reliable vapor detection devices for energetic materials, a priority of first responders is to first identify the components and, second, determine how much of the components are in the vapor above energetic materials (or IEDs).[20] Knowledge of the detectable compounds will aid in developing new and improving current energetic vapor detection devices. Moreover, knowledge of the expected concentrations of the detectable vapor compounds will make possible the standardization and calibration of explosive detection devices. This information will also allow for the advancement of canine training for explosive (and other material) detection.[21,22] Improving our detection capabilities should greatly reduce the number of false negatives and/or false positives.

Here, we present a method that both identifies and quantifies components (even trace components of low volatility) above energetic materials. This method is a modified headspace (HS) approach that makes use of cryoadsorption on short alumina-coated porous layer open tubular (PLOT) columns.

Headspace Collection with Cryoadsorption. Headspace sampling methods can be either static or dynamic. Static methods typically involve pressurizing a vial containing the sample with a gas and then sampling the gas with a gastight syringe, a multiport sampling valve, or solid phase microextraction (SPME).[23,24] Dynamic methods typically employ a flow of carrier (or sweep) gas to the vial containing the sample. The sweep gas (and any solutes in the headspace) are passed out of the sample matrix and vial and through a cryostat, adsorbent, or solvent to collect (or trap) the solutes.[25] After the solutes are collected (trapped), they are concentrated, separated, and analyzed, often with gas chromatography (GC).[26−30]

Headspace analysis is more difficult to apply to analytes that are of low volatility and those at trace quantity. Such applications of HS analysis typically require long collection periods to obtain sufficient sample mass for analysis and identification. Most commercially available purge and trap equipment was developed for measuring VOCs in aqueous samples; thus, these instruments typically have limited sweep periods for the purge cycle and limited temperature range for the sample holder (usually below 100 °C). These instruments are nearly impossible to use for the analysis of compounds of low volatility and/or at trace quantity, to obtain precise quantitative measurements, and for external studies performed as a function of collection temperature.

To overcome the limitations of commercially available HS analysis equipment, we have developed a high sensitivity, dynamic headspace analysis technique that makes use of cryoadsorption[31] on short alumina-coated PLOT columns.[25] We have used alumina as the adsorbent in most of our work with this technique because it is robust and can be used even with alkaline elution solvents if desired; however, when the measurement warrants, one can easily use silica, porous polymers, clays, organo-clays, pourous graphite, sol−gel phases, etc.[32−39] It is important to mention that SPME is not always a viable method for readily obtaining quantitative data, especially for compounds of low volatility and/or at trace quantities. Moreover, one must often salt-out the solutes of interest for SPME, which is not a feasible approach for in-the-field or "electronic nose" testing/analysis.[25]

After HS collection (see the Experimental Section for the experimental details), the cryoadsorber column is removed and the constituents are collected via desorption (usually solvent or thermal). Components of the headspace are separated, identified, and quantitated as a function of temperature, typically with GC

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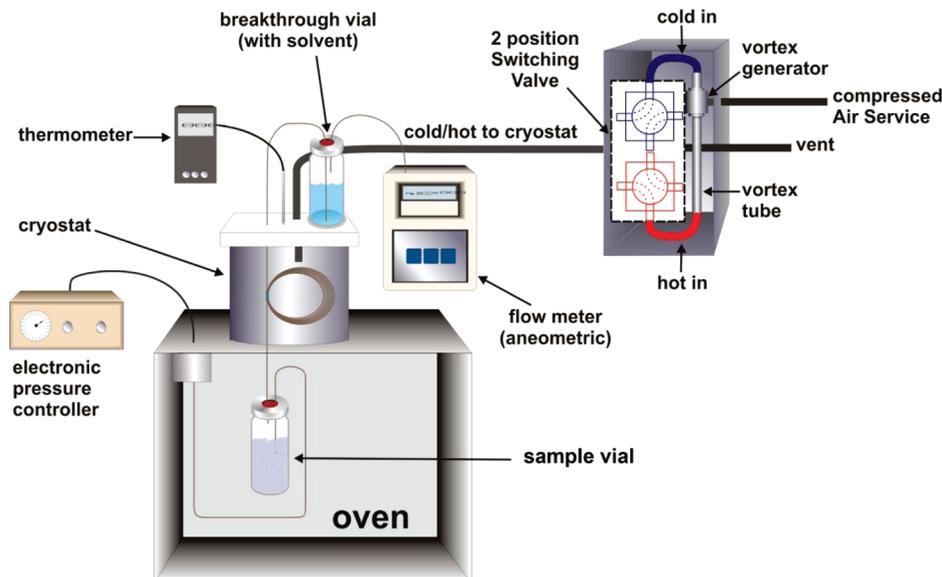
Figure 1. Schematic of the experimental apparatus used for quantitative and trace HS analysis with an adaptation of cryoadsorption.

