COMMUNICATIONS

Vapor Detection of TNT and RDX Using Atmospheric Pressure Chemical Ionization Mass Spectrometry with Counter-Flow Introduction (CFI)

Kyoko KOJIMA,^{*a)} Minoru SAKAIRI,^{a)} Yasuaki TAKADA,^{a)}
and Jun NAKAMURA^{b)}

(Received May 13, 2000; Accepted July 27, 2000)

To enable vapor detection of TNT and RDX, we have combined atmospheric pressure chemical ionization (APCI) mass spectrometry with counter-flow introduction (CFI) of sample vapors. The chemical ionization source, which enables high ionization efficiency and highly selective ionization, was attached to a quadrupole mass spectrometer. Using this modified mass spectrometer, we obtained negative mass spectra and detection chromatograms of trinitrotoluene (TNT) and 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) vapors at room temperature. The explosives detection could be done within 5 s. Our test results from this prototype system demonstrate that this technique is suitable for practical on-line explosives detection.

1. Introduction

The use of explosives-detection systems has increased worldwide in airline baggage control, customs inspection, at sensitive facilities, and so on. Explosives-detection technology can be classified into two categories: bulk detection and trace detection. Bulk detection technologies, such as X-ray imaging, are widely used. In contrast, trace-detection technologies, which focus on vapor of explosives have not been widely applied.

In recent years, however, vapor-detection technology has become increasingly necessary as security concerns have grown. In vapor-detection technologies, mass spectrometry is a major tool,^{1), 2)} because it offers high sensitivity, and a short detection interval. However, the vapor pressure of nitro explosives excluding ethylene glycol dinitrate and nitroglycerin, is generally very low, which makes vapor detection more difficult. For example, the saturated vapor pressure of TNT at room temperature is 5.8×10^{-6} Torr, and that of RDX is 4.6×10^{-9} Torr.³⁾ The vapor detection of RDX has is especially difficult by conventional techniques.

Recently, our laboratory developed an atmospheric pressure chemical ionization (APCI) source with counter-flow introduction to the discharge region. As we will explain, this ionization source improves ionization efficiency compared to that with a conventional APCI source. In addition, our ionization source has a superior structure for on-line gas sampling that enables large-volume sampling while suppressing contamination of the APCI source. We made a prototype explosives detector by combining this APCI source with a commercially available quadrupole mass spectrometer. We evaluated the developed mass spectrometer system by using it to detect vapors from nitro compounds.

2. Experimental

We modified a quadrupole mass spectrometer, the Hitachi M-1200 liquid chromatography/mass spectrometry (LC/MS) system, for on-line vapor detection as shown in Fig. 1. A gas-sampling probe evacuated at 15 L/min with a diaphragm pump, and an APCI source with counter-flow introduction to the discharge region (Fig. 2) were used. At the chemical ionization source, the obtained gas sample flows toward a corona-discharge electrode, where negative ions are generated. The negative ions are then sent in the direction opposite to the vapor flow exiting the system by an electric field, and are introduced into the mass analysis region. A voltage of -3 kV was applied to the discharge electrode.

When nitro compounds were placed close to the probe, air containing the vapor of the nitro compounds was drawn into the mass spectrometer. Part of the drawn gas sample (0.7 L/min) was introduced into the corona-discharge region, and atmospheric pressure chemical ionization took place.

The generated ions then passed into a mass analysis region through apertures in the differential pumping region. The differential pumping region was evacuated to about 1 Torr with a mechanical pump (900 L/min). The ions were focused by an electrostatic lens and were mass analyzed with the quadrupole mass spectrometer. The mass-analysis region was evacuated to 1×10^{-5} Torr with a turbo-molecular pump (200 L/s).

Open sample bottles were placed close to the probe for the explosives-vapor sampling.

The TNT and RDX were provided by an explosives manufacturer. They were used after recrystallization from acetone.

3. Results and Discussion

Negative mass spectra of TNT, RDX, and air were obtained by on-line vapor sampling with the mass spectrometer (Fig. 3). In the spectrum of air as a

^{*a)} Central Research Laboratory, Hitachi Ltd. (1-280 Higashi-koigakubo, Kokubunji, Tokyo 185-8601, Japan)

^{b)} National Research Institute of Police Science (6-3-1 Kashiwanoha, Kashiwa, Chiba 277-0882, Japan)

Fig. 1. Schematic diagram of the mass spectrometer for explosives-vapor detection.

