

Simple, Quantitative Headspace Analysis by Cryoadsorption on a Short Alumina PLOT Column*

Thomas J. Bruno[†]

Physical and Chemical Properties Division, National Institute of Standards and Technology, Boulder, CO

Abstract

The use of purge and trap methods for sampling volatile organic compounds prior to chromatographic analysis is a mature technology. Application to low volatility compounds has been far less facile and sensitive. Especially problematic has been applications that require precise quantitative analysis and analyses as a function of sample temperature, especially for low volatility analytes. In this paper, we have applied short lengths of alumina-coated PLOT columns as purge traps and operate the traps at low temperature during the collection cycles to improve efficiency in a method called cryoadsorption. We have applied the method as a function of temperature to a medium volatility solid, coumarin, as a demonstration, with further application to the pure explosive compound 2,4,6-trinitrotoluene (TNT) and the practical explosive C-4. We estimate that by use of mass spectrometry, the sampling method discussed in this paper can provide a detection limit of 0.0019 μg TNT per gram of substrate (determined with a 60 min sweep with the sample held at 60°C). Moreover, for quantitative results, we can achieve a percent standard deviation (coefficient of variation) of 10% with samples as low as 0.064 μg TNT per gram of substrate.

Introduction

Headspace analysis is a technique in which a gas that has previously been in contact with a condensed phase (solid or liquid) is examined for the presence of (typically volatile) compounds released into the gas (1,2). The partitioning of analytes into the gas phase can be understood or even predicted with thermodynamic considerations (3). This thermodynamic relationship in its simplest form is a plot of equilibrium concentration against temperature (embodied in the van't Hoff equation), and can sometimes make possible the approximation of analyte concentration in the original condensed phase. Headspace analysis is most easily accomplished if the solute approaches an ideal solution in the matrix (4). When attempts are made to measure analytes in the headspace of an aqueous solution, salting out is often used to boost the analyte concentration in the headspace (5,6). Moreover, when such headspace analyses are standardized, it is often desirable to salt out both the standards and analytes to minimize the ef-

fects of solutions with differing ionic strengths.

Sampling methods from headspaces can be either static or dynamic. In static methods, one typically pressurizes a sealed vial or vessel containing the condensed sample (to slightly above atmospheric pressure), then sampling is done of the pressurized headspace through a septum (7). Sampling can be done with a gas tight syringe (with or without a syringe valve), a multiport sampling valve, a solid-phase extraction cartridge (8,9), or with a solid-phase microextraction (SPME) fiber (10,11). In dynamic methods, a flow of carrier or sweep gas is applied to the matrix containing the analyte (12). The stream is then collected in a cryostat, adsorbent, or solvent, thus this method is often referred to as purge and trap. The sweep gas can be under a positive pressure or drawn through the sample at reduced pressure; either method has its advantages and pitfalls.

When the analyte in the headspace gas is at a trace level, or when an exhaustive analysis of all constituents is desired, purge and trap methods are usually preferred over static headspace or even modern SPME approaches (13–16). For analytes of very low volatility, longer collection times are required to collect sufficient sample for analysis (17). Moreover, static and SPME methods are often difficult to make quantitative and reproducible with such solutes. These techniques are often more suited to survey analysis, or to verify the presence of an analyte. They are often not suitable for temperature-dependent studies that are critical in the validation of other analytical methods.

It is often necessary to analyze the headspace of a solid to determine (i) the constituents of the headspace, (ii) the relative concentrations of constituents in the headspace, and (iii) how the constituents and concentrations can be changed with temperature (18,19). This latter aspect typically requires the correlation of equilibrium concentration data with the van't Hoff equation mentioned earlier. There are clear applications of such analyses in environmental forensics and in homeland security (18,20). The detection and analysis of explosives, residues, and taggents, especially such materials that are packaged to conceal the content, is an obvious example (21). In these instances, the major analytes may not be the compounds that were originally present in the largest concentrations. For example, in the case of explosives, the binder in a plastic explosive may be the most easily recovered or detected analyte. In many cases, analytes of this type are of very low volatility

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[†] Author to whom correspondence should be addressed: email bruno@boulder.nist.gov.

and are also very polar. These two characteristics make analyses and especially repeatable quantitation very challenging (19). Indeed, most of the commercially available purge and trap equipment are unsuitable without significant modifications. The common shortcomings include a limited sample holder temperature range (most are limited to below 100°C), a limited sweep time for the purge cycle, and sample carry-over or history effects. This latter problem is typically addressed with deactivation coatings on transfer lines, often with mixed results (that is, effective with some analytes and ineffective with others). Moreover, many of the commercial units are too limited or inflexible (in both hardware and control software) to be useful in research environments; they are intended for repetitive analyses running specific standard methods.

