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Surface detection of chemical warfare agent simulants and degradation products

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Abstract

Chemical warfare agent (CWA) simulants as well as their degradation and hydrolysis products were detected from surfaces using thermal desorption ion mobility spectrometry (TD-IMS). CWA simulant materials that closely mimic the chemical structures of real CWA G/V-type nerve and S-type vesicant simulants were used in this study. Reduced mobility constants (K_0) in air were reported for 20 compounds studied. Spectra for sample materials as low as 1 ng deposited on a paper filter were produced for most of the compounds. Detection limits as low as 15 pg of sample material with a sensitivity of 3.2×10^2 ampere per gram ($A\,g^{-1}$) were reported. TD-IMS, which is normally used for the detection of explosives and drugs of abuse, demonstrated the capability of separating and detecting mixtures of CWA simulants, degradation and hydrolysis products from surface samples. TD-IMS demonstrated clear advantages of speed, high throughput and versatility over chromatographic methods of analysis for detecting CWA simulants, degradation and hydrolysis products. Successful development of the technique may lead to a practical and simple sensor for CWA and related compounds that could be installed and used at sensitive locations around the USA and throughout the world.
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1. Introduction

Throughout history, the periodic use of chemical weapons for war and terror has created a need for the development of rapid detection and sensitive analytical methods and instrumentation. The use of nerve agents in 1988 that killed thousands in Kurdish villages and the 1991 gulf war further emphasized the threat of chemical warfare. The events in the United States in 2001, of course, again focused the world's attention on the specter of terrorist attack. The chemical weapons convention, [1] enforced in April 1997, bans the development, production, stockpiling and use of chemical weapons by member nations and produced a requirement for rapid detection schemes for nerve agents and their degradation and hydrolysis products. On-site verification procedures to monitor suspected production and storage facilities require methods for detecting and identifying chemical weapons, their degradation and hydrolysis products which are rapid, portable, selective and sensitive. Monitoring surfaces for trace quantities of deposited agents and/or their degradation products would provide a relative simple method for the determination of the presence or past presence of chemical warfare agents.

CW agents are commonly classified as nerve, vesicant or blood born agents. Nerve agents – Sarin (GB), Soman (GD), Tabun (GA), and VX – disrupt neurological regulation within biological systems through the inhibition of organophosphorous cholinesterase [2,3]. Vesicant agents – sulfur mustard gas (H, HD, HT), lewisite (L), nitrogen mustard gas (HN-1, HN-2, HN-3), and phosgene-oxime (CX) – are typically responsible for blistering action, damaging eyes, mucus membranes and the respiratory tract [4]. Blood born agents – hydrogen cyanide (AC), or cyanogen chloride (CK) – prevent tissue utilization of oxygen by inhibition of cytochrome oxidase [5,6].

All of these compounds hydrolyze to form stable degradation products [7–9]. The degradation pathway for G-type nerve agents is a quick hydrolysis to form alkyl phosphonic acid and esters [10]. V/VX type nerve agents degrade to form alkyl phosphonothioic acids, and various alkyl amino ethanol compounds

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[11]. The degradation products of sulfur mustard are thiodiglycol, thiodiglycol sulfone, thiodiglycol sulfoxide, thiodiglycol disulfide, 1,4-dithiane and 1,4-thioxane [12]. Finally, blood born agents such as AC initially hydrolyze to formamide, and subsequently to ammonium formate; while CK readily hydrolyzes to hydrogen chloride and unstable cyanic acid. The cyanic acid further decomposes to carbon dioxide and ammonia [13].

A widely established method for detecting these compounds has been derivatization followed by chromatography. Derivatization has been used to form fluorescing chromophores [14] for detection after liquid chromatographic separation or derivatization to make these compounds sufficiently volatile for analysis by gas chromatography–mass spectrometry (GC-MS) [15]. Both methods require extensive sample preparation and are generally expensive and time consuming. In recent years a number of rapid separation and sensitive detection systems have become available. Capillary zone electrophoresis (CZE) combined with indirect UV detection at 210 nm has been demonstrated to be another means to separate and detect hydrolysis products of nerve agents as well as hydrolytic or oxidative and degradation products of HD. Because of its relative ease of analysis its utility in the field and on-site analysis is feasible [16]. Liquid chromatography–electrospray ionisation–MS (LC-ESI-MS) was utilized as a rapid screening method for the hydrolysis products of nerve agents in aqueous samples and extracts [17]. In this same report the application of LC-ESI/APCI-MS and LC-ESI/APCI-MS-MS to the identification of dialkyl esters of phosphonic acids was described. High-resolution atmospheric pressure ESI-IMS-MS has also been used for the analysis of chemical warfare degradation products in which quantitative studies were reported [18].

