

# Detection of Military Explosives by Atmospheric Pressure Chemical Ionization Mass Spectrometry with Counter-Flow Introduction

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## Summary

To detect vapors from explosives, we have developed a new detection system based on a novel ion source for atmospheric pressure chemical ionization (APCI). The direction of the sample gas flow introduced into the ion source is opposite to that of the ion flow produced by the ion source. We call this technique “counter-flow introduction” (CFI). The CFI ion source has high ionization efficiency for nitro-compounds and is installed in an ion-trap mass spectrometer. Our tests on various military explosives show that this system is suitable for practical on-line explosive detection; namely major explosives can be detected within a few seconds without any pretreatment of the sample gases.

## 1 Introduction

Due to various changes in world circumstances, the threat of terrorism has become a serious problem for all countries. For example, military explosives are traded on the black market, and the general public can find out how to make explosives via the Internet. Therefore, to maintain a safe society, detection technologies for hidden explosives are being demanded.

Two types of detection methods are in main use: bulk detection (which uses x-rays to determine the existence of suspicious objects such as knives and firearms from their shapes), and trace detection (which detects the presence of explosives by chemically analyzing the vapor from nitro-compounds). Bulk detection has been widely used, but trace detection technologies have become increasingly necessary as security concerns have grown. For example, wiping tests for passengers and hand luggage by using ion mobility spectroscopy or chemiluminescence detection have been carried as part of aviation security. In the near future,

combined use of the bulk detection and trace detection will become more popular to improve security at important facilities.

However, the current trace detection methods mentioned above suffer several problems. For example, selectivity of ion mobility spectroscopy is not enough, resulting in false alarms in some cases. On the other hand, selectivity of chemiluminescence detection is good enough, but this method needs GC separation and is difficult to obtain quick responses for on-line use.

In the trace detection technologies, mass spectrometry is a good tool, because it offers high sensitivity, high selectivity, and a short detection interval<sup>(1)</sup>. However, the vapor pressure of nitro-explosives other than ethylene glycol dinitrate and nitroglycerin is generally very low, which makes vapor detection more difficult.

Recently, we have developed a flue-gas analysis system for on-line and real-time monitoring of heavily contaminated gases. This system has high-speed response, high sensitivity, and high selectivity. In this system, a novel atmospheric-pressure chemical ionization (APCI) source with “counter-flow introduction” (CFI) has been installed. This ion source improves the ionization efficiency beyond that of a conventional APCI ion source. We have developed a new detection system of explosives based on the flue gas monitor<sup>(2)</sup>.

## 2 Experimental Section

Figure 1 shows cross-sectional views of a conventional (a) and the newly developed APCI ion source (b). In the conventional ion source, sample gas flows directly into the corona discharge region. The sample gas and primary ions produced by the corona discharge are moved together towards the sampling aperture by the gas flow and an

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electric field produced between the needle electrode and the aperture electrode. In the new ion source shown in Figure 1(b), the sample gas flows into the secondary ionization region, then flows to the corona discharge region, where negative ions are generated. The negative ions are extracted in the direction opposite to the gas flow by the electric field.

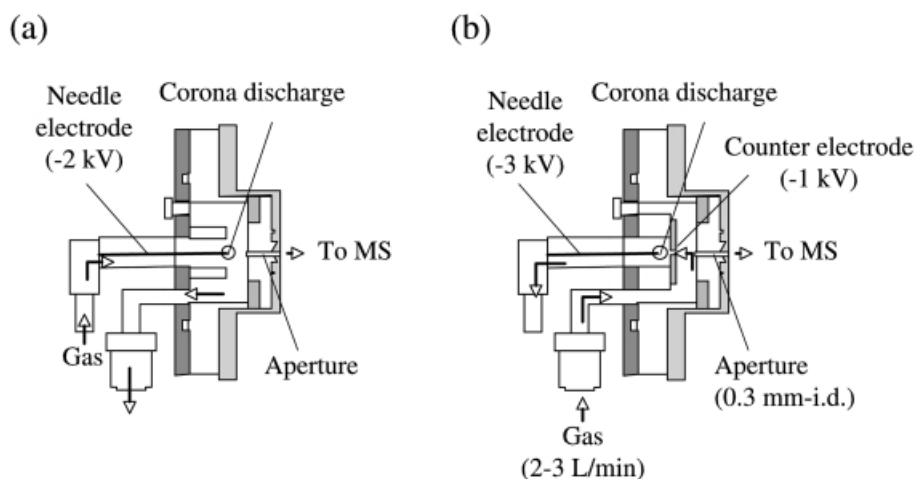
An on-line flue gas monitor (an ion trap mass spectrometer, Hitachi model CP-2000) with an APCI source operating in the negative mode<sup>(3,4)</sup> was modified to detect explosive vapors in air. Figure 2 shows a schematic diagram of the mass spectrometer. The gas-sampling probe is evacuated at 2–3 L/min with a diaphragm pump, and the gas sampled by the probe is introduced into the ion source. A gas introduction tube between the sampling probe and the ion source is kept at 200 °C by a heater to reduce adsorption of the sample molecules on the inner surface of the tube. The ions produced by the ion source are introduced through three apertures into a vacuum region. The differential pumping region is evacuated with a mechanical pump. The ions are focused by an Einzel lens and an electrostatic ion-guide and are mass analyzed by the ion trap mass spectrometer.