and mass spectrometry (GC/MS).[40,41] We have applied this technique to the analysis of pure TNT and coumarin (both obtained from a commercial supplier), spoiled poultry, and the detection of gravesoil.[25,42,43]

We present the data in the form of van't Hoff plots, which is useful for establishing the thermodynamic validity of the data. Thermodynamics predicts that for an equilibrium process a plot in this form should exhibit a linear slope that is equal to the negative of the standard reaction enthalpy, $\Delta_r H^{std}$, divided by the gas constant, R. For the HS collections here, $\Delta_r H^{std}$ is the equilibrium enthalpy of the mass transfer from the solid to the gaseous state. Thus, a linear fit to the data presented in the form of a van't Hoff equation plot gives the value of the equilibrium enthalpy and affords predictive capability with thermodynamic significance.

EXPERIMENTAL SECTION

The solvents used in this work (acetone and toluene) were obtained from a commercial supplier and were analyzed by GC (30 m capillary column of 5%-phenyl/95%-dimethyl polysiloxane having a thickness of 1 μm, temperature program from 50 to 170 °C at a heating rate of 5 °C per minute) with flame ionization and mass spectrometric detection.[40,44] These analyses revealed the purity of the solvent to be greater than 99%, and the fluids were used without further purification. The external standards (DMNB, γ-butyrolactone (γ-but), 3,5,5-trimethylcyclohex-2-en-1-one (isophorone), bis(2-ethylhexyl) adipate (EHA), tributyl acetylcitrate, tributyl aconitate, trinitroglycerin (NG), diethyl phthalate (DEP), and n-tetradecane) were purchased from a commercial supplier (purity greater than 97%) and were used as received.[45] The

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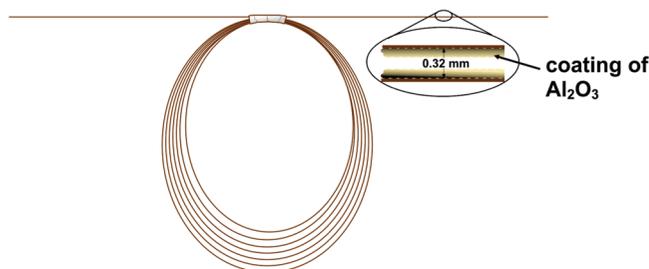
cryoadsorber trap

Figure 2. Schematic of the porous layer open tubular (PLOT) column used as a cryoadsorber trap. The PLOT column is coated with alumina, is approximately three meters long, and is coiled at a 3 in. diameter to allow the column to be housed in the cryostat chamber. (See Figure 1.)

compounds used in this work are relatively safe to work with and pose a danger only when ingested, inhaled, splashed on the eyes or skin, or ignited. Proper use of personal protective techniques (gloves, ventilation, and eye protection) and strict temperature and static control reduce these hazards.

The experimental apparatus developed in our laboratory, along with the associated PLOT column, are shown in Figures 1 and 2, respectively.[25] During a measurement, a crimp-sealed autosampler vial with a small amount (less than 100 mg) of sample was placed in a temperature-controlled chamber (the oven in Figure 1). An uncoated capillary was pierced through the septum to direct a flow of the sweep gas into the vial. Helium (He) was selected for the sweep gas because solutes diffuse readily through the He gas. Moreover, He has a high thermal conductivity, which is helpful in achieving thermal equilibrium.[25] An activated alumina-coated PLOT column (see Figure 2) was pierced through the septum to allow the sweep gas and the constituents in the HS to flow out of the vial and pass through the PLOT column. It is important to note that several different PLOT columns can be inserted into the vial's septum at the same period to collect samples on multiple phases and/or in parallel.

