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Analysis of ammonium nitrate headspace by On-Fiber solid phase microextraction derivatization with gas chromatography mass spectrometry

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ABSTRACT

A novel analytical method has been developed for the quantitation of trace levels of ammonia in the headspace of ammonium nitrate (AN) using derivatized solid phase microextraction (SPME) fibers with gas chromatography mass spectrometry (GC–MS). Ammonia is difficult to detect via direct injection into a GC–MS because of its low molecular weight and extreme polarity. To circumvent this issue, ammonia was derivatized directly onto a SPME fiber by the reaction of butyl chloroformate coated fibers with the ammonia to form butyl carbamate. A derivatized externally sampled internal standard (dESIS) method based upon the reactivity of diethylamine with unreacted butyl chloroformate on the SPME fiber to form butyl diethylcarbamate was established for the reproducible quantification of ammonia concentration. Both of these compounds are easily detectable and separable via GC–MS. The optimized method was then used to quantitate the vapor concentration of ammonia in the headspace of two commonly used improvised explosive device (IED) materials, ammonium nitrate fuel oil (ANFO) and ammonium nitrate aluminum powder (Ammonal), as well as identify the presence of additional fuel components within the headspace.

1. Introduction

Trace explosives vapor detection is a field of vital importance to homeland security, soldier protection, and various peacekeeping operations, worldwide. Numerous analytical trace explosives vapor detection methods have been developed for energetic compounds that include PETN [1], TNT [2,3], RDX [4], and TATP [5], each method incorporating a preconcentration step followed by thermal desorption to a multichannel detector such as a gas chromatography–mass spectrometer (GC–MS). The detection of ammonium nitrate (AN) based improvised explosive devices (IEDs), on the other hand, has been challenging due to the low vapor pressure of AN [6–11], as well as the relatively high background levels of ammonia present in the environment. AN is a salt which has been shown to decompose at room temperature into gaseous ammonia and nitric acid [6,10]. Detection of trace levels of ammonia using conventional GC–MS is problematic due to ammonia's low molecular weight, which pushes the low mass limits of common MS, and because of its extreme polarity, which is incompatible with common, low polarity GC phases. As a result of these shortcomings, AN is typically analyzed by ion chromatography (IC) or capillary electrophoresis (CE), instrumental approaches requiring vapor samples to be transferred into an aqueous phase prior to analysis and the subsequent loss of time and sensitivity [6]. Although chemical sensors continue to be actively pursued for the detection of ammonia at trace levels, e.g., carbon nanotubes, the univeral drawback limiting their applicability in explosives detection is the lack of selectivity when compared to GC–MS, for example [12–14].

A promising method for the detection of ammonia from AN dissolved in an aqueous basified solution or from the headspace of a basified solution of AN was first introduced by Brown et al. [11], using a derivatized solid phase microextraction (SPME) fiber. This sensitive and selective approach is based upon an akylchloroformate derivatized SPME fiber that directly converts sampled ammonia in vapor or dissolved in solution into a high molecular weight product, thereby enhancing the separation and detectability of ammonia when coupled to GC–MS (Fig. 1A) [11]. The benefits of this method are faster, more portable sampling when compared

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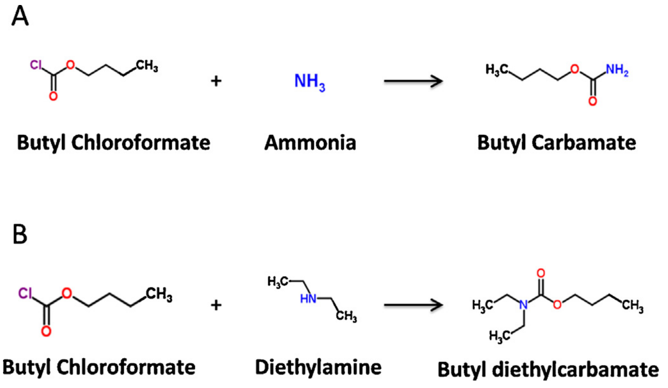

Fig. 1. Butyl chloroformate reacts with (A) ammonia to produce butyl carbamate, and (B) diethylamine to produce butyl diethylcarbamate (internal standard).

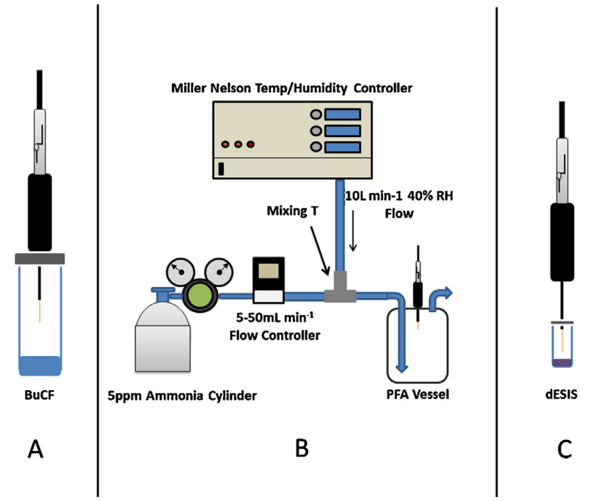

Fig. 2. (A) Polyacrylate fiber is exposed to butyl chloroformate; (B) calibration experimental setup; (C) sample exposure to dESIS.

to alternative techniques, rapid analysis, high sensitivity, and more importantly, the added capability of simultaneously detecting the presence of fuel along with the ammonia within a headspace, e.g., ammonium nitrate fuel oil (ANFO).

