



Short communication

Direct liquid deposition calibration method for trace cyclotrimethylenetrinitramine using thermal desorption instrumentation

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ABSTRACT

A simple method for establishing calibration curves with sorbent-filled thermal desorption tubes has been demonstrated for nitroaromatic and nitramine vapor samples using a thermal desorption system with a cooled inlet system (TDS–CIS), which was coupled to a gas chromatograph (GC) with an electron capture detector (ECD). The method relies upon the direct liquid deposition of standard solutions onto the glass frit at the head of sorbent-filled thermal desorption tubes. Linear calibration results and ideal system conditions for the TDS–CIS–GC–ECD were established for mixtures containing both cyclotrimethylenetrinitramine, a.k.a. RDX, and 2,4,6-trinitrotoluene (TNT). Because of the chemical characteristics of RDX, a higher TDS–CIS flow rate relative to the optimized approach for TNT was required for efficient RDX desorption. Simultaneous quantitation of TNT and RDX using the direct liquid deposition method with optimized instrumentation parameters for RDX were compared to results from a standard split/splitless GC inlet and a CIS.

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1. Introduction

Sensor development for the detection of trace explosives is of critical interest to both military and homeland security interests [1–6]. One of the most challenging problems facing sensor development is the validation of vapor generation methods at trace, sub-parts-per-million (ppm), concentrations because of the difficulty in generating known vapor concentrations of nitroaromatics and nitramines over a reasonable dynamic range [7–13]. Gas chromatography (GC) coupled to an electron capture detector (ECD) is widely recognized as a sensitive technique for quantitation of nitroenergetics in complex mixtures [14–16]. Because of the extremely low vapor pressures associated with these compounds [8,12], detection limits in the nanogram to picogram range are required and necessitate some form of vapor pre-concentration. In this respect, sorbent-filled thermal desorption tubes have shown great promise for calibrating vapor generators [9,11,13,17] and thermal desorption systems with a cooled inlet system (TDS–CIS) can now be coupled directly to a GC–ECD as a single commercial instrument, making nanogram to picogram detection limits a reality. Thus, explosives vapor generators for sensor development research can be calibrated and monitored

using sorbent-filled thermal desorption tubes and analyzed with a TDS–CIS–GC–ECD, provided there is an adequate understanding of the losses associated with the technique and a viable quantitation method.

A method for quantitation of 2,4,6-trinitrotoluene (TNT) vapors utilizing thermal desorption tubes and commercial TDS–CIS–GC–ECD instrumentation that corrects for analytical losses observed in the TDS, CIS, and adjoining transfer lines was recently developed [18]. However, an analytical method using TDS–CIS–GC–ECD instrumentation and thermal desorption tubes has not been developed for quantitating cyclotrimethylenetrinitramine, a.k.a. RDX, vapors, which has a vapor pressure approximately three orders of magnitude lower than TNT at room temperature ($\sim 5.0 \times 10^{-12}$ Torr for RDX and $\sim 7.0 \times 10^{-9}$ Torr for TNT) [8]. Herein, the direct liquid deposition method of standard solutions onto sorbent-filled sample tubes was extended to the quantitation of the chemically challenging nitroenergetic compound, RDX. In addition, three inlet systems were compared: a standard split/splitless GC inlet with liquid samples, a CIS with liquid samples, and a TDS–CIS with thermal desorption tubes using the direct liquid deposition method. The ability to simultaneously quantitate both RDX and TNT vapor samples collected on sorbent-filled sample tubes was also investigated and offers a significant advancement for the sensor development community in validating vapor generation methods of explosives.

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2. Experimental

2.1. Apparatus

All samples were analyzed with an Agilent 7890A gas chromatograph equipped with a μ ECD (Agilent Technologies, Santa Clara, CA, USA). An Agilent 7693A Automatic Liquid Sampler was used in conjunction with a standard split/splitless GC inlet in the front inlet position. A SiltekTM-coated glass liner was incorporated (Part No. 20800-214, Restek Corp., Bellefonte, PA, USA) to reduce the surface affinity of explosive analytes for the glass and improve the quantitative capability for TNT as previously demonstrated [18] and potentially for RDX. The GC was fitted with a 15-m RTX-5MS column (Part No. 12620; Restek Corp.). A helium carrier column flow rate of 5.6 mL min⁻¹ was used for separation while an ultra-high purity nitrogen auxiliary flow rate of 60 mL min⁻¹ was supplied to the μ ECD operated at 275 °C.

A cooled inlet system, also known more generally as a programmable temperature vaporization (PTV) inlet, (Part No. CIS-4; GERSTEL GmbH & Co. KG, Mülheim an der Ruhr, Germany) was installed in the back inlet position of the GC. A septum-less head (SLH; GERSTEL GmbH & Co. KG) was incorporated for liquid injections onto the CIS in the absence of the TDS. A SiltekTM-coated glass liner was utilized with the CIS (Part No. 014652-005-00, GERSTEL GmbH & Co. KG) for improved quantitation [18]. The CIS was operated in two modes depending upon the injection: split with the SLH and solvent vent with the TDS. In split mode, the split ratio was varied from 1:10 to 1:100 with total flow rates varying from 60.5 to 556 mL min⁻¹ with a constant GC carrier column flow rate of 5.6 mL min⁻¹.

