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Development of portable mass spectrometer with electron cyclotron resonance ion source for detection of chemical warfare agents in air

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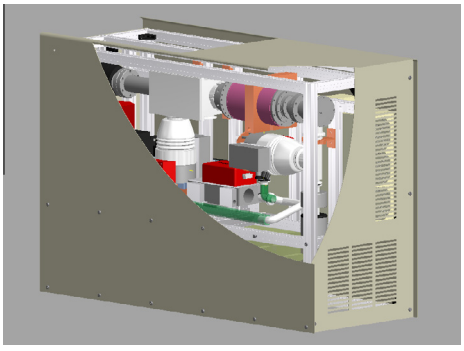
HIGHLIGHTS

- We developed a portable mass spectrometer (miniECRIS-MS).
- The miniECRIS-MS had great advantages (a fast response, high sensitivity and a small body size) for real time monitoring.
- We measured three types of chemical warfare agents (CWAs) for counter terrorism.
- The miniECRIS-MS successfully detected target signals from the CWAs in air.
- We showed the potential of miniECRIS-MS for on-site detection of CWAs in the future.

GRAPHICAL ABSTRACT



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ABSTRACT

A portable mass spectrometer with an electron cyclotron resonance ion source (miniECRIS-MS) was developed. It was used for *in situ* monitoring of trace amounts of chemical warfare agents (CWAs) in atmospheric air. Instrumental construction and parameters were optimized to realize a fast response, high sensitivity, and a small body size. Three types of CWAs, i.e., phosgene, mustard gas, and hydrogen cyanide were examined to check if the mass spectrometer was able to detect characteristic elements and atomic groups. From the results, it was found that CWAs were effectively ionized in the miniECRIS-MS, and their specific signals could be discerned over the background signals of air. In phosgene, the signals of the $^{35}Cl^+$ and $^{37}Cl^+$ ions were clearly observed with high dose–response relationships in the parts-per-billion level, which could lead to the quantitative on-site analysis of CWAs. A parts-per-million level of mustard gas, which was far lower than its lethal dosage (LCt_{50}), was successfully detected with a high signal-stability of the plasma ion source. It was also found that the chemical forms of CWAs ionized in the plasma, i.e., monoatomic ions, fragment ions, and molecular ions, could be detected, thereby enabling the effective identification of the target CWAs. Despite the disadvantages associated with miniaturization, the overall performance (sensitivity and response time) of the miniECRIS-MS in detecting CWAs exceeded those of sector-type ECRIS-MS, showing its potential for on-site detection in the future.

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Introduction

Chemical warfare agents (CWA) have a lethal effect on the human body and are regarded as weapons of mass destruction [1]. They are classified into gaseous CWAs (blood agents, choking agents), volatile CWAs (nerve gases, blister agents), semi-volatile CWAs (vomit agents, lachrymators (tear gases)), based on their physical properties and influence on the human body. The real-time monitoring and rapid detection of CWAs *in situ* is an urgent need for homeland security. Various technologies have been developed for the on-site detection of CWAs in air: manual gas detection tubes [2], ion mobility spectrometry (IMS) [3], surface acoustic wave detection [4], gas chromatography [5], chemical sensors [6] and also mass spectrometry techniques based on electron ionization instruments with hydrophobic membranes [7] and atmospheric pressure chemical ionization [8]. Some of them are even commercially available as portable instruments. However, they are limited by their low sensitivity, low specificity (frequent false alarms), and long response and recovery times because of the strong adsorption of CWAs on them [9]. Though some mass spectrometers and IMS instruments are capable of sensitive and real-time detection of specific chemicals, versatile detection of all kinds of CWAs is impossible, because of the instrumental complications involved.

In our previous report [10], a new technology for the detection of gaseous CWAs using an element analysis system with an electron cyclotron resonance (ECR) ion source was discussed. Its versatile detection of CWAs with specific elemental markers was its unique advantage. Hydrogen cyanide (AC) and CWA simulants such as diisopropyl fluorophosphate (DFP) were measured, and their characteristic monoatomic ions or atomic groups (CN^+) were successfully detected. We plan to use this ECR technique together with IMS to conclusively identify CWAs. The ECR technique offers fast response and diversity for the elemental detection of CWAs and compensates the disadvantage of IMS that leads to false positives. However, several challenges had to be addressed to make our technology suitable for on-site and real-time monitoring: (1) high sensitivity was needed for detection at the parts-per-million level, (2) a fast response against an atmospheric air sample was necessary (within 1 min), and (3) the size of the instrument had to be optimized for portability and ease of use. We addressed these challenges by developing a new compact mass spectrometer with an ECR ion source (miniECRIS-MS). In this paper, the detection performance of the miniECRIS-MS for CWAs was studied, and the results are presented. The purpose of this study is to demonstrate the ability of miniECRIS-MS for the on-site, real-time and versatile detection of CWAs in air.

