Analytica Chimica Acta 865 (2015) 39–52

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Ion mobility spectrometric analysis of vaporous chemical warfare agents by the instrument with corona discharge ionization ammonia dopant ambient temperature operation

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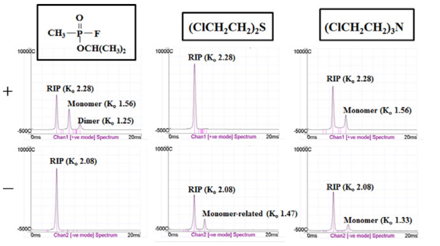
HIGHLIGHTS

- Ion mobility spectrometer with corona discharge ionization and ammonia doping was used.
- Nineteen chemical warfare agents were analyzed in addition to simulants and organic solvents.
- Relationship between the reduced ion mobility and the molecular mass was investigated.

GRAPHICAL ABSTRACT



Ion mobility spectrometry with corona discharge ionization and ammonia dopant

ARTICLE INFO

Article history:
Received 24 August 2014
Received in revised form 6 November 2014
Accepted 3 February 2015
Available online 4 February 2015

Keywords:
Ion mobility spectrometry
Chemical warfare agents
Simulants
Organic solvents
Performance evaluation

ABSTRACT

The ion mobility behavior of nineteen chemical warfare agents (7 nerve gases, 5 blister agents, 2 lachrymators, 2 blood agents, 3 choking agents) and related compounds including simulants (8 agents) and organic solvents (39) was comparably investigated by the ion mobility spectrometry instrument utilizing weak electric field linear drift tube with corona discharge ionization, ammonia doping, purified inner air drift flow circulation operated at ambient temperature and pressure. Three alkyl methylphosphonofluoridates, tabun, and four organophosphorus simulants gave the intense characteristic positive monomer-derived ion peaks and small dimer-derived ion peaks, and the later ion peaks were increased with the vapor concentrations. VX, RVX and tabun gave both characteristic positive monomer-derived ions and degradation product ions. Nitrogen mustards gave the intense characteristic positive ion peaks, and in addition distinctive negative ion peak appeared from HN3. Mustard gas, lewisite 1, *o*-chlorobenzylidenemalononitrile and 2-mercaptoethanol gave the characteristic negative ion peaks. Methylphosphonyl difluoride, 2-chloroacetophenone and 1,4-thioxane gave the characteristic ion peaks both in the positive and negative ion mode. 2-Chloroethylethylsulfide and allylisothiocyanate gave weak ion peaks. The marker ion peaks derived from two blood agents and three choking agents were very

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Abbreviations: CWAs, chemical warfare agents; GB, sarin; IMS, ion mobility spectrometry; GC, gas chromatography; MS, mass spectrometry; TICs, toxic industrial compounds; GD, soman; GA, tabun; GF, cyclohexylsarin; RVX, Russian VX; DF, methylphosphonyl difluoride; HD, mustard gas; L1, lewisite 1; HN1, nitrogen mustard 1; HN2, nitrogen mustard 2; HN3, nitrogen mustard 3; CS, o-chlorobenzylidenemalononitrile; PS, chloropicrin; CN, 2-chroroacetophenone; DFP, diisopropylfluorophosphate; DMMP, dimethylmethylphosphonate; TMPO, trimethylphosphate; TEPO, triethylphosphate; CEES, 2-chloroethylethylsulfide, 1,4-thioxane; ME, 2-mercaptoethanol; AITC, allyl isothiocyanate; AC, hydrogen cyanide; CK, cyanogen chloride; CG, phosgene; CL, chlorine; RIP, reactant ion peak; RIP(+), reactant ion peak in the positive ion mode; RIP(−), reactant ion peak in the negative ion mode; K_o, reduced mobility constant; OP, organophosphorus; LOA, limit of alarm; LC_{50}, median lethal concentration; LDT, long drift tube.

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http://dx.doi.org/10.1016/j.aca.2015.02.004

close to the reactant ion peak in negative ion mode and the respective reduced ion mobility was fluctuated. The reduced ion mobility of the CWA monomer-derived peaks were positively correlated with molecular masses among structurally similar agents such as G-type nerve gases and organophosphorus simulants; V-type nerve gases and nitrogen mustards. The slope values of the calibration plots of the peak heights of the characteristic marker ions versus the vapor concentrations are related to the detection sensitivity, and within chemical warfare agents examined the slope values for sarin, soman, tabun and nitrogen mustards were higher. Some CWA simulants and organic solvents gave the ion peaks eluting at the similar positions of the CWAs, resulting in false positive alarms.

1. Introduction

Chemical warfare agents (CWAs) [1,2] are fast-acting and toxic low-molecular-weight synthetic compounds. With respect to physical properties, they can be classified as gaseous "blood agents", gaseous "choking agents", volatile "nerve gases", volatile "blister agents", non-volatile "vomiting agents" and non-volatile "lachrymators (tear gases)". The physical and toxicological properties of CWAs vary with respect to molecular mass, melting point, vapor pressure, vapor density, durability in air, lethal concentration, incapacitating concentration, smell, water solubility, stability in water, effect on skin and possibility of effective antidote [3]. Deadly poisonous nerve gases and toxic blister agents are registered as scheduled compounds in the Chemical Weapon Convention (http://www.opcw.org). Although CWAs show toxicity not only by direct inhalation, but also by contact with skin, in cases of chemical warfare and disposal of chemical weapons, inhalation toxicity against CWAs vapor should be given priority. On-site measurement technologies are mainly focused on detecting CWAs in the vapor form.