There are many other examples of applications beyond the homeland security issues discussed earlier. Pesticides deposited on soils subject to weathering effects are an example of an environmental analysis in which headspace analysis plays a critical role. Other applications are in the measurement of the vapor concentrations of fire retardants, plasticizers in beverage bottles, and volatile chemical markers for food spoilage.

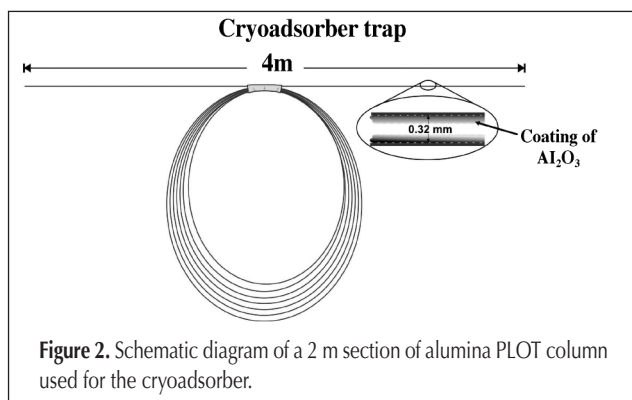
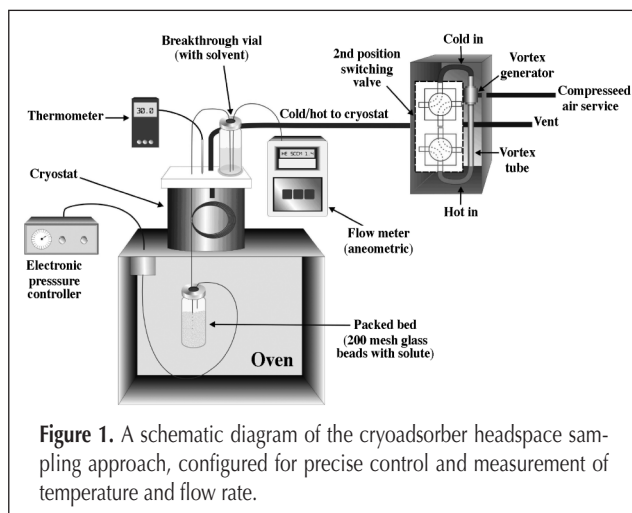
Experimental

Any approach to quantitative purge and trap headspace sampling requires a sweep gas of controllable, measurable flow rate and pressure, a leak-tight sample holder that can be thermostatted, and a sample collection device that is efficient (to minimize measurement times) and has sufficient capacity (to avoid problems of sample breakthrough). Also required is a timer to measure the duration of the measurement, from which the total flow through the sample holder is established. As alternatives to the time-based measurement, a flow integrator (or totalizer) can be used to establish the total flow, or a mass measurement can be used along with an accurate equation of state (22). The apparatus should be simple, convenient to use, and inexpensive, yet applicable over a wide range of solute vapor pressures and concentrations. The sampling approach developed to make quantitative headspace measurements as a function of temperature is shown schematically in Figure 1. It is a combined approach that utilizes both an adsorbent (23–25) and reduced temperatures (14,26).

The apparatus was made from a surplus gas chromatograph that was equipped with electronic pressure control (EPC). The EPC module was used in constant pressure mode to control the sweep gas, and the column oven serves as a thermostat for the sample holder. Constant pressure mode was preferred over constant flow mode because the pneumatics were consistently more stable in that mode. A length of uncoated fused silica capillary tubing (0.32 mm inside diameter) was connected to a split/splitless injection (under EPC) port inside the oven. The other end of this tube was connected to the sample holder, as will be described later. The oven temperature stability was improved by the addition of braids of copper grounding wire, and copper blocks on the sides and bottom of the oven, whereas without it was no better than 1°C. The uncertainty in the oven temperature with these modifications was 0.1°C. When sub-ambient sample temperatures are desired, we apply a vortex chiller on the chromatographic oven (27).