Table 1. Details for the GC/MS Programs Used to Separate and Identify the HS Components for Each PBX

column[a]	injection volume (μL)	isobaric head pressure (psig)	oven program
semtex-1A polar	3	12	48 °C for 1 min, 48−150 at 80 °C/min, 150−240 at 10 °C/min
semtex-H nonpolar	2	10	50−150 at 30 °C/min, 150−300 at 10 °C/min
tagged-C4 nonpolar	2	12	70 °C for 1 min, 70−150 at 50 °C/min, 150−300 at 15 °C/min
detaflex polar	3	12	70 °C hold for 1 min, 70−150 at 30 °C/min, 150−250 at 10 °C/min hold for 1 min
detcord nonpolar	3	12	50 °C, 50−150 at 30 °C/min, 150−300 at 10 °C/min, hold for 1 min

[a] 30 m nonpolar column, (5%-phenyl)-methylpolysiloxane, or polar column, (50%-cyanopropyl)-methylpolysiloxane.

To increase the collection efficiency, most of the length of each PLOT column was housed in a cryostat (a low-temperature chamber) that was cooled with a vortex tube (see Figure 1).[46] Temperatures as low as −40 °C are easily attainable with this arrangement. In practice, it is not always necessary to use temperatures below 0 °C, which is the temperature that was utilized in this study. Sample breakthrough from the cryoadsorber capillary was checked by allowing the sweep gas exiting the PLOT column to bubble through a vial with solvent (acetone) and a small amount of *n*-tetradecane to serve as a keeper. This solution was then analyzed for solute carryover.

The flow rate of the He carrier gas at the exit end of the PLOT column was monitored with a high precision digital flow meter having an uncertainty of 3%. Flow rates were approximately 0.5−1.2 mL/min. Note that, although we desire a relatively low flow rate to avoid turbulence and mechanical disturbance to the sample, the actual flow rate value is not very important. It is only critical that the flow rate be uniform, an aspect of the technique that has been discussed previously.[25] Headspace collection periods varied depending on the collection temperature. Lower sample temperatures required longer collection periods. The crimp-sealed sample vials were used only once to minimize the development of leaks and sample carryover.

After HS collection, analytes were removed from the PLOT column by solvent desorption with reagent grade acetone or 50/50 v/v acetone/toluene. We emphasize that the cryoadsorption technique is not limited to solvent desorption, and one should ascertain the advantages and feasibility of the use of thermal or other more sophisticated desorption techniques when developing a new application. Analytes eluted from the PLOT column were subsequently analyzed with GC/MS on either a nonpolar column (30 m capillary of 5% phenyl-95%/dimethyl polysiloxane having a thickness of 0.25 μm) or polar column (30 m capillary of (50% cyanopropyl−methylpolysiloxane having a thickness of 0.25 μm). The GC/MS temperature programs varied from sample to sample to provide chromatographic optimization. (See Table 1.)

We used GC with MS detection because numerous components are collected from the HS above PBXs. Component peaks
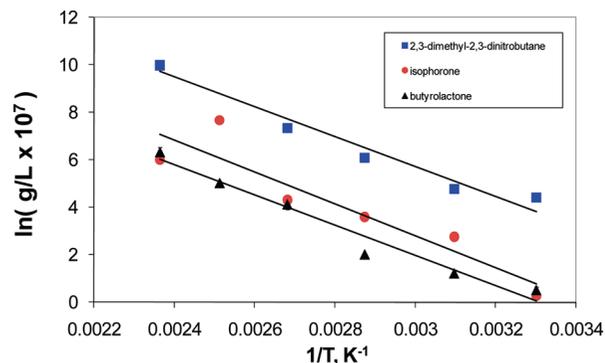
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Figure 3. Recovered mass (grams per liter × 10⁷) of DMNB (■), isophorone (●), and γ-butyrolactone (▲) as collected with an alumina-coated PLOT column from the headspace of Semtex-1A.

