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Profiling of volatile impurities in tetramethylenedisulfotetramine (TETS) for synthetic-route determination

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ABSTRACT

This study investigated the feasibility of using volatile impurities from the rodenticide tetramethylenedisulfotetramine (TETS) for the discrimination of TETS produced by three synthetic routes. Each route was used to make one batch of TETS by reacting sulfamide with one of three formaldehyde analogs in the presence of either trifluoroacetic acid (TFA) or hydrochloric acid. Ten impurities useful for differentiating the three TETS batches were discovered and tentatively identified by headspace solid-phase microextraction comprehensive two-dimensional gas chromatography–mass spectrometry (HS-SPME/GC × CG–MS). Of the ten identified impurities, the alkyl trifluoroacetate and alkyl chloride impurities distinguished TETS routes based on their use of either TFA or HCl as catalyst. On the other hand, four 6-carbon ketone impurities appeared to be batch specific rather than route specific and hence potentially useful for sample matching. Interestingly, 1,3,5-trioxane was not found in the TETS batch where it was used as a reactant, but instead was found in the two batches that did not have 1,3,5-trioxane as the reactant. In brief, the limited work discussed in this paper supports: (1) the feasibility of sampling and detecting volatile organic impurities from a solid chemical-threat agent, (2) the probable forensic benefit of catalysts acting as reactants in side reactions, (3) the uniqueness of a synthetic batch's impurity profile for potential sample matching, and (4) the possibility that some impurities, such as formaldehyde analogs, are not forensically helpful and may lead to an incorrect estimate about the synthetic route if not supported by sound chemical knowledge.

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1. Introduction

Tetramethylenedisulfotetramine, also known as tetramine or TETS, is a highly toxic, odorless, tasteless, water–soluble, solid rodenticide [1–3]. A dose of 7–10 mg of TETS is considered lethal to humans [1,4]. Even though it has been banned worldwide, over a thousand TETS poisonings have occurred in recent years primarily in China [1,4–7]. In most cases, exposure to TETS was through the ingestion of intentionally contaminated foods. Given this obvious public threat, researchers have developed methods for its analysis in biological and food matrices [8–14]. These methods have focused on the detection of TETS at trace levels. This manuscript is the first to investigate the potential of obtaining forensic information from the impurity profiling of TETS. The main goal of this paper was to determine if impurities in TETS could provide information specific to the routes used for synthesizing it. Given the relatively high to moderate volatilities of most reagents used in making TETS, it was decided to investigate the volatile impurities in TETS by headspace (HS) sampling with solid-phase microextraction (SPME).

SPME is a sample preparation technique initially developed in the 1990s and typically coupled with gas chromatography–mass spectrometry (GC–MS) for the analysis of volatile to semi-volatile compounds [15]. SPME is well suited for the sampling of complex mixtures because it typically permits the direct extraction and concentration of target compounds from the original matrix in a single step. Recently, SPME-GC–MS has been used for the determination of TETS in the headspace of several spiked food samples with a limit of detection from 0.9 to 4.3 ng TETS/g food matrix [8,13]. Herein, HS-SPME was also applied on TETS except the focus was on the impurities found in TETS rather than on TETS itself. The fact that SPME is a solventless extraction technique was an important consideration for selecting it because potential chemical interference between reactant or solvent signatures with chemical background was presumably reduced by the lack of solvent handling. In this paper, the use of comprehensive two-dimensional gas chromatography–mass spectrometry (GC × GC–MS) also reduced the likelihood of forensic impurities interfering with one another or with the chemical background because of the larger chromatographic separation space provided by GC × GC. This increased the likelihood of obtaining fully resolved mass

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spectra for greater confidence in chemical identification by mass spectrometry.

In this feasibility study, three batches of TETS produced by three published synthetic routes were sampled and analyzed in duplicate by HS-SPME/GC × GC–MS for synthetic route determination. The impurity profiling work described here has precedence in previous forensic research on other chemical-threat agents and precursors [16–18]. In those studies, the feasibility of obtaining forensic information from impurity profiling for sample matching and possible route and source determination were demonstrated. Here the effort continued by providing a better understanding of the possible role of impurity profiling in forensic investigations following chemical attacks. Specifically, this study investigated impurity profiling for route determination using TETS made from three synthetic routes as opposed to previous work on a chemical-threat simulant made from a single route [18].

2. Experimental

2.1. TETS synthesis

Three stocks of crude TETS (>90% purity) were provided by researchers at Lawrence Livermore National Laboratory, Livermore, CA. Each TETS stock originated from separate batches produced by different published synthetic routes. In this paper, the three TETS routes or stocks are called TETS 1, TETS 2, and TETS 3. Their reaction schemes are shown in Fig. 1 while their synthetic steps are described below.

2.2. TETS 1

The procedure for the synthesis of TETS was a modified version of Kang's published protocol [19]. Sulfamide (2.4 g, 25 mmol) and paraformaldehyde (1.5 g, 50 mmol) were dissolved in 12.5 mL trifluoroacetic acid (18.5 g, 162 mmol) at room temperature. The reaction was stirred at room temperature and then heated overnight. The resulting mixture was filtered, washed with hexane, and air dried to provide crude TETS.

