REAL-TIME DETECTION OF SULFUR MUSTARD AND LEWISITE IN AIR THROUGH LONG TUBING USING ATMOSPHERIC PRESSURE CHEMICAL IONIZATION ION TRAP MASS SPECTROMETRY

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Abstract

An atmospheric pressure chemical ionization ion trap mass spectrometer (APCI-ITMS) was used for the real-time detection of low levels of blister agents, sulfur mustard (HD) and lewisite (L), in air through long tubing. HD was found to generate a mass spectral peak more intense than that of the protonated HD molecule at the normal humidity level in our laboratory. The peak was utilized as the detection marker for HD. L was found to generate several mass spectral peaks that were more intense than that of the molecular-related negative ion at the same humidity level. One of the peaks was utilized as the detection marker for L. Single or double-stage tandem mass spectrometry (MS/MS or MS/MS/MS) was used for the detection of HD or L to increase specificity and resultantly, the signal-to-noise ratio. The three-sigma detection limit through a 35-m heated Teflon tube (120°C) was about 1 $\mu g/m^3$, or the sub-part per billion level for both agents at sampling intervals of 1.2 seconds.

Introduction

Real-time monitoring of low levels of chemical warfare agents (CWAs) in air is needed for security against terrorism or leakage from chemical weapons abandoned or buried by former military forces. Sulfur mustard (HD) and lewisite (L) are blister agents widely used for chemical weapons. Gas chromatography has been used to detect low levels of these agents in air[1]. However, it usually takes several minutes or more for one measurement, and furthermore, a derivatization process[2] is usually necessary to efficiently detect L, which is labile and easily decomposes in heated tubing.

We have been developing a direct air-sampling real-time detection system utilizing atmospheric pressure chemical ionization (APCI) with a counter-flow configuration for sensitive and specific ionization[3] and an ion trap mass spectrometer (ITMS) for specific detection based on multi-stage tandem mass spectrometry (MS^n) and have applied it for detection of explosives[3,4], dioxin precursors[5], PCBs[6], narcotics, and CWAs.

With this system, we found that HD gives a mass spectral peak that is more intense than that of the protonated HD molecule in the positive ion mode at the normal humidity level of our laboratory. This peak was utilized as a detection marker for HD. We also found that L gives several mass spectral peaks that are more intense than that of the molecular-related ion in the negative ion mode at the above-mentioned humidity. One of these peaks was utilized as a detection marker for L. Using these markers, detection limits of the system for HD and L were evaluated as being at the sub-$\mu g/m^3$ or sub-ppb level when no extra tubing was connected to the system.

Because the system is too heavy to be carried, long tubing may often be utilized for drawing air into the inlet of the system. Here, we evaluate the detection limits for HD and L when using a long tube. The three-sigma detection limit was at the sub-$\mu g/m^3$ or sub-ppb level when a 35-m Teflon tube was used.

Experimental

HD or L was dissolved in n-hexane, injected into a heated container to be vaporized, and drawn into the inlet of an APCI-ITMS (Hitachi, DS-1000C) through a 35-m Teflon tube. The container was Teflon-coated stainless steel with a 10-L capacity and was heated to 120°C. The experimental setup is shown in Fig. 1. A 5-μL sample solution was injected into the container filled with room air, and after two minutes the gas inside the container was drawn with room air at 1.2 L/min. The calibration curve was formed based on the relation between the system response and the concentration of the injected sample solution. The background was measured for five minutes, without using the container, by sucking room air from the inlet of the tube. The detection limit was obtained as three times the standard deviation of the background divided by the slope of the calibration curve. Before evaluating the detection limit through long tubing, three different tube materials (stainless steel, fused silica, and Teflon) were tested by injecting the sample solution directly into the inlet of shorter tubes (1.8 and 7

m) for convenience. As a result, Teflon gave the most intense signals for both agents for each tube length. Thus, we used only Teflon thereafter.
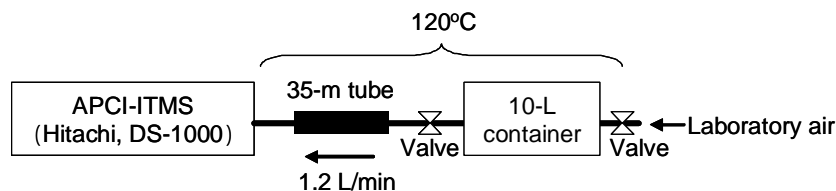

Figure 1. Experimental setup. Sample solution is injected with syringe into container through injection inlet (not shown here) and sucked into detector by opening valves.