The Japanese doomsday cult group, AUM Shinrikyo, used sarin (GB) in Matsumoto (Japan) in 1994 and in the Tokyo Subway System in 1995, poisoning and killing many defenseless people [4]. Since then, governmental organizations have strengthened their crisis management systems at the national level for civil defense [5]. Monitoring of CWA vapors in public places and security checks at territorial borders, airports and venues where large public events are held, could protect society against terrorism and promote the health of workers at these sites. Rapid on-site detection is the most important criterion for minimization of a CWA disaster, particularly in criminal investigations and emergency life-saving. That is because it takes significant time to transport specimens sampled on-site to laboratories for analysis. Various types of measurement technologies have been used for on-site detection [6,7]. We previously evaluated the performance of commercially available field-deployable portable CWA detectors [5,8–12]. These included the gas detection tube (Draeger safety) [13], handheld detectors [14–17] based on ion mobility spectrometry (IMS) [18–20], arrayed surface acoustic wave detector (ChemSentry) [21] and a gas chromatography (GC)–mass spectrometry (MS) (Hapsite) [22]. The required detection performance for field utilization by first responders involves consideration of detection sensitivity, detection accuracy, response time, recovery time and operational performance; at present a detector that can meet all these requirements is not available. Low alarm sensitivity, frequent false alarms and strong adsorption of CWAs on the surface of the inlet of the detectors are particularly serious problems [12]. Among field-deployable CWA detection equipment, IMS detectors have been extensively developed and utilized for personal protection and early screening against dangerous materials such as CWAs, explosives and illicit drugs because of their light weight and portability, ease of operation and real time detection [23].

Several portable field-deployable IMS systems have been commercially available for the previous two decades [24,25], particularly for homeland security application [23]. Such instruments can differ with respect to ionization mode, ion separation mode, dopant (reagent gas) usage and drift tube temperature control. For ionization, radioactive source such as ^{63}Ni and ^{241}Am are mainly used. Target compounds with high proton affinity offer favorable detection [26]. Machines based on laser desorption ionization [27] or corona discharge ionization [28], which are free from the regulations of radioisotope usage, have recently been used. For ion separation mode, a straight drift tube with parallel voltage and reverse airflow is most popular: generated ions move from the shutter to the collector in the direction of the drift voltage, and the drift time is measured [26,29]. Usually, the electric field is weak, namely several hundred volts per centimeter. An aspiration type detector [30,31] is also available where the produced ions traverse from the shutter through an airflow, change direction as a result of a perpendicular drift voltage, and several sensor cells receive the ions depending on the size, shape and charge of the molecules. Essentially, the drift tube temperature [32] and drift gas species [33], and especially the moisture level [34,35], are essential parameters for ion mobility behavior of the reactant ion peak (RIP) and the target ions. In the ionization and drift regions, there are many ion/molecule reactions leading to the characteristic ion mobility spectra [36]. High-field asymmetric waveform IMS and differential mobility spectrometry are newly developed technologies [23,37,38]. Hyphenated technologies such as IMS combined with GC as pre-separation [39,40] or MS as post-analysis [41] have been widely reported. For dopant usage [42–44], various solvents (e.g., ammonia, acetone, dichloromethane) have been used. By introducing the dopant molecules into the ion source and the drift region, the production of the reactant ions is facilitated or the production of interfering ions suppressed, or the target ions are well discriminated from the other ions, resulting in increased sensitivity and specificity. In a non-dopant IMS system, RIPs are produced from background air molecules such as water, nitrogen and oxygen. Target compounds are ionized indirectly by reaction with these RIPs, providing characteristic marker ions.

We previously evaluated the aspiration-type IMS instruments with ^{241}Am ionization, ambient temperature control and non-air purification (M90 D1-C [16] and ChemPro100 ver. 1 [14], all manufactured by Environics Oy (Finland)); the straight drift tube-type purified-drift-air-driven instruments with corona discharge ionization, simultaneous positive and negative ion measurement, ambient temperature operation and ammonia dopant (LCD 3.2E [15]); and with long drift tube (LDF), ^{63}Ni ionization, calibrant-adoption and high temperature control (SABRE 4000 [17]), both manufactured by Smiths Detection. The proto-type LCD (light-weight chemical detector) was developed by Graseby Dynamics Ltd. [45], and successively improved into the LCD 3.3, which includes an alarm warning for ten CWAs, compared with LDC 3.2E which has an alarm featuring only two CWA classes. The LDT IMS instrument (SABRE 4000 system [17]) has the advantage of providing semi-quantitative identification of ten and nine agent names as the detection alarm, respectively. In contrast, most portable detectors are limited in terms of specifying agent alarm