2.3. TETS 2

The procedure for the synthesis of TETS was a modified version of Hecht and Henecka method [20] as well as a 40 times scale down of the protocol described in Kang's manuscript [19]. Sulfamide (1.2 g, 12.5 mmol) was dissolved in 12.5 mL of concentrated hydrochloric acid (conc. HCl, 37% HCl, 0.13 mol) at room temperature and then mixed with 2.03 mL of 37% formaldehyde/water solution (37% formaldehyde, 25 mmol). The reaction mixture was stirred and another 2.03 mL of 37% formaldehyde solution was added followed by 2 h of stirring and then filtration. The solid was washed with hexane and air dried overnight to provide crude TETS.

2.3.1. TETS 3

The procedure for the synthesis of TETS was from Esser's published protocols [21]. 1,3,5-trioxane (0.72 g, 8.0 mmol) and sulfamide (1.16 g, 12.0 mmol) were dissolved in 30 mL of trifluoroacetic acid (0.39 mol) at 0 °C. The reaction mixture was stirred at 0 °C for 3 h and then at room temperature overnight. The next morning, a white solid was observed in the reaction flask. The reaction mixture was cooled in an ice bath and stirred. The reaction mixture was filtered and the resulting solid was washed with hexane and vacuum-dried to provide crude TETS.

2.4. Sample preparation

Two portions of approximately 15–22 mg of TETS were taken from each TETS stock and placed into separate 10 ml borosilicate–glass headspace vials. Each vial was capped with a septum screw-on cap. Table 1 lists the name and the amount of TETS for each sample. Each duplicate sample was distinguished by a decimal one or decimal two following the name of its TETS stock; for example, TETS 1.1 and TETS 1.2 were duplicates taken from the TETS 1 stock. Also included were two method blanks (BLK 1 and BLK 2) that were capped vials consisting of the lab air present during TETS handling.

2.5. HS-SPME/GC × GC–MS analysis

The SPME fiber used in this study was 2 cm in length and composed of three phases (30 μm carboxen, 50 μm divinylbenzene, polydimethyl siloxane, Supleco Corp., Bellefonte, PA). The SPME procedure involved sampling the headspace of a capped 10 mL vial for 68 min at 40 °C. The fiber was then introduced into a LECO Pegasus 4D GC × GC–MS (LECO corp., ST. Joseph, MI, USA) and desorbed at 250 °C for a total of 3 min. The TETS samples and two method blanks were each analyzed once in random order and with instrumental blanks between analyses to address any sample carryover.

The LECO GC × GC–MS instrument was equipped with a heated injection port connected to a first column of 30 m length, 250 μm inner diameter, SolGel-Wax (SGE-Phenomenex) with 0.25 μm film thickness, and a second column of 2 m length, 100 μm inner diameter, Quadrex 1701 stationary phase with 0.4 μm film thickness. Ultra high purity helium was utilized at a constant flow of 1.0 mL/min. Temperature programming for the oven housing the first column began at 35 °C, which was held for 10.00 min, then ramped to 250 °C at 5 °C/min and held at this final temperature for 5.00 min. Temperature programming for the second column oven began at 45 °C, which was held for 10.00 min, then ramped to 260 °C at 5 °C/min and held at this final temperature for 5.00 min. A temperature offset of +25 °C relative to the first column oven temperature was selected for the modulator block with modulation period of 5 s. The transfer line to the mass spectrometer was set to 250 °C while the ion source temperature of the mass spectrometer was set to 200 °C and the electron energy set to −70 eV. The mass spectrometer was set to collect signal starting 1 min and ending 58 min after sample introduction from ions having *m*/*z* 35–300 at 100 spectra/s using a detector voltage of 1650 V.

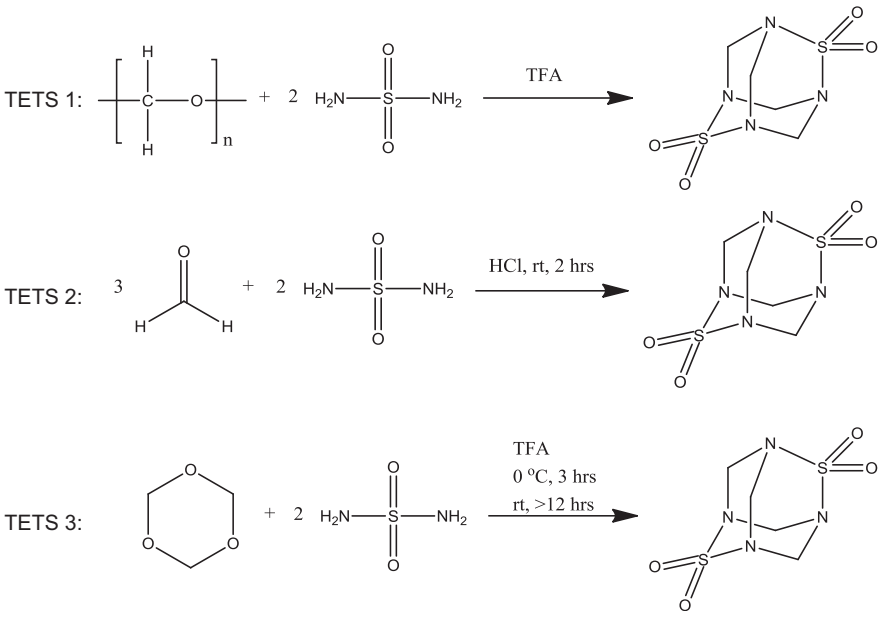

Fig. 1. Reaction schemes for TETS.

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