The system responded poorly to low levels of L through the 35-m Teflon tube, possibly due to adsorption and/or decomposition inside the tube, so we used another experimental setup (Fig. 2) that made it possible to increase the flow rate. In this setup, dry air was fed through the container at 2 L/min, mixed with a 3-L/min stream of humidity-controlled air that was generated with a gas generator (GL Science), fed through a 35-m tube at 5 L/min, and drawn into the inlet of the mass spectrometer at 1.2 L/min. The excess stream (3.8 L/min) was vented into a draft hood. The background was measured for five minutes by drawing room air from the inlet of the tube at 1.2 L/min.
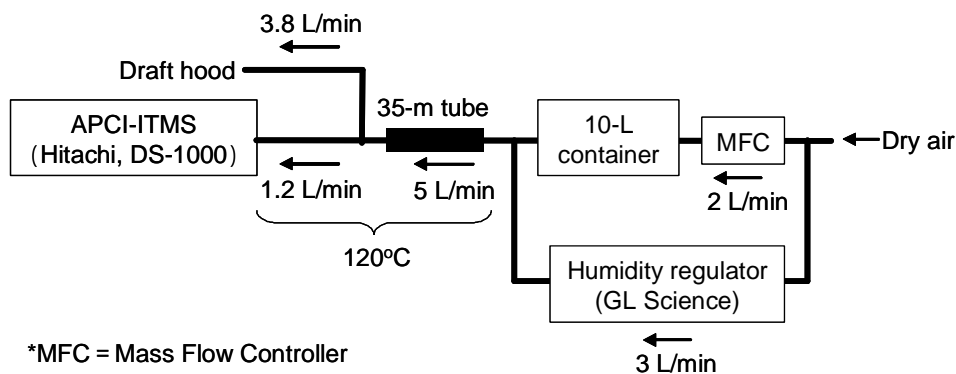

Figure 2. Experimental setup. Sample solution is injected with syringe into container through injection inlet (not shown here).

We used single or double-stage tandem mass spectrometry (MS/MS or MS/MS/MS) for HD or L to improve specificity and consequently, the signal-to-noise ratio. Ions generated in the APCI were introduced into an ion trap for 300 ms, isolation and dissociation processes for MS/MS or MS/MS/MS were carried out, and the intensity of a fragment ion was measured. This cycle was repeated three times, and the average intensity was plotted. Under these conditions the sampling interval was about 1.2 seconds.

Results and Discussion

Figure 3 plots the system response through the 35-m Teflon tube for various initial concentrations of HD inside the container. For each concentration, the signal intensity was averaged over two minutes after three minutes had passed from the beginning of drawing the HD gas, and plotted against the concentration to form a calibration curve, shown in figure 4.

Figure 5 shows the system response through the 35-m Teflon tube for various concentrations of L. As shown in the figure, the system seems to respond to L for about fifteen minutes for each concentration. As the dry air drawn through the 10-L container is 30 L in total for fifteen minutes and is diluted by 2/5 when mixed with the humidity-controlled air, the average concentration of L introduced into the mass spectrometer for the fifteen minutes is roughly 2/15 of the initial concentration in the container. These concentrations are indicated in the

figure. Figure 6 shows a calibration curve for L formed by plotting the average signal intensity for the fifteen minutes against the concentration at the inlet of the mass spectrometer.
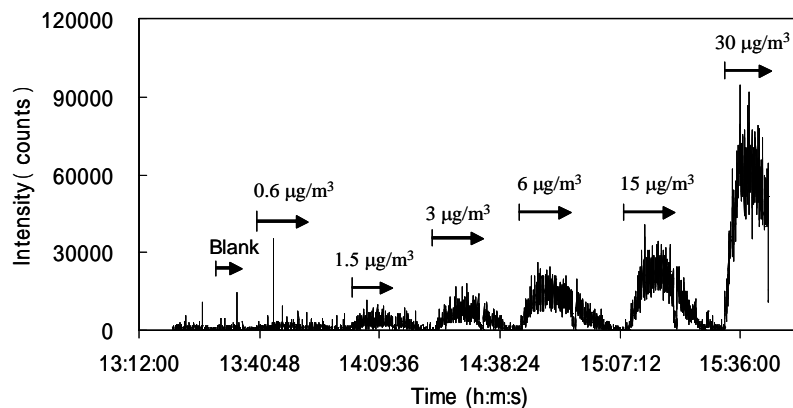