spectrometer (inner radius  $r_0$  of 16 mm, and maximum  $m/z$  of 300 amu). The mass-analysis region is evacuated to  $1 \times 10^{-5}$  Torr with a turbo-molecular pump.

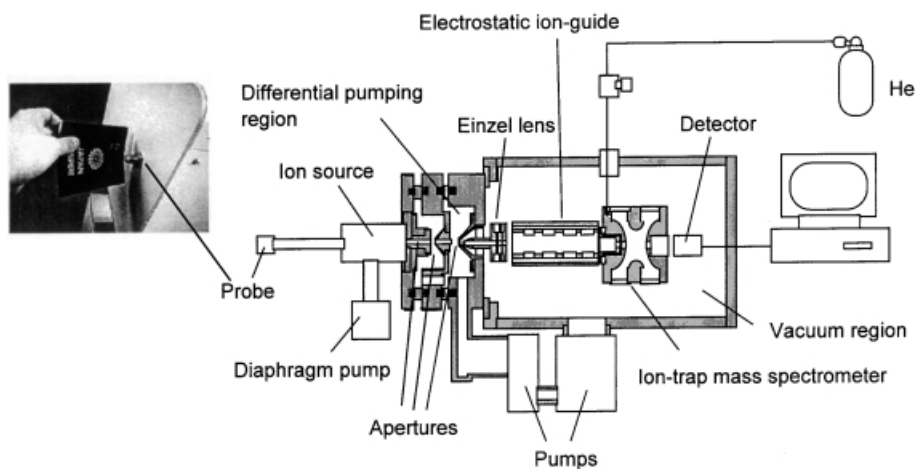
To evaluate the detection limits of our system, we used a temperature-controlled gas generator as shown in Figure 3(a). A small amount of 2,4,6-trinitrotoluene (TNT) powder (about 5 mg) is placed in the gas generator, and the temperature of the gas generator is set at 40 °C. Room air flows into the gas generator, and the gas including the TNT vapor is separated by a T-connector for sampling by three impingers as shown in Figure 3(b). The sampled gas is quantitatively analyzed by liquid chromatography with a UV detector, and the concentration of the TNT gases is calculated then compared to the S/N ratio monitored by our system.

### 3 Results and Discussion

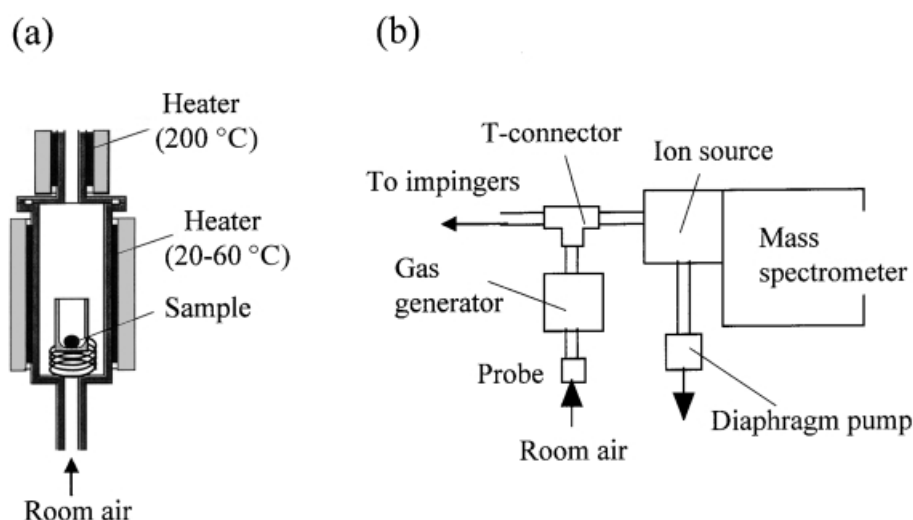
We chose 2,4-dichlorophenol (DCP) as a model compound to evaluate the new ion source because it is easily