After completing the liquid injections with the CIS via the SLH, a thermal desorption system (TDS; Part No. TDS-3; Gerstel GmbH & Co. KG, Mülheim an der Ruhr, Germany) was coupled to the CIS via a heated (300 °C) deactivated stainless steel transfer line (0.74 mm OD). Commercially available thermal desorption sample tubes (Tenax[®] 60/80 sorbent material; Part No. 009947-000-00; Gerstel GmbH & Co. KG) were used in conjunction with the TDS.

2.2. Reagents

Analytical standards for 3,4-dinitrotoluene (DNT, CAS No. 610-39-9), 2,4,6-trinitrotoluene (TNT, CAS No. 118-96-7) and cyclotrimethylenetrinitramine (RDX, CAS No. 121-82-4) were purchased from AccuStandard, Inc. (New Haven, CT, USA). The internal standard used in this work was 3,4-DNT because of its previous utility in trace explosive vapor quantitation [18]. All solution standards were prepared in acetonitrile (CAS No. 75-05-8, Sigma-Aldrich, St. Louis, MO, USA).

2.3. Procedure

For liquid injections, a 1 μ L aliquot was injected from a 10 μ L syringe (back inlet: Part No. 002810, front inlet: Part No. 002821; SGE Analytical Science, Victoria, Australia) into either the front or back inlet operating in split mode at a constant inlet temperature of 250 °C. For TDS injections, a 5 μ L aliquot of internal standard and analyte mixture was applied to the glass frit at the head of the Tenax[®]-filled sample tube using a micropipette, and the solvent was allowed to evaporate for at least 15 min. The internal standard mixture consisted of 3,4-DNT at a constant concentration of 0.3 ng μ L⁻¹ with 1.5 ng deposited onto the sample tubes, and the concentration of RDX and TNT was appropriately varied for each analysis to establish a calibration curve over the dynamic range of the detector. After a suitable evaporation time, the sample tubes were inserted into the TDS at a constant temperature of 25 °C and the TDS-CIS-GC-ECD sequence was initiated.

To desorb analyte from a sample tube, the TDS was ramped from an initial temperature of 25–250 °C at 40 °C min⁻¹ with a final hold time of 2.0 min, and the helium flow rate through the TDS was varied from 50 to 550 mL min⁻¹. Throughout the TDS temperature profile, the CIS was held constant at 0 °C. During the first 2.0 min of the TDS temperature profile, the solvent vent state of the CIS was “on” in order to purge excess solvent from the system, and for the remainder of the TDS temperature profile, the solvent vent state was “off”. At the conclusion of the TDS temperature profile, the CIS temperature was ramped from 0 °C to 250 °C at 12 °C s⁻¹. The GC oven was held constant at 40 °C for 2.0 min and then ramped at 40 °C min⁻¹ to 210 °C, where the temperature was held constant for 1.0 min followed by a second ramp at 40 °C min⁻¹ to 250 °C where it was held constant for 1.0 min. A blank acetonitrile injection was carried out after each set of replicate injections; a negligible amount of carryover was observed. All sample tubes were analyzed within one day.

3. Results and discussion

The direct liquid deposition of solution standards onto sorbent-filled thermal desorption tubes was an effective method for establishing calibration curves for TNT quantitation [18]. Several critical parameters were identified for effective TNT quantitation: the internal standard, liner surface treatment, initial CIS temperature, and TDS flow rate. An internal standard of 3,4-DNT enabled normalization of the analyte peak area to account for variability in instrument response and help determine analytical losses, thus it was also used for RDX method development. A SiltekTM-coated glass liner in both the CIS and standard split/splitless GC inlet was found to be a critical element for effective quantitation of TNT and was used for RDX method development. Furthermore, an initial CIS temperature of 0 °C with a TDS flow rate greater than 200 mL min⁻¹ was required to minimize losses, and a flow rate dependent desorption mechanism was observed. Thus, the flow rate through the CIS and TDS-CIS was the initial focus for RDX method development.

3.1. Impact of CIS flow rate on RDX quantitation

Evidence of a flow rate dependent vaporization mechanism within the CIS for TNT suggested that the impact of CIS flow rate on RDX quantitation be explored independent of TNT and the TDS [18]. Fig. 1(A) shows the change in RDX and 3,4-DNT peak areas as a function of CIS flow rate for liquid injections at a 0 °C initial CIS temperature. The RDX and 3,4-DNT solution concentrations were adjusted based on the split ratio to theoretically yield an identical mass of 1.5 ng injected onto the GC column at each flow rate. Ideally, one would expect the RDX and 3,4-DNT peak areas to remain constant regardless of CIS flow rate; however, the peak areas decrease as the CIS flow rate increases. This trend is most likely due to incomplete cryo-focusing, or trapping, at elevated CIS flow rates. Differences in absolute peak area between RDX and 3,4-DNT at any particular flow rate are possibly linked to differences in detector sensitivity with the μ ECD. Fig. 1(B) shows the normalized peak area for RDX as a function of CIS flow rate, with 3,4-DNT as an internal standard. The normalized peak area appears relatively constant regardless of CIS flow rate, suggesting losses associated with incomplete cryo-focusing are analyte agnostic and normalization can account for variations in CIS flow rates.

3.2. Effect of TDS-CIS flow rate on RDX quantitation

The TDS was attached to the CIS in order to assess the impact of TDS-CIS flow rate upon RDX quantitation with thermal desorption sample tubes. Identical masses of RDX and 3,4-DNT, 1.5 ng, were deposited onto the glass frit of the Tenax[®]-filled sample tubes

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