were identified with the aid of the NIST-EPA mass spectral database with the mass spectrometer used in scanning mode (m/z range from 15 to 550).[40,41] Peak identifications were corroborated with the peak retention times of the pure compounds. Quantitation of the recovered mass for each analyte was done on the basis of selected ion monitoring (SIM). This process required external standardization with the pure compounds.[41,47] Four concentrations of each pure compound were prepared by diluting the external standard in acetone; each sample and standard solution was subjected to seven replicate analyses to quantify the recovered analyte masses. The recovered masses were corrected for the amount of solvent used to desorb analytes from the PLOT columns and the amount of sweep gas used during the HS collection. Before each cryoadsorber tube was used for sampling, a blank was run by eluting the capillary with acetone and analyzing the resulting solution to ensure against cross contamination.

The sources of uncertainty in evaluating the recovered mass of trace components from the headspace are 2-fold; there is uncertainty in the area quantitation and in the calibration. The overall uncertainty (with a coverage factor of $k = 2$), associated with the recovered mass for trace compounds, was determined to be 3% at the low concentrations encountered in this work.

RESULTS

Headspace Measurements with PBXs. The headspace above detonating cord and PBXs including Semtex-1A, Semtex-H, tagged C-4, and sheet explosive was measured with the cryoadsorption technique described above. The data in Figures 3−7 are presented in the form of van't Hoff equation plots. The linear relationship of the vapor pressure as a function of inverse collection temperature is a confirmation of the thermodynamic consistency and predictive capabilities of the methodology employed here. The trace quantities of recovered masses are expressed in grams per liter of sweep gas used during HS collection. In all figures, the uncertainty bars presented indicate the excellent repeatability of the analytical sampling method. In most cases, the uncertainty bars are smaller than the size of the plotting symbol and, thus, are not visible.

Semtex. There are three main versions of Semtex: Semtex-1A (red Semtex, used mainly for blasting), Semtex-H (orange Semtex, used mainly for welding, forming, and hardening applica-

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tions), and Semtex-10SE (black Semtex, also used mainly for welding, forming, and hardening applications).[48] These materials differ in the secondary explosive: Semtex-1A contains 76.0%–86.0% PETN and 0%–4.6% RDX, Semtex-H contains 31.9%–37.9% PETN and 47.0%–53.0% RDX, and Semtex-10SE contains 72%–76% PETN.[48] Semtex-1A and Semtex-H contain approximately 15% binder (butadiene–styrene + oil); Semtex-10SE contains approximately 20% binder (polystyrene + dibutylphthalate + Teflon + silicon dioxide).[8] Each material contains at least 0.1% taggant DMNB or EGDN and plasticizer (e.g., dioctyl phthalate and tributyl acetylcitrate).[48]

Semtex-1A. The taggant DMNB, along with the solvents γ-but and isophorone, was identified (see the Supporting Information, Table S-5) and quantitated as a function of HS collection temperature (Figure 3) above Semtex-1A samples with the cryoadsorption technique. It is not surprising that PETN was not detected, because it has a very low vapor pressure at 20 °C ($\sim 8.3 \times 10^{-6}$ Pa). Quantitation was done by use of external standards and SIM of $m/z = 69$, 84, and 100 for DMNB, $m/z = 41$, 56, 86, and 137 for γ-but, and $m/z = 82$, 95, and 138 for isophorone. The solvent γ-but is known to be used for the recrystallization of RDX,[49] and isophorone most likely comes from the binder system.[50,51]

