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On-line monitoring system for chemical warfare agents using automated capillary micellar electrokinetic chromatography

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ABSTRACT

We present an automated analysis system for the detection of the chemical warfare blister agents, sulfur mustard (HD) and lewisite (L), in aqueous samples without any chemical derivatization. The system is compact in size and designed to operate in the field in a safe, autonomous manner for near real-time monitoring applications. It uses anionic surfactant-based capillary micellar electrokinetic chromatography (MEKC) to separate the sample followed by UV detection. The analysis time is sufficiently fast to allow direct detection of HD which enabled the estimation of effective hydrolysis rates in the aqueous sample matrix. The estimated hydrolysis half-life of HD in our system was 4.85 ± 0.05 min. The detection limit of HD was determined to be 10 ppm with a signal to noise ratio of 5. By contrast, L hydrolyzed too rapidly in aqueous samples to enable direct detection. Instead the first hydrolysis product 2-chlorovinyl arsonous acid (CVAA), also considered a blister agent, was detected with a detection limit of 0.7 ppm with a signal to noise ratio of 5.

1. Introduction

Although much of the world's stockpiles of chemical warfare agents (CWA) have been destroyed in compliance with the Organization for the Prohibition of Chemical Weapons (OPCW) treaty, which entered into force in 1997, the United States and many other countries continue to deal with problems associated with legacy and discarded World War I and II era chemical warfare munitions at land and ocean dump sites throughout the world [1,2]. There continues to be a great need for analysis methods of CWA to help locate and monitor these sites and to determine the dispersion and effects of the agents. There is also a need for more rapid analysis of CWA to help minimize the time and cost to remediate munitions and dump sites.

One such remediation approach is the Explosive Destructive System (EDS) developed by Sandia National Laboratories for the U.S. Army Non-Stockpile Chemical Materiel Project to provide on-site treatment of chemical warfare materiel in a safe, environmentally sound manner [3]. The EDS uses cutting charges to explosively open chemical munitions, eliminating their explosive capacity prior to chemical agent neutralization. The main component of the EDS is a sealed, stainless steel vessel, which contains all the blast, fragments and any vapor resulting from the process. The treatment level is confirmed by sampling residual liquid from the vessel prior to reopening the EDS vessel. An on-line near real-time monitoring system for the EDS will enable better definition of how soon this sampling can begin.

CWA present unique challenges to the development of monitoring and analysis methods. Treaty obligations and security precautions make the acquisition of agents necessarily impossible for all but a select authorized few. As a result, analytical methods are frequently developed using simulants and degradation products but not validated using the real agents. In addition, aspects of treaty compliance as well as variations in legislation from state to state, makes transport of agents to centralized laboratories problematic. Consequently there is a very great need for on-site testing capabilities [4,5].

Moreover, the agents themselves often present analytical challenges. The high toxicity requires that safety precautions be employed for handling and disposing of agent. CWA are most often assayed using gas chromatography (volatile compounds) or liquid chromatography, often in combinations with various mass spectrometry techniques [6–8]. CWA, in particular the blister agents such as distilled sulfur mustard (bis-(2-chloroethyl)sulfide, HD, $C_4H_8Cl_2S$, CAS No. 505-60-2), are a challenge to detect and quantify, particularly in aqueous samples because of rapid hydrolysis. The reported hydrolytic half-life of HD at 25 °C in distilled water ranges

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from 4 to 9 min [9,10]. Fast optical based detection methods are limited because of the lack of good chromophores or reactive moieties [11]. Various derivatization techniques have been reported but can add additional preparation time, ultimately leading to poor sensitivity and or reproducibility [12,13].

Methods that employ solid phase extraction or solid phase microextraction [14–17] prior to gas chromatography or mass spectrometry have been shown to be highly successful in laboratory settings; these may lead to an extra level of complexity for on-site field testing scenarios or prototype hardware. Furthermore, for agents that hydrolyze rapidly, there will be a trade-off between the concentration benefits of solid phase extraction and the material lost through hydrolysis resulting from the additional processing time [4]. The most practical method for on-site monitoring of CWA would be a rapid analysis method that can detect agent directly in aqueous samples without the need for chemical derivatization.

