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Identification of chemical warfare agents from vapor samples using a field-portable capillary gas chromatography/membrane-interfaced electron ionization quadrupole mass spectrometry instrument with Tri-Bed concentrator

Hisayuki Nagashima [a], Tomohide Kondo [a,1], Tomoki Nagoya [a], Toru Ikeda [b], Naoko Kurimata [b], Shohei Unoke [b], Yasuo Seto [a,*]

[a] National Research Institute of Police Science, 6-3-1, Kashiwanoha, Kashiwa, Chiba 277-0882, Japan
[b] INFICON Co., Ltd., NARA Bldg. II 5F, 2-2-8, Shin-Yokohama, Kohoku-ku, Yokohama, Kanagawa 222-0033, Japan

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ABSTRACT

A field-portable gas chromatograph–mass spectrometer (Hapsite ER system) was evaluated for the detection of chemical warfare agents (CWAs) in the vapor phase. The system consisted of Tri-Bed concentrator gas sampler (trapping time: 3 s^{-1} min), a nonpolar low thermal-mass capillary gas chromatography column capable of raising temperatures up to 200 °C, a hydrophobic membrane-interfaced electron ionization quadrupole mass spectrometer evacuated by a non-evaporative getter pump for data acquisition, and a personal computer for data analysis. Sample vapors containing as little as 22 μg sarin (GB), 100 μg soman (GD), 210 μg tabun (GA), 55 μg cyclohexylsarin (GF), 4.8 μg sulfur mustard, 390 μg nitrogen mustard 1, 140 μg of nitrogen mustard 2, 130 μg nitrogen mustard 3, 120 μg of 2-chloroacetophenone and 990 μg of chloropicrin per cubic meter could be confirmed after Tri-Bed micro-concentration (for 1 min) and automated AMDIS search within 12 min. Using manual deconvolution by background subtraction of neighboring regions on the extracted ion chromatograms, the above-mentioned CWAs could be confirmed at lower concentration levels. The memory effects were also examined and we found that blister agents showed significantly more carry-over than nerve agents. Gasoline vapor was found to interfere with the detection of GB and GD, raising the concentration limits for confirmation in the presence of gasoline by both AMDIS search and manual deconvolution; however, GA and GF were not subject to interference by gasoline. Lewisite 1, and *o*-chlorobenzylidene malononitrile could also be confirmed by gas chromatography, but it was hard to quantify them. Vapors of phosgene, chlorine, and cyanogen chloride could be confirmed by direct mass spectrometric detection at concentration levels higher than 2, 140, and 10 mg/m^3 respectively, by bypassing the micro-concentration trap and gas chromatographic separation.

1. Introduction

Chemical-warfare agents (CWAs), which are fast acting and sometimes lethal even at low levels [1], include nerve agents, blister agents, choking agents, blood agents, vomit agents, and lachrymators. They were used in World War I and II, and during the Cold War, and are still being produced and stockpiled [2]. In 1992, a treaty prohibiting the development, production, stockpiling, and use of chemical weapons, and calling for their destruction was ratified and came into force in 1997 [3]. Even so, in the 1980s Iraq used sarin (GB) and sulfur mustard (HD) in the Iran–Iraq conflict [4]. The Japanese cult group AUM Shinrikyo poisoned many by dispersing GB in Matsumoto (1994) and the Tokyo subways (1995) [5,6]. VX has also been used for committing suicide [5]. Just after the September 11, 2001 terrorist attacks in the United States, letters contaminated with anthrax spores were sent to a number of addresses resulting in five deaths [7]. Since then, governmental organizations have strengthened their crisis management systems at national levels for civil defense [8]. Nevertheless, in 2013 GB was used again during the civil war in Syria [9].

* Corresponding author. Tel.: +81 471358001; fax: +81 471339173.
E-mail address: seto@nrips.go.jp (Y. Seto).
[1] Present address: Tokyo Metropolitan Police Department, 2-2-1, Kasumigaseki, Chiyoda-ku, Tokyo 100-8929, Japan.

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Suspected use of CWAs in chemical terrorism cases calls for immediate detection and confirmation, as transport to and analysis at an off-site laboratory would take too long. Portable CWA detection equipment is effective for the personal protection of first responders and for early warning in crisis management situations [10,11]. Several types of on-site equipment for detecting different agents and with varied sensitivity, accuracy, and detection performance are being used by military forces, police mobile teams, coast guards, and fire defense teams [11,12]. We have previously evaluated several commercially available on-site detection systems [13–19], such as handheld gas detection tubes [20], ion mobility spectrometry (IMS) instruments [21–26], and arrayed surface acoustic wave (SAW) sensors [27]. In addition, we have developed new field-deployable detection equipment such as an amperometric sensor for HD detection [28], an atmospheric pressure counter-flow chemical ionization ion trap mass spectrometer (MS) for the detection of a wide range of CWAs [29–31], an electron cyclotron resonance ion source MS instrument for the detection of blood agents, choking agents, and blister agents [32,33], and a low temperature plasma ionization MS technology against nonvolatile CWAs [34]. Mass spectrometers based on Direct Analysis in Real Time (DART) [35,36], glow discharge electron ionization cylindrical ion trap MS [37], selective ion flow MS [38], and chemical ionization reaction time-of-flight MS [39] are other candidates for field-deployable technologies for the detection of CWAs.