To illustrate the precision of the cryoadsorption method, the HS above Semtex-1A was sampled at 150 °C, a total of seven times. Three of the samplings were done in parallel and four samplings were independently (separately) run experiments. To sample the HS in parallel, an empty crimp-sealed vial (the staging vial) was set up with four capillaries attached; one to allow He gas to flow in at 2.1 kPa (0.3 psi) and three capillaries to connect the staging vial to three separate crimp-sealed sample vials containing Semtex-1A. A different PLOT column was attached to each of the sample vials. In keeping with the van't Hoff equation presentation, we evaluated the recovered mass for DMNB and present the values as the ln(mass) normalized by the gas volume. The values for the DMNB that were collected for the three experiments run in parallel were 6.9, 7.3, and 7.3; and the values for the four collections that were run separately were 6.7, 7.6, 8.4, and 8.0. These seven values are in excellent agreement, with an average of 7.5, a standard deviation of 0.6, and a percent coefficient of variation of 8%.

Semtex-H. We examined the components of the HS above three different blocks of Semtex-H, differing only in handling history with the cryoadsorption technique. We use the following notation to differentiate the Semtex-H samples. Semtex-H1 refers to a slice taken off of the end of an unopened block; Semtex-H2 refers to a core sample from an unopened block, and Semtex-H3 refers to a slice taken off of the end of a block that had been previously opened. The components of the HS above Semtex-H samples were examined with the cryoadsorption technique at HS collection temperatures from 30 to 150 °C. Several hydrocarbon compounds indicative of motor oil (linear and branched alkanes) were identified in the HS above each Semtex-H block at each collection
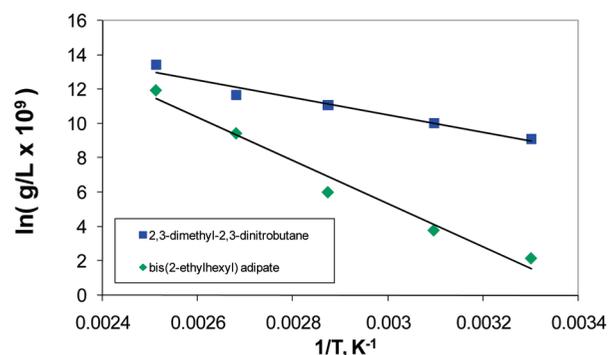

Figure 4. Recovered mass (grams per liter × 10⁹) of DMNB (■) and EHA (◆), as collected with an alumina-coated PLOT column from the HS of C-4.

temperature. Tables S-6–S-8 in the Supporting Information present the following compounds, which were found at only the highest temperature HS collection (150 °C): benzaldehyde, heptanonitrile, benzonitrile, nitrobenzene, 1,4-butanedioldinitrate, and NG (and its byproducts). NG (and its byproducts) is commonly found in smokeless powder.[52] Additionally, at the collection temperature of 150 °C, isophorone was identified only in the HS above Semtex-H2, and the taggant DMNB was identified only in the HS above Semtex-H2 and Semtex-H3.

Tagged C-4. Tagged C-4 contains 89.9%–92.0% RDX, 5.3%–5.9% plasticizer (e.g., dioctyl adipate or dioctyl sebacate), 2.1%–2.5% binder (e.g., polyisobutylene), 1.4%–1.6% motor oil, and 1%–1.5% taggant (DMNB). Both DMNB and the plasticizer EHA were identified (see the Supporting Information, Table S-9) and quantitated as a function of collection temperature (Figure 4). Isophorone and cyclohexanone were also observed; however, these compounds were found just above baseline noise. Quantitation was done by use of external standards and SIM of $m/z = 69.1$, 84.1, and 100.1 for DMNB and $m/z = 112.1$, 129, 147.1, and 241.2 for EHA.

Detaflex. Detaflex is the sheet explosive made for the military; Flex-X, Primasheet, and Detasheet are common sheet explosives made for industry.[8] These materials may include RDX, PETN, nitrocellulose binder, plasticizers (e.g., diphenylmethane-4,4′-diisocyanate), xylene, and kerosene. Two plasticizers, tributyl acetylcitrate and tributyl aconitate, composed the majority of the compounds found in the HS and probably originated from the polymeric fraction. A previous study found both of these plasticizers in polyvinylchloride (PVC), polyglycolide, and PVC copolymer with nitrile butadiene rubber.[53] Table S-10 in the Supporting Information presents these compounds along with the other interesting compounds that were identified (γ-but, 1-nitro-2-propanone, and dibutyl itaconate). Dibutyl itaconate is a monomer that may also be present in PVC and polyglycolide.[53] Quantitation was done by use of external standards and SIM of $m/z = 86$, 56, and 42 for γ-but, $m/z = 329$, 259, 185, 157, and 129 for tributyl acetylcitrate, and $m/z = 269$, 213, 157, and 112 for tributyl aconitate, and the recovered masses are presented in Figure 5.