Fig. 2. Cross-section of the atmospheric pressure chemical ionization (APCI) source with counter-flow introduction (CFI) to the discharge region.

background, two major peaks are monitored. One was assigned to O_2^- ($32\ m/z$), and the other at 60 could be a O_2^- species ($[O_2^-(N_2)]$, $[O_2^-(N_2O)]$, $(NO)_2^-$).⁴⁾ We detected TNT at $227\ m/z$ as a molecular anion (M^-), and minor fragment peaks of $[M-O]^-$ at 211, and $[M-NO+H]^-$ at 198 (Fig. 3(b)). On the other hand, RDX was detected at 268 as a cluster ion, $[M+NO_2]^-$ (Fig. 3(c)). The ionization of the nitro compound molecule (M) was as follows:

negative corona discharge

negative corona discharge

(X: neutral molecule)

In reaction (2), TNT is ionized by an electron-transfer reaction from an oxygen radical anion. In reactions (3) and (4), RDX forms a cluster anion with NO_2^- . This stable cluster formation is caused by collisions between M_{RDX} , NO_2^- , and another neutral molecule X .⁵⁾

These ionization reactions were progressed highly selectively and highly efficiently. This can be explained as follows. In our chemical ionization source, the generated ions move in a direction opposite to the

Fig. 3. Mass spectra of air (a), TNT (b), and RDX (c).

sample gas flow. This suppresses formation of inert NO_3^- , as shown by reactions (5) and (6), which has very strong acidity and inhibits ionization of the nitro compounds. The NO_3^- generation is suppressed because there is less overlap between the O_2^- rich region and the

Fig. 4. Detection of TNT (a) and RDX (b) with vapor sampling.

NO rich region due to the opposite directions of movement.

negative corona discharge

The ions pass through the main gas current provided by the diaphragm pump, and selective secondary chemical ionization (reaction (2) or (4)) takes place. This low-energy secondary ionization means there is little fragmentation of the nitro compounds, which increases the sensitivity of the explosives detector.

A selected-ion-monitoring (SIM) mode measurement program is then used for on-line detection of the vapors of nitro compounds at room temperature. Figure 4(a) shows a chromatogram of TNT vapor detected from a passport contaminated with TNT (sampled as shown in

Fig. 2(b)). Figure 4(b) shows the result of RDX vapor detection using an open sample bottle. When vapor sampling started, the intensity of the monitored major ion immediately increased, and the intensity quickly returned to the initial level when sampling was ended. Detection was completed within 5 s. The estimated sensitivity of the detector was within the saturated vapor pressure of each nitro compound. The vapor sampling could also be repeated without frequent maintenance of the system.

4. Summary

Vapor detection of the explosives TNT and RDX was achieved using a quadrupole mass spectrometer equipped with an atmospheric pressure chemical ionization source with counter-flow introduction to the discharge region. This detection technique enables high sensitivity, highly selective ionization, and a short detection/response interval compared with other vapor detection methods.

Acknowledgments

Important contributions to the experiments were made by Dr. Y. Hirabayashi, Mr. Y. Hashimoto and Mr. M. Suga of the Hitachi Central Research Laboratory.

References

- 1) W. R. Scott, D. Green, and A. Mercado, *Proc. SPIE*, **2276**, 87 (1994).
- 2) W. A. Bryden, R. C. Benson, S. A. Ecelberger, and T. E. Phillips, *Proc. SPIE*, **2511**, 153 (1995).
- 3) B. C. Dionne, D. P. Rounbehler, E. K. Achter, J. R. Hobbs, and D. H. Fine, *J. Energetic Mater.*, **4**, 447 (1986).
- 4) (a) M. W. Siegel and W. L. Fite, *J. Phys. Chem.*, **80**, 2871 (1976).
(b) K. Hiraoka, S. Fujimaki, K. Aruga, and S. Yamabe, *J. Phys. Chem.*, **98**, 8295 (1994).
- 5) S. A. McLuckey, D. E. Goeringer, K. G. Asano, G. Vaidyanathan, and J. L. Stephenson, Jr., *Rapid Commun. Mass Spectrom.*, **10**, 287 (1996).

Keywords: Atmospheric pressure chemical ionization, Corona discharge, Nitro compounds, TNT, RDX