Ion mobility spectrometry (IMS) is a rapidly advancing technique that has wide applications for explosives, narcotics and CWAs. While attempts to place some analytical methods into field venues have been frustrated by weight-power requirements, IMS instruments have been developed which are portable and hand-held analyzers [19,20]. Changes in the gas composition in the IMS can be used to enhance sensitivity and selectivity in the IMS response. For example, gas phase chloride ions from a suitable dopant increase sensitivity of IMS towards vapors of explosives. Doping the ion source of the IMS with acetone improves its selectivity towards organo-phosphorous compounds, including nerve agents as used in chemical agent monitors [21–23].

Detection of CWA with IMS has, for the most part, been limited to gas phase samples using a ^{63}Ni or corona ionization source. For verification of the past presence of CWA it is necessary to detect these compounds or their degradation products on the surfaces on which they have settled or condensed. ESI has been used for the detection of CWAs in water, but the ability of IMS to separate and detect CWAs and their degradation products deposited on surfaces has not been investigated. In this paper we described a novel use of IMS for the detection of chemical warfare agent simulants and degradation products from surfaces.

2. Experimental

2.1. Materials and reagents

Because of the high toxicity of CWAs, less toxic structural analogs that directly mimic or imitate the actual CWAs were utilized to evaluate instrumental response. A total of 20 compounds comprising of five CWA simulants, two CWA degradation products and 13 CWA hydrolysis products were studied. Five of the 20 compounds studied (dimethyl methyl phosphonate, DMMP; pinacolyl methylphosphonate, PMP; diethyl phosphoramidate, DEPA; 2-chloroethyl ethyl sulfide, 2-CEES; and 2-(butylamino) ethanethiol, 2-BAET) were chosen to mimic or imitate the actual CWAs. DMMP was chosen as a simulant for the presence of a P=O, P-CH_3 and P-OCH_3 functional groups that are found in both GB and GD. PMP was chosen as a simulant because its structure are identical to that of GD, except that the fluorine atom in GD is substituted by an OH group. DEPA was chosen as a simulant because it contains a P=O, P-NH_2 and P-OCH_2CH_3 functional groups which is found in GA. Similarly, 2-BAET was selected as a simulant because it possesses both C–S and C–N bonds found in the functional groups of VX which are attached to the phosphorus atom. One of these simulants, 2-CEES, was used as a structurally identical simulant for HD with the exception of a missing chloride atom. Thus, the CWA simulants used in this study were the following: 97% DMMP, 97% PMP, 98% DEPA, 97% 2-BAET, and 98% 2-CEES were obtained from Sigma Aldrich Chemical Company (St. Louis, MO). CWA hydrolysis and degradation products – 1,4-dithiane (1,4-DT), 1,4-thioxane (1,4-TO), thiodiglycol sulfoxide (TDS), ethyl methyl phosphonic acid (EMPA), cyclohexyl methyl phosphonic acid (CHMPA), and diisopropyl methyl phosphonate (DIMP) were obtained as 1 mg ml^{-1} certified reference materials (CRM) from Cerilliant (Auston, TX). Alkyl amines – cyclopentylamine (CPA), cyclohexylamine (CHA), cycloheptylamine (CHPA), cyclooctylamine (COA), dipropylamine (DPA), tripropylamine (TPA), *n*-butylamine (NBA) dihexylamine (DHA) and decylamine (DA) were obtained from Sigma Aldrich Chemical Company (St. Louis, MO), purity $\geq$ 99%.

Standards were prepared using a micropipette (Brinkmann, Westbury, NY). A known amount of the analyte was pipetted into 30 ml polypropylene nalgene vials (Fisher Scientific, Tustin, CA). The resulting transfer was diluted with methanol (J.T. Baker, Phillipsburg, NJ) to 10 ml total volume. This was followed by serial dilutions where necessary. The stock solutions were stored in the refrigerator at 4 °C when not in use. In Table 1, the structures and CAS numbers for all compounds are shown.

Sample introduction into the instrument was achieved by pipetting a 1 μl aliquot of sample onto a paper disk, 50 μm thick × 90 mm wide (GE Ion Track, Wilmington, MA) or a gold seal® micro glass slide (VWR, Brisbane, CA). Concentrations of the liquid test standards were the following: DMMP (0.12 mg cm^{-3}), PMP (0.10 mg cm^{-3}), DEPA (0.09 mg cm^{-3}), 2-CEES (0.11 mg cm^{-3}), 2-BAET (0.09 mg cm^{-3}), 1,4-DT (1 mg cm^{-3}), TDS (1 mg cm^{-3}), EMPA (1 mg cm^{-3}), CHMPA

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