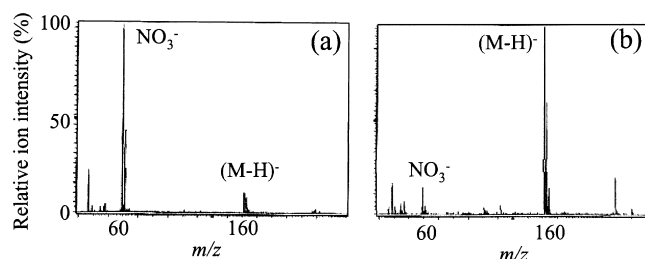
**Figure 1.** Cross-sectional view of (a) the conventional atmospheric-pressure chemical ionization (APCI) ion source, and (b) the APCI ion source with counter-flow introduction (CFI).



**Figure 2.** Schematic diagram of the new mass spectrometer for explosive-vapor detection.

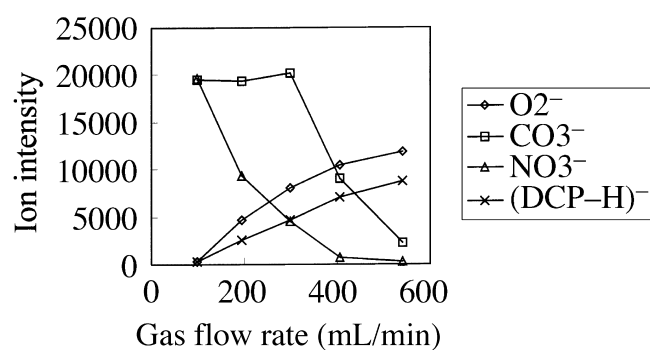


**Figure 3.** Evaluation of detection limits of our system by using TNT vapor. (a) Temperature controlled gas generator to produce TNT vapor, and (b) setup for sampling of the TNT vapor.



**Figure 4.** Negative APCI mass spectra of 2,4-dichlorophenol (DCP) obtained by (a) a conventional ion source and (b) the new ion source.

ionized by using negative-APCI mode. Typical mass spectra of DCP obtained with a conventional ion source and the new ion source are shown in Figures 4(a) and 4(b), respectively. The observed ion intensity of the DCP ions was greatly improved by using the new ion source, although the ion intensity of  $\text{NO}_3^-$  was reduced. Figure 5 shows the relationship between the gas flow rates and observed ion intensities of various ions. The intensities of the  $\text{O}_2^-$  and DCP ions increased with increasing gas flow rate, but that of  $\text{NO}_3^-$  decreased.



**Figure 5.** Relationship between the gas flow rate and observed ion intensity.

The ionization process of the DCP molecule (M) consists of two steps:

$\text{O}_2 + \text{e}^- \rightarrow \text{O}_2^-$  (primary ionization by negative corona discharge),

then

$\text{O}_2^- + \text{M} \rightarrow (\text{M}-\text{H})^- + \text{HO}_2$  (secondary ionization by ion-molecule reaction).

However, nitrogen monoxide (NO) is also produced by the corona discharge, and NO reacts with  $\text{O}_2^-$  to produce  $\text{NO}_3^-$ . This reaction reduces the concentration of  $\text{O}_2^-$  and affects the ionization efficiency of the sample molecules. In our new ion source, neutral NO molecules are eliminated from the secondary ionization region by the gas flow.

Eliminating the NO produced by the corona discharge from the secondary ionization region gives another advantage; i.e.,  $\text{NO}_x$  (NO and  $\text{NO}_2$ ) molecules dissociated from nitro-compounds can be analyzed by using the new ion source. In other words, our system can analyze concentrations of NO and  $\text{NO}_2$  at the same time, although the current Abel heat test simply checks  $\text{NO}_2$  concentration evaporated from explosives<sup>(5)</sup>. Decomposition processes of various explosives are very complicated, because they depend on the composition of chemicals, interaction between stabilizers and nitro-compounds, temperature of the explosives, and the amount of time from the date of manufacture. Therefore, independent analysis of NO and  $\text{NO}_2$  would be very useful for quality control of explosives. Analysis of the decomposition processes of various explosives will be a future task of the new system.