In this work we present a stand-alone analysis platform designed for the EDS or other comparable remediation technologies. Given that the on-line monitoring system will need to be mounted on the EDS during treatment of the CWA materiel, this requires that the technology must be relatively compact, automated, and the system should not require large quantities of consumable reagents. Capillary electrophoresis based approaches would appear to be ideal candidate technologies as they are miniaturizable and do not use large amounts of reagents. The compact platform presented here automatically loads and separates samples by capillary-based micellar electrokinetic chromatography (MEKC) and detects the agent directly without any derivatization via an on-column UV absorbance detector. Cheicante et al. reported on a MEKC method for separation of hydrolysis products including the primary hydrolysis product of HD, thiodiglycol (TDG, $C_4H_{10}O_2S$, CAS No. 111-48-8) [5] and MEKC is appropriate for analysis of HD as well. Because it relies on the hydrophobicity of the analytes partitioning into and out of the negatively charged micelles, it is inherently suitable for both neutral and charged analytes [18,19]. Neutral compounds that would otherwise not resolve in traditional zone electrophoresis are resolved in MEKC; charged compounds which do not partition into the negatively charged micelles will separate via the combination of their charge characteristics and electroosmotic flow (EOF). As a result the method is versatile and suitable for more than one agent class. Specifically in this paper, we present our results on the performance of our system for HD and L agent analysis and demonstrate the monitoring utility of our platform by determining the hydrolysis rate for HD. This prototype technology represents the first step toward an EDS-mountable device for monitoring destruction of sulfur mustard and other CWA during chemical decontamination processes.

2. Materials and methods

2.1. Materials

Caution: The handling of CWA should only be conducted in properly certified facilities with personnel trained and certified for surety operations.

Isopropyl alcohol, sodium borate and sodium dodecyl sulfate (SDS) were from Sigma–Aldrich Chemical Co. (St. Louis, MO). Sodium chloride, thiodiglycol (TDG) and 1,4-dithiane were from Sigma Chemical Co. (St. Louis, MO). Sulfur mustard (HD) and lewisite (L) were diluted from 10 000 ppm stock solutions in isopropyl alcohol to minimize hydrolysis prior to use. Standards of 2-chlorovinyl arsonous acid (CVAA, $C_2H_4O_2AsCl$, CAS No. 85090-33-1)) and 2-chlorovinylarsonic acid (CVAOA, $C_2H_4O_3AsCl$, CAS No. 64038-44-4) were diluted from stocks in distilled water adjusted to pH 5 with HCl. All tests with CWA were carried out at Edgewood Chemical and Biological Center (Edgewood Area Aberdeen Proving Ground, MD) using approved protocols. All reagents were used without further purification.

2.2. Automated system

The system is a relatively compact (~16 in. × 14 in. × 9 in.) one-man portable capillary electrophoresis system capable of drawing in a sample, injection of the sample onto the capillary, followed by absorbance detection by a commercial, miniature UV detector. The platform is designed to fit in a sealed case and incorporates a combination of commercial off the shelf components (COTS) as well as in-house designed custom components (SNL). Fig. 1 illustrates the system schematic which comprises two key functions: fluid handling and integrated electrophoresis with UV detection.

The fluid handling is composed of PSD4 syringe pumps to aspirate the sample (Hamilton; Reno, NV) and a two-position 10-port VICI switching valve (Valco; Houston, TX) to backflush the sample line. Aspirated sample is delivered through low-dead volume fluids fittings and tubing (Upchurch; Murrieta, CA) to load the 10-nL internal loop of a 4-port VICI injection valve (Valco; Houston, TX) in line with the electrophoresis unit. The separation capillary was mounted in the detector head and was connected to the injection valve at one end and placed in the buffer reservoir at the cathode. The electrical path was completed by a section of capillary extending from the injection valve to the second buffer reservoir (anode). Two additional Sandia designed valves were used to pressurize the electrophoresis buffer reservoirs to approximately 70 psi to minimize bubble formation. The valves could be independently vented to atmospheric pressure to enable rapid forward or backward flushing of the capillary in preparation for the next separation run.

Large electrode reservoirs (~5 mL) were used to minimize the effects of buffer depletion. Buffer depletion is a consequence of extended electrophoresis which over time can result in changes in pH and buffer composition in the anode and cathode reservoirs [20]. In an automated system such as this which may be exposed to hazardous agents, it was desirable to maximize the amount of time before maintenance was required. As configured, the system could be operated for at least 50 samples before the running buffer reservoirs needed to be refreshed to compensate for buffer ion depletion.

The integration of the injection loop in-line with capillary appears to be a unique design in the field of capillary MEKC. Its key advantage is that it allows a defined and reproducible sample volume to be injected into a running MEKC separation while streamlining the sample introduction and automating the fluidics. Because this necessitated that the sample loop be in the electrical path during electrophoresis, this required electrical isolation of the valve actuator from the sample injection valve. This was achieved by having a custom fabricated all PEEK design (rotor, stator and "stand-off") as well as locating the high voltage power supply at the detector end (negative voltage), allowing the injection end of the separation to be close to electrical ground. The second challenge associated with this design was the additional surfaces and interfaces associated with the fluid transport through the injection valve. The resultant bubble generation was essentially eliminated through an external pressure applied to the electrophoresis reservoirs (compressed air), much the way it is done in analyses involving capillary electrochromatography [21].

Electrophoresis was performed in positive polarity (inlet at anode and outlet at cathode) using −11 kV; currents were