(48) Ribbands Explosives, England, MSDS for Semtex RX-1A, Semtex RX-1H, and Semtex RX-10SE.

(49) Kim, D.-Y.; Kim, K.-J. *J. Chem. Eng. Data* **2007**, *52*, 1946–1949.

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(53) Report ND05o610/01; Screening of plastic toys for chemical composition and hazards – Market surveillance in the Netherlands; Food and Safety Authority (VWA): Netherlands, 2005.
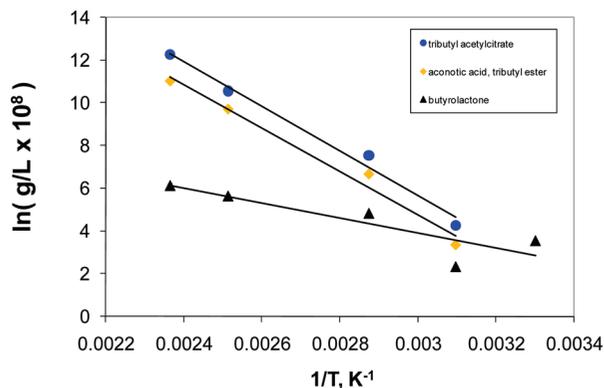
Figure 5. Recovered mass (grams per liter $\times$ 10^8) of tributyl acetylcitrate (●), tributyl aconitate (◆), and γ-butyrolactone (▲) as collected with an alumina-coated PLOT column from the HS of Detaflex (Flex-X).
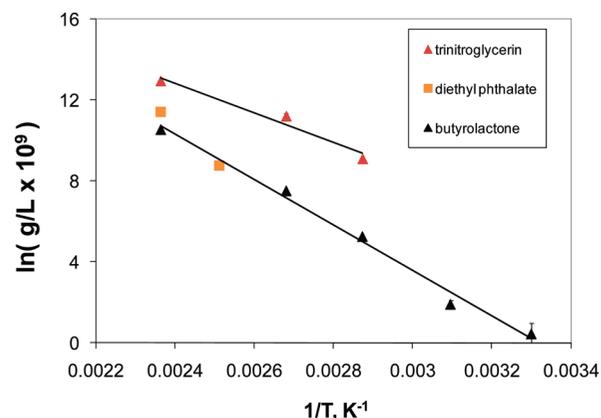

Figure 6. Recovered mass (grams per liter $\times$ 10^9) of nitroglycerin (red ▲), diethyl phthalate (■), and γ-butyrolactone (black ▲), as collected with an alumina-coated PLOT column from the HS of detcord.