The sample holder consisted of a narrow-mouth auto-sampler vial with an aluminum crimp cap closure and a PTFE/silicone sandwich septum. To connect the sample holder to the sweep gas source, one simply pierces the septum of the vial with the fused silica tube. We have shown in other work that this can be facilitated with rubber padded hemostat clamps (28). The seal made by the septum to the tube is surprisingly tight. We have noted that a seal made in this way can withstand up to 3 atm without leaking either at the pierce point or at the crimp seal. Naturally, during the purge and trap cycle, the pressures are much lower than this. The sample contained in the vial can consist of a dispersed, powdered solid, a solid deposited on glass beads (as shown in Figure 1) from a solution, monolithic chunks, or a film produced from a melt. All of these types of preparations have been used, and all are suitable. The tube from the sweep gas source typically extends to the bottom of the sample holder vial.

The sample collection device used for this work was a cryoadsorber made from a 2-m length of an alumina porous layer open tubular (PLOT) column (0.32 mm inside diameter). The alumina coating on this capillary is a highly retentive, polar adsorbent. The column that was used for this work had been used previously for natural gas analysis, so before using the sections as cryoadsorbents, the column was washed thoroughly with mixed polar and aromatic solvents, then dried and activated at 225°C in a gas chromatographic (GC) oven. Of course, one can use lengths of new PLOT columns, and PLOT columns with silica, sol-gel, or porous polymer layers can be



used when desired. The length of PLOT column was formed into a 6 cm diameter coil and secured with short lengths of heat-shrink tubing of the type used to insulate electrical connections, as shown in Figure 2. The coil was then placed in the cryostat chamber (an insulated cylinder secured to the top of the GC oven) so that the coil, which comprises most of the length of the column, is contained in the cryostat. We have found that cryoadsorbers so prepared can be reused many times before cracks develop in the fused silica tubing.

The PLOT capillary was connected to the sample holder in the same way that the sweep gas was connected, by piercing the fused silica tube into the sample holder septum. In this case, however, the tube was inserted to a depth of only ~ 1 mm below the septum surface. The direct connection of the cryoadsorber to the sample holder completely eliminates the difficulties of transfer line carry-over that plague many commercial instruments. The sample holder is then left suspended in the middle of the GC oven, held only by the two fused silica tubes piercing the septum. The top of the cryostat is covered with an insulated PTFE plate, which contains provisions for a breakthrough vial (also a crimped cap autosampler vial connected by piercing), a temperature probe, and a venting muffler (the reason for which will be explained later). The breakthrough vial can be an adsorbent (such as glass wool) or a solvent; in Figure 1, we show a solvent in the vial. For many low vapor pressure solutes, the breakthrough vial may be eliminated after experimental verification that breakthrough does not occur.

In earlier work, we noted that cryotrapping applications need not require liquid nitrogen temperatures; indeed, very efficient collections can be obtained at between 0 and -40°C . To achieve this temperature, we used a vortex tube to produce a cold air stream that was used to chill an uncoated cryotrap to this temperature range. A vortex tube is a simple device (with no moving parts) used to produce low (and high) temperature air streams from a source of compressed air (29). Desorption in that apparatus was easily done by valving to the hot air stream of the vortex tube (160°C). The same sort of valve arrangement is shown in Figure 1, although, here we do not use the thermal desorption feature. We simply use the cold air stream to chill the PLOT column to a low enough temperature to assist in solute trapping. The temperature stability of the cryostat is 2°C at -40°C . The muffler on the top of the cryostat serves as the vent for the cold air and also reduces the noise produced by the escaping cold air stream. After leaving the breakthrough vial, a length of uncoated fused silica tubing connects to an anemometric flow meter calibrated for the sweep gas. In addition, an integrator is available for connection to the anemometer, although it is not shown in Figure 1. Flow rates ranged from 1.0 to 1.8 mL/min, decreasing as the temperature increased as a result of the viscosity of the sweep gas. The typical uncertainty in the flow rate measurement was 3%, coefficient of variation (COV) (30).