We evaluated the detection limit of our system by using TNT vapor. In the mass spectrometry (MS) analysis mode, the detection limit was determined according to chemical noise of about 10–20 ppt. However, in the mass spectro-

metry/mass spectrometry (MS/MS) analysis mode, the detection limit was lowered by reducing chemical noise. So a concentration of 0.3 ppt can be detected within a few seconds. In the MS/MS mode, detection limit depends on the analysis time, so it will be further reduced by setting a longer detection interval.

We tested our system in detecting military explosives. Figure 6 shows the TNT signal from the piece of the explosive Composition B at room temperature. The sample was taken out from a hand grenade made in Belgium.

$M^-$  ions of TNT were monitored ( $m/z = 227$ ). When the sample was placed near the sampling probe, a strong signal was observed on the mass chromatogram. The detection time was about one second, and the S/N ratio was about 50. In this case, MS analysis mode was used, but the sensitivity and selectivity of the system could be further improved if the MS/MS analysis mode was used.

Figure 7 shows the detection of TNT from an anti-personnel land mine. The mine was made in the United

States in 1944. It looks like an all-metal block, but there is a small hole for setting the blasting cap. Vapors from the internal explosives come out through the hole, and attach to the surface of the mine. Because we could not carry the mine into our laboratory, we wiped the surface of the mine with a cotton swab. The next day, we checked the swab by our system. When the swab was moved close to the sampling probe, a TNT signal was detected. This result shows that our system is suitable for a simple wiping test as well as on-line real-time detection.

Figure 8 shows the detection of nitro-compounds from plastic explosives C-4. 1,3,5-Trinitro-1,3,5-triazacyclohexane (RDX) was detected by MS/MS analysis. The observed  $m/z$  was 46 ( $NO_2^-$ ), which is the result of fragmentation of ions dissociated from larger molecular ions with  $m/z$  268 ( $NO_2^-$  adduct ion of RDX). Low vapor pressure explosives such as RDX can be detected in a few seconds without any pretreatment of samples; namely, no heating, no concentration, or no cleaning up of gases.

Checking hands by using a trace detector is one of the important measures for counterterrorism, because nitro-compounds are easily adsorbed on the hands when handling explosives. Figures 9(a) and 9(b) show that the detection of TNT stuck to a hand. When the TNT-contaminated hand was moved close to the sampling probe a strong signal was detected on the mass chromatogram (Fig. 9(a)). After washing the hand several times in soap and water very carefully, the TNT signal was still detected as shown in Figure 9(b).

The above described results show that detection speed, sensitivity and selectivity of this explosive detection system are good enough for on-line use in various applications such as baggage checking for airport security.

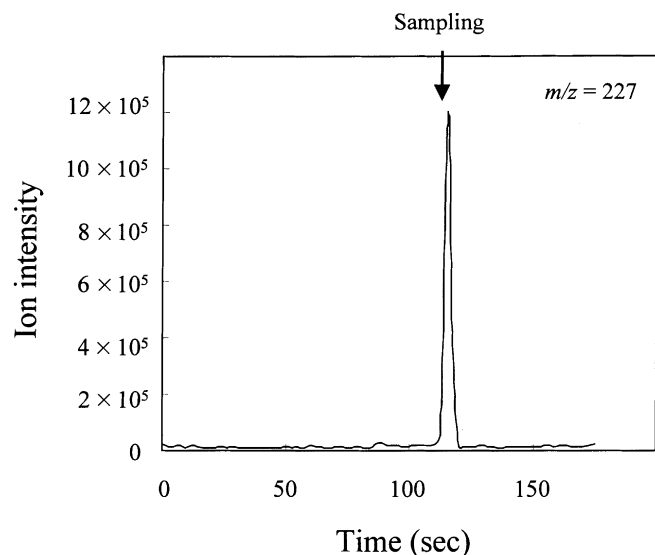


Figure 6. TNT signal from Composition B.