Experiment

Equipment

A schematic of the miniECRIS-MS is shown in Fig. 1. The specifications of the permanent magnet used for the confinement of the ECR plasma can be found in [11]. The plasma chamber with an outer casing was inserted inside the center of the magnet. The length and diameter of the chamber were 150 mm and 35 mm, respectively. A microwave with a frequency of 5.91 GHz was fed to the plasma chamber from a solid-state-type microwave amplifier with a signal generator. A microwave power of 1.3–10 W for the plasma chamber was supplied using a monopole antenna.

The ions generated by ECR plasma in the plasma chamber were led to the ion transfer chamber through an extraction electrode set at a potential of 120–150 V. On the flight-path of the ions, two einzel lenses, an XY deflector, and double deflector lenses were installed. The double deflector lenses were responsible for offsetting

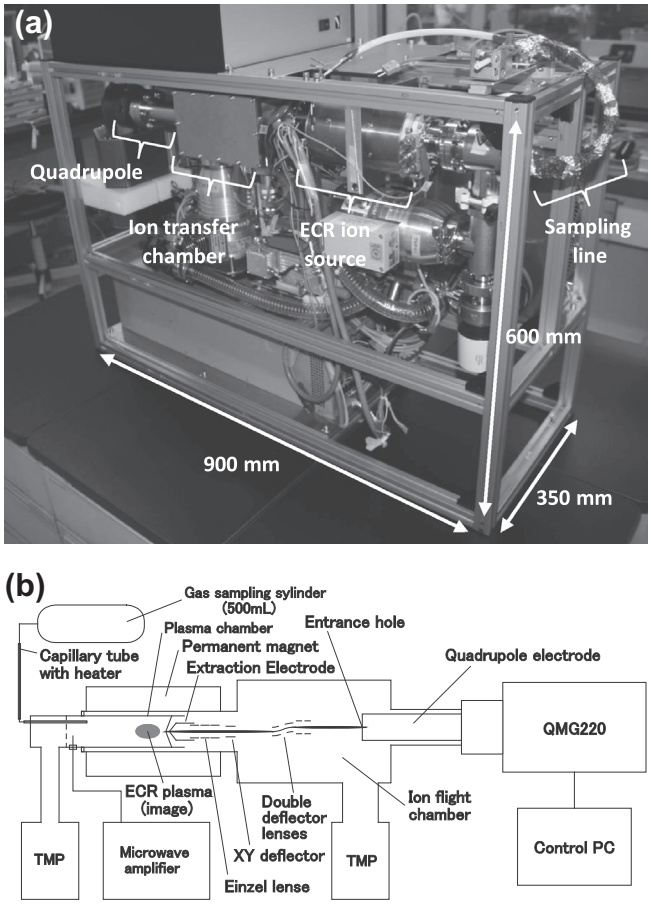

Fig. 1. (a) Photograph and (b) schematic diagram of the miniECRIS-MS.

the flight axis of the extracted ions. They were installed to prevent noise caused by the light of the plasma going into the detector.

The vacuum system was composed of two turbo-molecular pumps (TMP, 80 L s^{-1}) and a diaphragm pump. The diaphragm pump served as a back-up for the turbo-molecular pumps. The two turbo-molecular pumps were set for the plasma chamber and the ion transfer chamber, respectively. The vacuum pressure set by the head position of the turbo-molecular pump in the plasma chamber was 8×10^{-6} Pa.

A customized quadruple mass spectrometer (QMG220, Pfeiffer Vacuum GmbH, Asslar, Germany) was used for mass analysis, in the m/z range 4–50 with unit resolution. The commercial ion source attached to the head of the quadruple electrode was removed, leaving a hole at the entrance for ions to enter. The Faraday cup and secondary electron multiplier (SEM) within the QMG220 instrument were used for the detection of ions.

A customized power supply with multiple outputs was used for supplying electric power to all the electrodes; a customized microwave power supply and a programmable controller (e-RT3, Yokogawa Electric Corporation, Tokyo, Japan) for the customized power supply were also a part of the setup. All the above-mentioned devices were assembled into an aluminum framework with outside dimensions of 600 × 350 × 950 mm and weight of 90 kg. For the actual application of the device, electric power is fed to all electrical components using a lithium ion battery. The duration for the practical on-site application is approximately 1 h for a single battery unit.

CWA measurement

The CWAs (phosgene (CG), mustard gas (HD), and AC) used in this study were prepared at the National Research Institute of