The choice of sweep gas is a relatively minor consideration because the main desire is transport. In earlier work on the measurement of very low vapor pressures with the gas saturation method, we argued that sulfur hexafluoride was the best choice despite its high cost because it minimized back diffusion at low flow rates, and the relatively high mass allowed the

flow to be determined by a precise mass measurement (31). Here, for an analytical sampling application, the flow rates are higher, and such a precise measure of the mass is not needed. Our choice for sweep gas in this application is helium. The high thermal conductivity of this gas improves the performance of the cryoadsorber, and the solute diffusion to the adsorbent through the helium is favorable.

The approach discussed here allowed us to address the shortcomings in current approaches while providing additional advantages. The sample holder can be operated from -40°C to $\sim 300^{\circ}\text{C}$, and there is no restriction on collection times. Sample carryover or breakthrough is explicitly measured. Multiple analyses are possible for each sampling with the cryoadsorber. In addition, we can insert multiple cryoadsorbers into a given saturator for even better reliability. This provides the unique opportunity to utilize different adsorber phases for specific applications. Thus, while here we have only used alumina PLOT phases, it is clearly possible to use porous polymers, sol-gel phases, or silicone phases. Moreover, these can be used simultaneously, as stated earlier.

To operate the apparatus, the sample holder and cryoadsorber are assembled as shown in Figure 1. With the sweep gas turned off, the oven temperature is set to the desired value, and compressed air is applied to the vortex tube to chill the cryotrap. After thermal equilibration, the sweep gas is applied and the resulting flow is measured by the anemometer. The timer on the GC is simultaneously activated to measure the duration of the measurement. This duration is determined on the basis of solute vapor pressure; longer measurement periods, up to 72 h, may be needed for very low vapor pressure solutes at lower temperatures (for example, below room temperature). At the end of an experiment, the sweep gas is stopped, and the oven is cooled. The cryoadsorber is removed from the sample holder and the cryostat and is eluted with solvent into a weighed vial. Elution is easily accomplished by piercing the cryoadsorber into a septum vial filled with an appropriate solvent, and pressurizing the vial (with a 50 mL syringe or a compressed air source) to force the solvent flow. The collected solution is then analyzed for the solute. The use of multiple cryoadsorbers makes it possible to elute and analyze one measurement while the next one is running.

Results and Discussion

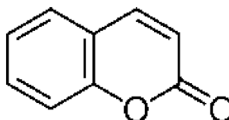
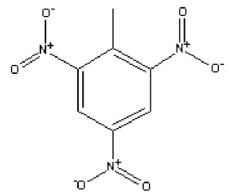
The operation of the cryoadsorber approach to quantitative headspace analysis was tested with two polar solid solutes with very different vapor pressures: coumarin and 2,4,6-trinitrotoluene. Coumarin was chosen for the development of this technique because it has a vapor pressure in the range of some taggents used for explosives. Moreover, it is far less toxic than many taggents used to mark explosives. Some basic information on each of these solutes is provided in Table I. The coumarin was solvent deposited on 200 mesh glass beads that were then placed in the sample holder. The apparatus was connected as described earlier, and measurements were done for eight different temperatures (10, 30, 50, 70, 80, 90, 100, and 110°C) with helium as the sweep gas. Collection

times varied from 60 min at 110°C to 240 min at 10°C. The flow rate was maintained at 1.0 mL/min with an uncertainty of 3% COV. The cryoadsorbents were eluted with acetone and analyzed by a GC-MS method (splitless injection, 30 m open tubular column coated with cross linked 50%-cyanopropyl-methylphenylpolysiloxane, isobaric head pressure at 4.5 psig, column temperature programmed 150°C to 225°C, at 15°C per minute, single ion monitoring for $m/z = 89, 90, 118, \text{ and } 146$). The analyses were standardized externally with coumarin solutions in acetone. For this solute, the recovered mass was expressed per liter of sweep gas. A plot of the recovered mass per liter against reciprocal thermodynamic temperature is provided in Figure 3. A linear relationship in mass recovered is obtained, despite the relatively short collection times and

low flow rates. The linearity on this plot is the result of the van't Hoff relation, which relates the temperature change to the equilibrium constant; the mass recovery being controlled by the phase equilibrium. We have performed multiple measurements of this solute and can overlay successive plots within the experimental uncertainty indicated on the figure. Indeed, we make routine use of this solute as a diagnostic sample to verify proper functioning of the apparatus. We can use this plot to predict a low temperature limit, or a collection time limit, for this solute. For other solutes in this vapor pressure range, one would also have to consider the analytical factors such as detector responses. These data are presented merely to demonstrate the operation of the technique; the main application of the method is with solids of much lower vapor pressure.