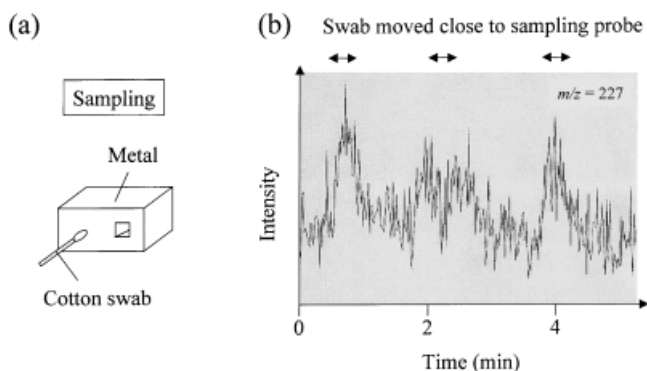


Figure 7. Detection of explosives from an anti-personnel land mine. (a) Sampling of explosives by cotton swab, and (b) TNT signal from the swab.

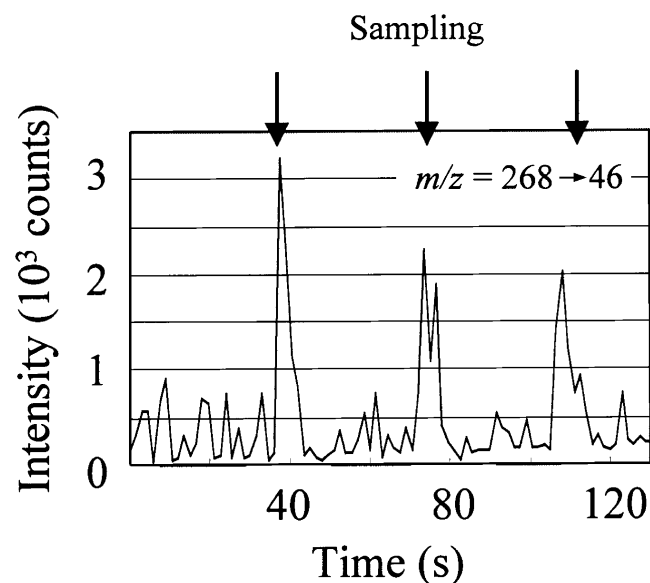
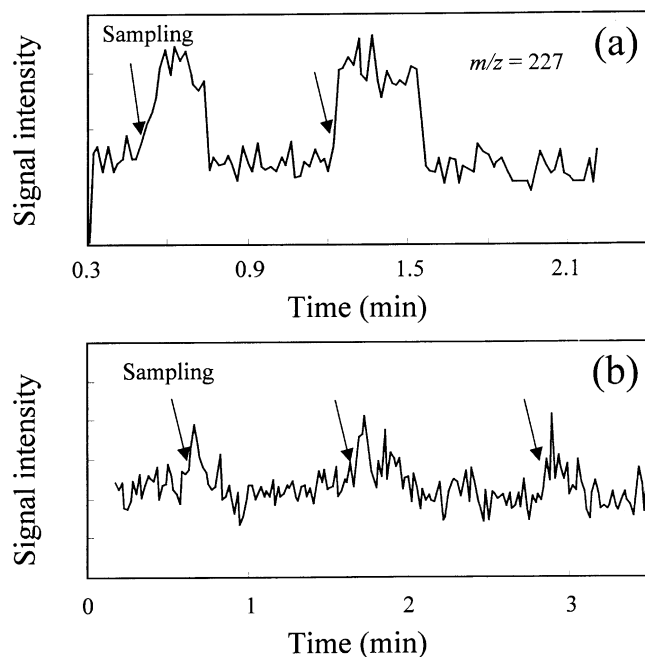


Figure 8. Detection of the plastic explosive C-4. Signals from main component RDX.



**Figure 9.** TNT signal stuck to a hand: (a) after wiping the hand by a cloth, and (b) after washing the hand several times in soap and water.

#### 4 Conclusion

To detect vapors from military explosives, we have developed a new detection system based on the novel ion

source for atmospheric pressure chemical ionization. Our test results show that the system is suitable for on-line detection of explosives; that is, it can detect major conventional explosives within a few seconds without sample pre-treatment. In the near future, we will further reduce the size and cost of the system for use in practical security fields.

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#### Acknowledgements

We would like to thank Dr. Tsuchihashi and Dr. Miki of Osaka Prefectural Police Headquarters and Mr. Torii of NOF Corporation for their helpful comments. We also thank Dr. Kojima of Hitachi, Ltd., for her technical support.

(Received December 12, 2001; Ms 2001/066)

Henrikus Steen (Hrsg.)

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