Detcord. There are several different manufactures of detcord. Some trade names include Primaline, Primacord, Low Flex, and Fireline cord.[8] Table S-11 in the Supporting Information section presents the compounds identified (NG, the solvent γ-but, and the plasticizer DEP). Standards were unavailable for definitive identification of the remaining compounds (1,4-butanediol dinitrate, 1,2,3-propanetriol-1,3-dinitrate, propyl nitrate, and the taggant EGDN). DEP is common to several consumer products (e.g., cosmetics, insect repellants, perfumes) and has industrial and military applications (food packaging materials, solid rocket propellants).[54] Some compounds were found in the HS of detcord only when HS collections were performed at high temperatures; e.g., diethyl phthalate was detected in the HS of detcord at only 125 and 150 °C, and 1,2,3-propanetriol-1,3-dinitrate and nitroglycerin were collected at only 100, 125, and 150 °C. Quantitation was done by use of external standards and SIM of m/z = 86, 56, and 42 for γ-but, m/z = 76, 46, and 30 for nitroglycerin, and m/z = 178 and 149 for DEP. The recovered masses as a function of inverse HS collection temperature are displayed in Figure 6. Normalized peak areas for EGDN are presented separately in Figure 7.
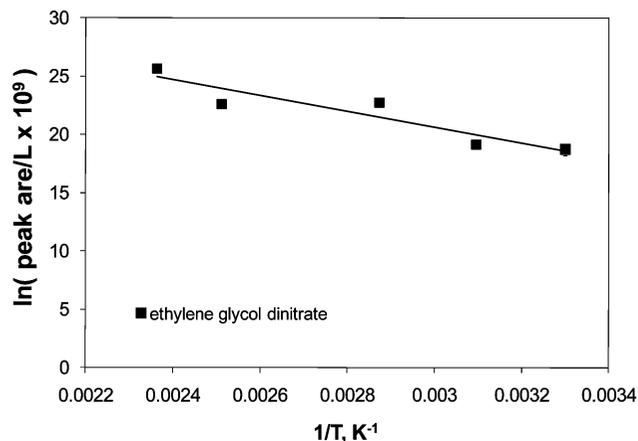
(54) *Diethyl phthalate*, *Environ. Writer*, **2006**; http://www.environmentwriter. org/resources/backissues/chemicals/diethyl_phthalate.htm; Access Date: Dec, 2008.

Figure 7. Normalized peak area (per liter $\times$ 10^9) of EGDN, as collected with an alumina-coated PLOT column from the HS of detcord.
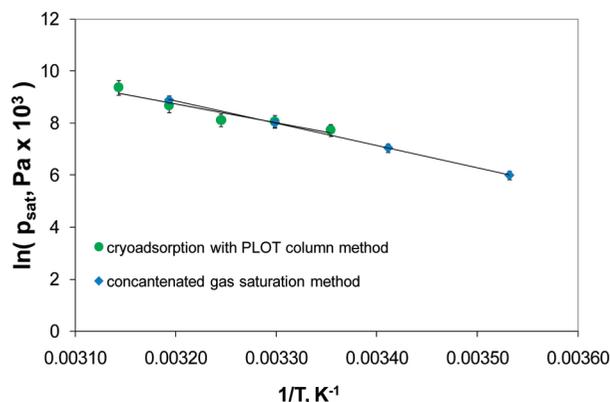

Figure 8. Vapor pressure (Pa $\times$ 10^3) of *n*-tetradecane, as collected with an alumina-coated PLOT column from the headspace above tetradecane adsorbed onto 1 mm glass beads (●). The data is compared with vapor pressure data obtained previously by Widegren and Bruno[6] by use of the concatenated gas saturation apparatus technique (◆).

Consistency Measurements with *n*-Tetradecane. It is important to measure a control sample as an experimental consistency check. We chose the pure compound *n*-tetradecane because it is stable and unreactive and we routinely use it for the same purpose in our measurements of low vapor pressure.[6,55] Figure 8 presents the data in the form of van't Hoff equation plots. The data are compared with vapor pressure data obtained by use of the concatenated gas saturation apparatus technique.[6,56] While we observe excellent agreement in the data sets obtained with both techniques, it is important to note that the concatenated gas saturation apparatus was developed specifically for the measurement of vapor pressure explicitly addressing all major sources of uncertainty. The dynamic headspace technique presented here is designed for determining the components in the headspace above complex mixtures of PBXs, and thus, the results were presented in trace quantities of recovered masses, expressed in grams per liter of sweep gas used during HS collection (not in vapor pressures, a pure component property).

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Table 2. Predicted Recovered Masses (ng/L) for the Compounds Detected Experimentally in the Headspace above Semtex-1A, Tagged-C-4, Detaflex, and Detcord[8] [a]

	compounds in the headspace	recovered mass (ng/L)	
		(20 °C)	(40 °C)
semtex-1A	isophorone	102	440
	γ-butyrolactone	51.0	205
	DMNB	2240	8850
tagged-C-4	bis(2-ethylhexyl)adipate	1.1	17.5
	DMNB	4460	13560
detaflex	γ-butyrolactone	116	250
	tributyl acetalcitrate	37.3	367
detcord	γ-butyrolactone	0.35	4.07
	nitroglycerin	224	1110
	diethyl phthalate	0.0006	0.03

[a] Predictions were made with van't Hoff relationships that were presented in Figures 3−7.