This manuscript will detail advancement of the butyl chloroformate (BuCF) derivatized SPME approach with two primary goals in mind: (1) demonstration of headspace vapor phase sampling of dry, solution free AN based samples, and (2) improvement of run-to-run reproducibility, a factor limiting quantitative capability of this technique. Previous work by Brown et al. [11] was restricted to SPME sampling of either AN in a basified aqueous solution or the headspace of a basified solution of AN. We establish the viability of utilizing BuCF derivatized SPME with headspace analysis of dry AN and IED mixtures of AN with fuels such as fuel oil and aluminum powder. Although the BuCF derivatized SPME approach was shown to have many attractive benefits with regards to the sensitive and selective detection of trace levels of ammonia arising from AN, one of the biggest drawbacks, and a problem that affects most SPME-based techniques, is the lack of reproducibility stemming from fiber-to-fiber inconsistencies and fiber degradation while in use. Despite the well-recognized advantages of utilizing the internal standard method for overcoming reproducibility issues, there have only been a few examples applied to SPME methods. MacCrehan et al. used an externally sampled internal standard (ESIS) method in order to account for fiber differences in underivatized bare fibers while evaluating vapor time profiles by SPME [15,16]. The ESIS method relies upon exposure of the fiber to analyte for a short enough period of time that the fiber does not become saturated with analyte; the fiber is then exposed to an internal standard and analyzed via GC–MS. We discuss here a new internal standard method, derivatized externally sampled internal sample (dESIS), that is applicable to derivatized SPME fibers such as the BuCF derivatized SPME approach for ammonia detection (Fig. 1B). By implementing a derivatized externally sampled internal standard (dESIS), run-to-run reproducibility, which is inclusive of fiber-to-fiber reproducibility, was greatly increased. With this enhanced reproducibility, we demonstrate the quantitation of ammonia from two commonly used improvised explosive device (IED) materials, ammonium nitrate fuel oil (ANFO) and ammonium nitrate aluminum powder (Ammonal).

2. Materials and methods

2.1. Calibration apparatus

Ammonia trace analysis was performed by first derivatizing an 85 µm partially cross-linked polyacrylate (PA) SPME fiber (57304; Sigma-Aldrich; St. Louis, MO) with butyl chloroformate (BuCF, Sigma Aldrich). A manual SPME fiber holder (57330-U; Sigma-Aldrich) was used to expose the fiber to the headspace over 2 mL of BuCF in a 20 mL headspace vial for 1 min. Ammonia calibration samples were generated using a flowing gas ammonia standard (5 ppm in air, Matheson Tri-Gas, Waverly, TN) controlled via a 5–50 mL min^{-1} mass flow controller (Smart Track 2, Sierra Instruments, Monterey, CA) and diluted with a humidified air control system (10 L min^{-1}, HCS 501; Assay Technology, Boardman, OH) for delivery to a sealed PFA sample chamber (102-0475-01; Savillex, Eden Prairie, MN). The sealed vessel was modified to accept SPME fibers by using a $^{1}/_{16}$” NPT to ¼” Swagelok compression fitting utilizing a standard Agilent GC septa (Fig. 2B).

2.2. SPME protocol

The SPME fibers were conditioned to manufacturer's specifications and run several times before use. Next they were inserted through the septa and exposed to the headspace vapor for 5 min; different sample times were considered, but 5 min provided the best overall efficiency. Calibration points were run in triplicate at 0, 5, 12.5, 25 ppb ammonia at 40% RH. Humidity data was obtained at a set concentration of 12.5 ppb ammonia. A specific fragment ion for butyl carbamate, *m/z* 62, was monitored via the MS in order to integrate and quantitate the SPME exposure to ammonia. This peak was first identified from a total ion chromatogram (TIC) collected from a BuCF saturated polyacrylate (PA) SPME fiber following exposure to a sealed container containing AN.

2.3. Headspace generation

For headspace sample collection above the AN fuel mixtures, approximately 2 g mixtures were prepared in an open 22 mL PFA sample vial (200-022-12; Savillex). The PFA vial containing the mixture was placed inside another 240 mL PFA jar (100-0240-01; Savillex); a 70 mm lid with two ¼” outer diameter tube ports was used to seal the jar (600-070-28; Savillex). One port was capped while the other was fitted with a septa. The jars were allowed to sit for at least 24 h to ensure an equilibrated headspace. The SPME fiber was inserted through the septa and exposed to the headspace for 5 min. Three data points were collected for each mixture. Different volumes between 240 mL and 1000 mL were tested with solid AN and no significant differences were noted.

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