Figure 3. System response through 35-m Teflon tube for various concentrations of HD. Initial HD concentrations in 10-L container are indicated.
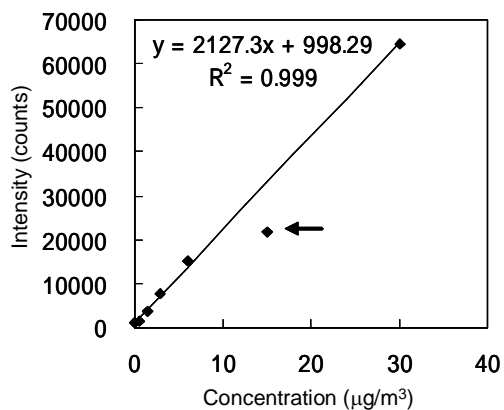

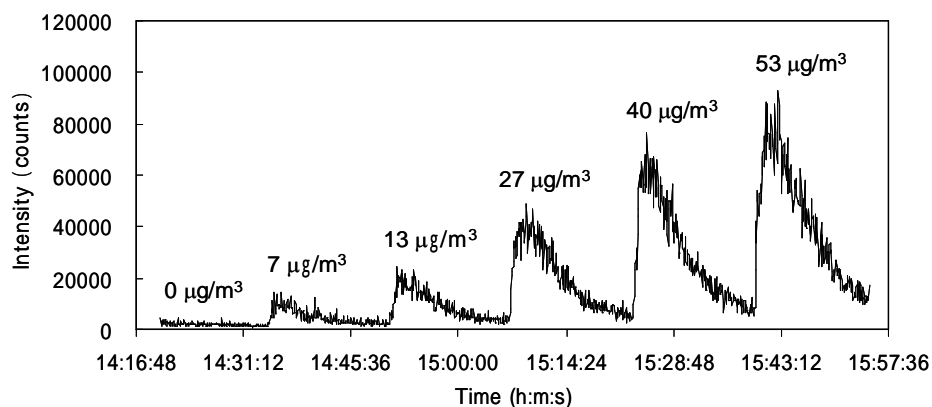Figure 4. Calibration curve for HD. Data indicated by arrow was omitted when plotting the curve.

Figure 5. System response through 35-m Teflon tube for various concentrations of L. Average concentrations at the detector inlet are indicated.
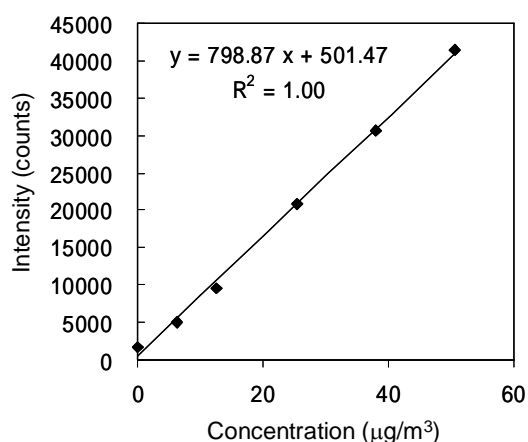
Figure 6. Calibration curve for L.

Table 1 shows the system's sensitivity, standard deviation of background, and detection limit for HD and L. The detection limit was 1.0 and 0.98μg/m^3 for HD and L, respectively.

Table 1. Sensitivity, background, and detection limit for HD and L.

	HD	L
Sensitivity [counts/(μg/m^3)]	2100	800
Background standard deviation [counts]	700	260
Three-sigma detection limit [μg/m^3]	1.0	0.98

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