DISCUSSION

Figures 3−8 present the data in the form of van't Hoff equation plots. These data exhibit a linear relationship of the natural log of the recovered mass as a function of inverse collection temperature. Thus, not only can we predict the analyte recovery for these compounds at temperatures in addition to those that were selected for experimental measurements but also the predicted values are thermodynamically consistent. Table 2 presents the predicted recovered masses for the compounds detected experimentally in the headspace above Semtex-1A, C-4, detcord, and Detaflex at both 20 and 40 °C.

The slope of the data in the form of a van't Hoff equation also provides insight into the important equilibrium process (e.g., enthalpies of adsorption, absorption, or vaporization) that dictate the mass transfer from the solid PBX material to the vapor phase. This equilibrium process is complicated by mixture effects and different component interactions. A linear fit to the data presented in Figure 3 provides the slopes for the equilibrium concentrations of the compounds collected in the HS above Semtex-1A: DMNB, γ-but, and isophorone. The slope multiplied by the ideal gas constant, R, is 5.2×10^7 J/kmol for DMNB, 5.3×10^7 J/kmol for γ-but, and 5.6×10^7 J/kmol for isophorone. These values for the equilibrium enthalpies of γ-but and isophorone are remarkably similar to the enthalpies of vaporization for these compounds at 303 K ($\Delta H_{vap} = 5.3 \times 10^7$ J/kmol for γ-but and $\Delta H_{vap} = 5.0 \times 10^7$ J/kmol for isophorone).[3] Thus, the equilibrium concentration of γ-but and isophorone in Semtex-1A is controlled by the enthalpy of vaporization of these compounds. A direct measurement for the enthalpy of vaporization for DMNB is not available in the literature; however, the enthalpy of vaporization has been evaluated indirectly from the measurements of the enthalpy of sublimation and the enthalpy of fusion.[57,58] These studies report the calculated value for the ΔH_{vap} for DMNB at 473 K (5.5×10^7 J/kmol with a reported error of 0.1×10^7 J/kmol)[57] and at 308 K (6.5×10^7 J/kmol).[58] These values are very close to the value we determined (5.2×10^7 J/kmol).

The γ-butyrolactone is also present in the HS above Detaflex and detcord. (See Figures 5 and 6.) The slope multiplied by the ideal gas constant, R, is 2.9×10^7 J/kmol for γ-but in Detaflex and 9.3×10^7 J/kmol for γ-but in detcord. The variability of the enthalpies of γ-but in different PBX packages, once again, indicates that the enthalpy of vaporization is not always the controlling mechanism and illustrates the importance of considering matrix effects when determining equilibrium concentrations with headspace analysis as a function of collection temperature.

The observation of NG in detcord and Semtex-H was somewhat surprising. We are unaware of NG in any formulation of these explosives. The possible sources of contamination are at the plant, during handling, and from our lab. We routinely tested the PLOT columns for contamination and found none. We also sampled the ambient air with a motorized pipetter and an activated alumina-coated PLOT column. The solutes were collected from the PLOT column with solvent desorption. We also sampled various surfaces in our laboratory including the lab bench, the hood surface, the inlet and outlet of the tube that connects the cryostat to the oven, the balance, the secure magazine where the explosive materials are stored, and various tools that were used to prepare samples and vials for headspace collection. Cotton swabs were used as swipes for these tests, which were subsequently soaked in solvent. These solutions obtained from both sampling the air and surface wipes were analyzed with GC/MS. No contamination from NG or any other energetic material or compound was found. Thus, we conclude that the NG detected in the HS above detcord and Semtex-H is from the samples. These compounds might originate from the manufacturing facility or from storage of these materials with other energetic materials containing NG.[59]

SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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