The sample of 2,4,6-trinitrotoluene, a low vapor pressure polar solid, was placed in the sample holder as a melt that coated the sides of the autosampler vial. The apparatus was connected as described earlier, and measurements were done for five temperatures (30, 60, 75, 100, and 125°C), also with helium as the sweep gas. Measurements for this solute were allowed to run much longer than those for coumarin because of the much lower vapor pressure (see the Antoine coefficients in Table I). Collection times ranged from 120 min at 125°C to ~4000 min for 30°C. The flow rate varied from 1.8 mL/min at 30°C to 1.0 mL/min at 125°C, as a result of changes in helium viscosity with temperature, but was maintained constant at each temperature with an uncertainty of 3% COV. The cryoadsorbents were eluted with acetone and analyzed by a GC-MS method (splitless injection, 30 m open tubular column coated with cross linked 50%-cyanopropyl-methylphenylpolysiloxane, isobaric head pressure at 12 psig, column temperature programmed 160°C to 260°C, at 19°C/min, single ion monitoring for $m/z = 63, 89, 180, \text{ and } 210$). The vapor pressure of 2,4,6-trinitrotoluene is more than two orders of magnitude lower than that of coumarin, as shown by the Antoine coefficients (to the hyperbolic fit of vapor pressure data, derived from the Clausius-Clapeyron equation) provided in Table I (32,33). Moreover, the difference in vapor pressure between these two solutes is greater at lower temperatures.

We present the TNT mass recovery data from the cryoadsorbents for a typical experiment in Table II, along with volume

Table I. Information on the Solutes Used in This Work.	
Coumarin:	
	CAS No: 91-64-5 InChI=1/C ₉ H ₆ O ₂ /c10-9-6-5-7-3-1-2-4-8(7)11-9/h1-6H
Other names: ² H-1-benzopyran-2-one; cis-o-coumarinic acid lactone; o-hydroxycinnamic acid lactone; benzo- α -pyrone; coumarinic anhydride; Rattex; tonka bean camphor; 1,2-benzopyrone; 2-propenoic acid, 3-(2-hydroxyphenyl)-, δ -actone; ² H-benzo(b)pyran-2-one; o-hydroxycinnamic lactone; cinnamic acid, o-hydroxy- δ -lactone; 2-oxo-1,2-benzopyran; ² H-1-benzopyran, 2-oxo-; ² H-chromen-2-one; H-1-benzopyran-2-one.	
$T_b = 301^\circ\text{C}$; $T_f = 71^\circ\text{C}$; RMM = 146; $\rho = 0.935 \text{ g/mL}$; Antoine coefficients: A = 5.31529; B = 2797.239; C = -37.541 (106–291°C)	
2,4,6-trinitrotoluene:	
	CAS No: 118-96-7 InChI=1/C ₇ H ₅ N ₃ O ₆ /c1-4-6(9(13)14)2-5(8(11)12)3-7(4)10(15)16/h2-3H,1H3
Other Names: benzene, 2-methyl-1,3,5-trinitro-; toluene, 2,4,6-trinitro-; α -TNT; s-trinitrotoluene; s-trinitrotoluol; Tolite; Tritol; Trotyl; TNT; 2-methyl-1,3,5-trinitrobenzene; 2,4,6-trinitrotoluene; syn-trinitrotoluene; sym-trinitrotoluol; NCI-C56155; Entsof; Tnt-tolite; Triton; trojnitrotoluen; 2,4,6-trinitrotolueen; 2,4,6-trinitrotoluol; Tolit; sym-trinitrotoluene; Trotyl oil; UN 0209; UN 1356; 1-methyl-2,4,6-trinitrobenzene; 2,4,6-TNT.	
$T_b = 295^\circ\text{C}$ (decomposes); $T_f = 80.4^\circ\text{C}$; RMM = 227.131; $T_{ig} = 295 \text{ C}$; $\rho = 1.654 \text{ g/mL}$; $\Delta H_{act} = 147 \text{ kJ/mol}$; VOD = 7,028 m/s Antoine Coefficients: A = 5.37280; B = 3209.208; C = -24.437 (230–250°C)	
T_b = boiling temperature, normal; T_f = freezing temperature; RMM = relative molecular mass; ρ = density; T_{ig} = ignition temperature; ΔH_{act} = Enthalpy of activation; VOD = velocity of detonation The Antoine coefficients are used to fit saturated vapor pressure data for pure compounds. The equation is: $\log P = A - B / (C + T),$ where P is the vapor pressure, A, B, and C are the Antoine coefficients, and T is the temperature.	