Currently, person-portable on-site detection instruments utilized by first responders and handheld IMS detectors [40] are regarded as ideal initial detection devices for screening hazardous vapors. If dangerous vapors are detected in this screening stage, confirmation can be obtained using hyphenated techniques consisting of gas chromatographic (GC) separation and specific detection or spectrometry [41]. A combination of on-site (hot zone) Tenax TA adsorbent vapor sampling [42] with off-site (cold zone) GC–MS analysis using a mobile laboratory has been considered [43,44]. As an alternative, sophisticated on-line technologies for on-site analysis [41] have been developed combining GC with IMS [45] or SAW sensing [46]. However, MS is preferable to IMS or SAW because of its higher resolution. In order to overcome the drawback of time-consuming separations using typical capillary column methods, isothermal GC temperature programs have been adopted [47]. Just prior to 2000, resistive column heating (low thermal-mass (LTM)) technology, an innovation in the field of GC that enabled fast temperature ramping, has been developed [48,49]. As a result, GC–MS became more feasible for on-site confirmation of a wide range of CWAs. Some instruments are now commercially available for this purpose [50,51]. An instrument consisting of a GC system with a nonpolar LTM capillary column, helium carrier gas, and an electron ionization (EI) toroidal ion trap MS [52] provides on-site CWA identification by off-line connecting with solid-phase microextraction (SPME) from vapor, liquid, and solid samples [53]. Self-chemical ionization induced by prolonging the ionization time aids in the identification of VX and related degradation products that do not show any characteristic EI spectrum under conventional ionization conditions [54]. A Hapsite, equipped with a Tenax TA micro-concentration trap, an LTM capillary column GC using nitrogen as the carrier gas, a quadrupole MS with a hydrophobic membrane interface, and a non-evaporative getter (NEG) vacuum system [55], enables on-site CWA identification of vapor samples [56]. Hapsite has been used as field analysis instrument for mainly quantifying volatile organic chemicals [57]. The latest version of the Hapsite ER [58] provides extended target analysis by adopting SPME and a thermal desorbing device at the inlet [49]. This inlet system is reported to be superior to the original sampling probe, which was found to have a hard memory effect due to condensation of less volatile compounds in the probe [59]. The constancy of the sample gas drawing flow rate has been improved in Hapsite ER machine compared to the flow rate fluctuation in the former version machine [55], by adopting mass flow controller.

Previously, we reported on the performance of the first version of the Hapsite system where G-type nerve agents, GB, soman (GD), tabun (GA) and blister agent HD could be successfully identified [60]. We are currently examining the latest version of the Hapsite ER for the potential for confirmation of a wider range of CWAs. The Hapsite is ideally used for confirmation after an initial IMS positive result is obtained. As many kinds of CWAs as possible should be confirmed for those which are detected by screening IMS instruments.

In this paper, we present details of our evaluation results and confirmation of the capabilities of a Hapsite ER system equipped with a standard sampling probe and Tri-Bed concentrator trap for the determination of vapor phase CWAs, including five G-type nerve agents (GB, GD, GA, cyclohexylsarin (GF), VX), five blister agents (HD, nitrogen mustard 1, 2, 3 (HN1, 2, 3), Lewisite 1 (L1)), one blood agent (cyanogen chloride (CK)), three choking agents (chloropicrin (PS), phosgene (CG), chlorine (CL)), and two lachrymators (2-chloroacetophenone (CN) and *o*-chlorobenzylidene malononitrile (CS)). The chemical structures and toxicological properties of these compounds are shown in Fig. 1.

2. Materials and methods

2.1. Instrumental methods

A Hapsite ER system (Inficon, East Syracuse, NY, USA) was used in this study. It is an integrated field-portable GC-MS instrument (46 cm (L) × 43 cm (W) × 18 cm (H), 19 kg). The instrument consists of a main body and a sampling probe connected by a 1.75 m inert PEEK tube (I.D.: 1.65 mm). When the front panel is opened for viewing, an NEG pump, canisters for carrier gas (N_2) and internal standard, a micro-concentration trap and a rechargeable NiMH battery are observed. Gas chromatograph and mass spectrometer (quadrupole) are located behind these parts. The Hapsite ER was installed with Tri-Bed micro-concentration trap as recommended by the supplier. Tri-Bed tube is a multi-bed type adsorbent tube composed of carbon materials (information from the supplier). Mass spectrometric tuning prior to the analysis, control of GC–MS analysis and acquired data analysis were all performed using a personal computer (Windows 7, GC–MS control and data analysis software installed). The NEG pump temperature was maintained at 400 °C. For our laboratory experiments, the carrier gas N_2 was provided from a laboratory N_2 line (>99.99% purity, Tomoe Shokai Co. Ltd., Tokyo, Japan), and the electricity was supplied by external laboratory power source using the AC to DC Power Converter.

Air sampling was performed with the sampling probe; its connection line was maintained at 50 °C. The inlet flow rate was set to 100 ml/min and for the first 1 min air sample was purged from the system (line purge). Next, air was drawn into a micro-concentration trap (Tri-Bed 15 mg packed) maintained at 70 °C for 3 s (ppm method) to 1 min (ppb method). Then, both the ends of the trap line was closed and the trapped analytes were desorbed by raising the trap temperature to over 450 °C within 8 s. The trapped analytes was then introduced into the DB-1 column (polydimethylsiloxane fused silica, 15 m × 0.25 mm ID, 1 μm film thickness) maintained at 60 °C with an N_2 flow of 2 ml/min for 30 s; then the flow lines were switched so that the micro-concentration rap line was cleaned by purging with the N_2 flow to outside the machine, and the carrier-gas (N_2) was flowed to the column at 2 ml/min. The temperature