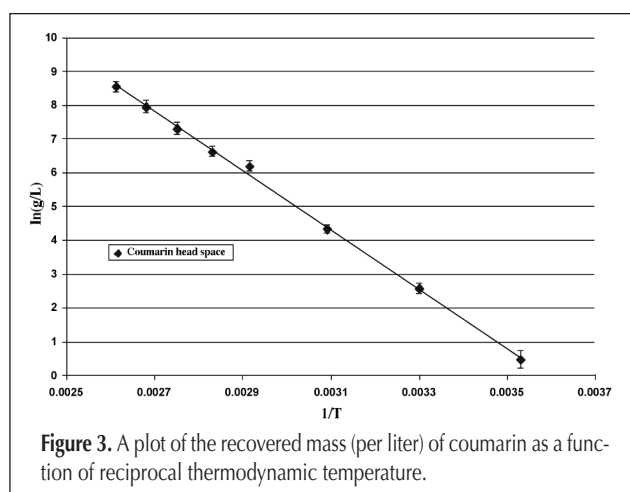


Figure 3. A plot of the recovered mass (per liter) of coumarin as a function of reciprocal thermodynamic temperature.

of sweep gas used, and the mass normalized per liter of sweep gas. The recovered masses are much smaller for this low vapor pressure solute than they were for the coumarin. The masses listed were calculated from the chromatograms, and have an uncertainty ranging from 1% COV at 125°C (where a relatively large quantity of solute is recovered) to 16% COV at 30°C (where far less solute is recovered). These uncertainties are presented in mass terms parenthetically in Table II. Included in this uncertainty is the repeatability of seven chromatographic measurements on eluted solutions, and the uncertainty in the chromatographic calibration. Since a larger volume of sweep gas was used for TNT, we present the mass recoveries graphically on the basis of 10^5 liters in Figure 4. The uncertainty bars in this figure also include the uncertainty in the volume of the sweep gas, discussed earlier. Note that only the uncertainty bars for the lowest two temperatures are large enough to be seen on this logarithmic plot of the van't Hoff formulation; the others are smaller than the plotting symbols. We see that again a linear relationship is obtained re-

Table II. The TNT Mass Recovery Data from the Cryoadsorbents for a Typical Experiment*

Temperature (°C)	Mass of TNT Recovered (g)	Sweep gas volume (mL)	Mass of TNT per liter of sweep gas (g/L)
30	0.000344 (0.000055)	10118 (303)	0.000034 (0.000007)
60	0.000157 (0.000016)	1439 (43)	0.000109 (0.000014)
75	0.000343 (0.000015)	433 (13)	0.000792 (0.000058)
100	0.000349 (0.000015)	148 (4)	0.002359 (0.000165)
125	0.001327 (0.000013)	118 (3)	0.011246 (0.000396)

* The uncertainty of each quantity (with a coverage factor $k = 2$, that is, two standard deviations) (30), determined from replicate measurements, is provided in the parentheses.

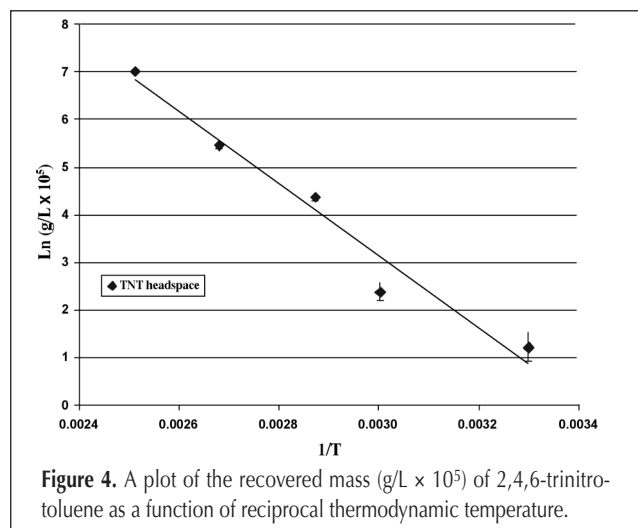


Figure 4. A plot of the recovered mass ($\text{g/L} \times 10^5$) of 2,4,6-trinitrotoluene as a function of reciprocal thermodynamic temperature.

lating the mass recovered to temperature, thus allowing a predictive capability. Here, such a predictive relation is critical, as the development of metrology to detect energetic materials is important to homeland security.

On the basis of the response obtainable from the analytical method, we can predict the lower bound for which this sampling method can be used for TNT headspace sampling.

We can approximate the minimum detectable quantity of the technique as it is applied to this solute by preparing spiked samples of TNT on the matrix (in this case, the glass beads). This was done for TNT by spiking small quantities of TNT on the glass bead matrix. We found that after a sweep time of 60 min, with the sample held at 60°C (an intermediate temperature for the TNT measurements we have presented earlier), samples with 0.064 $\mu\text{g/g}$ TNT on the glass bead matrix could be detected and quantitated with repeatability of 10% COV. A detection response of three times the baseline noise could be obtained with a spiked sample with 0.0019 $\mu\text{g/g}$ TNT on the glass bead matrix.

Of course, the application of more sensitive detectors, where appropriate, will extend this to a lower level. We have applied mass spectrometric detection here to provide qualitative identification as well.

In both example cases presented here, the solutes are pure components. Usually, samples are presented for purge and trap analyses as mixtures, often as complex mixtures. The method reported here can also be used with these types of samples. As an example, we used the approach for one measurement of the headspace of a sample of tagged C-4 (a modern plastic explosive). The sample holder was maintained at 100°C, and collection was done for 240 min. We were able to identify numerous components of the motor oil matrix, a taggant, as well as a plasticizer. These components are listed in Table III. The most abundant compound recovered was the plasticizer. We do not provide quantitative data here because this mixture is only presented as an example. Clearly, quantitation would be readily performed provided the pure components are used in the preparation of a calibration, or if internal standardization is done.

Note that the principal energetic material of C-4 (hexahydro-1,3,5-trinitro-1,3,5-triazine, or RDX) was not among the

Table III. Components detected in the headspace of tagged C-4, after a helium purge cycle of 240 min at 2 mL/min, with the sample held at 100°C.

Motor Oil Matrix Components:

2,4,6-trimethyloctane
n-decane
 2,2,9-trimethyldecane
 2,6-dimethylundecane
 2,5-dimethyltetradecane
 4-ethyl-2,2,6,6,-tetramethylheptane

Taggant:

2,3-dimethyl-2,3-dinitrobutane

Plasticizer:

Bis(2-ethylhexyl)hexadecanoic acid ester
 (dioctyl adipate)

compounds detected in the headspace. This is not a disadvantage because an identification can be made on the combined basis of the detected plasticizer and taggant. The suite of compounds listed earlier can provide the basis for the identification of improvised explosive devices that are made with C-4. The fact that RDX is not among the compounds is negative information that is also of great importance. It is a critical issue for field personnel to know what not to waste time and resources looking for with a particular technique. Moreover, the potential to develop such information as a function of temperature is also important because it provides the guidelines as to what temperatures might be needed in the application of the metrology for in the field detection.

Conclusions

In this paper we have demonstrated the application of cryoadsorption on short lengths of alumina PLOT columns as a method of quantitative headspace sampling. The sampling columns can be used under positive or negative pressure of an inert sweep gas to trap the desired analytes. The method is especially applicable to polar analytes such as explosives, and can be used in the laboratory or as a field sampling technique. It provides a very simple and inexpensive sample collection method with no compromise in efficiency or increased uncertainty. Moreover, the ability to obtain reproducible, quantitative measurements is a significant advantage over other approaches. The cryoadsorbents made from PLOT columns are durable and can be used many times before cracks develop in the fused silica tubes. We also note that it is possible to utilize multiple adsorbents simultaneously, and in so doing utilize more than one trapping phase in a single experiment. The preliminary results indicate that the method can collect samples that are at the ppb or lower range, although this is dependent upon the specific analytical combination utilized (injection and detection methods). We are currently applying this method to a series of practical explosives, and also examining the minimum periods required to provide a valid go-or-no-go identification of an explosive compound or a matrix component. This will be reported in the future.

Acknowledgement

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