

Continuous Real-time Monitoring of Chemical Warfare Agents with High Sensitivity by Atmospheric Pressure Chemical Ionization Mass Spectrometry (APCI-MS)

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Objective

Continuous real-time monitoring of low levels of CWAs in air

Method

APCI-MS* with direct air-sampling

*Atmospheric pressure chemical ionization mass spectrometry

Results

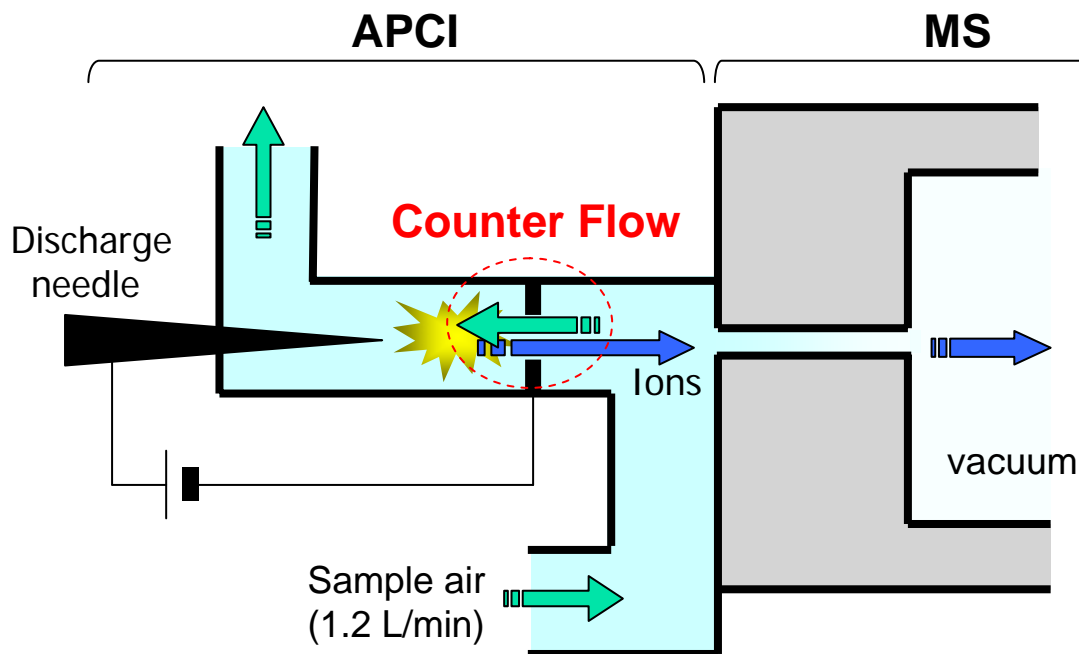
Detection limit (in real-time, 1s):

Sub $\mu\text{g}/\text{m}^3$ for various CWAs

Detection limit (in real-time, 1s) through 35-m tube:

1 $\mu\text{g}/\text{m}^3$ for HD and L1

APCI with Counter Flow Introduction (CFI)



APCI: Soft ionization → molecular weight information

APCI with CFI: Less unwanted ion-molecule reactions
→ simple spectra (**specific** and **sensitive** detection)

Mass Spectrometer

Quadrupole mass spectrometer (Single mass spectrometry)

- High sensitivity
- Small size



DS-100 (Hitachi, Ltd.)

Ion trap mass spectrometer (Tandem mass spectrometry, MS/MS)

- High selectivity
→ Low detection limit

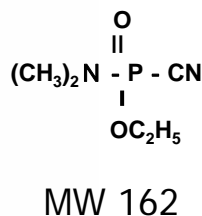
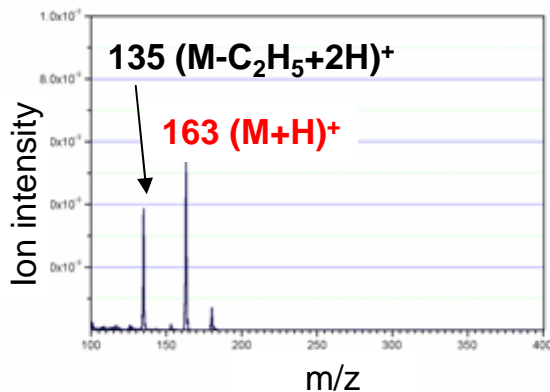


DS-1000 (Hitachi, Ltd.)

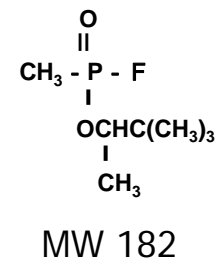
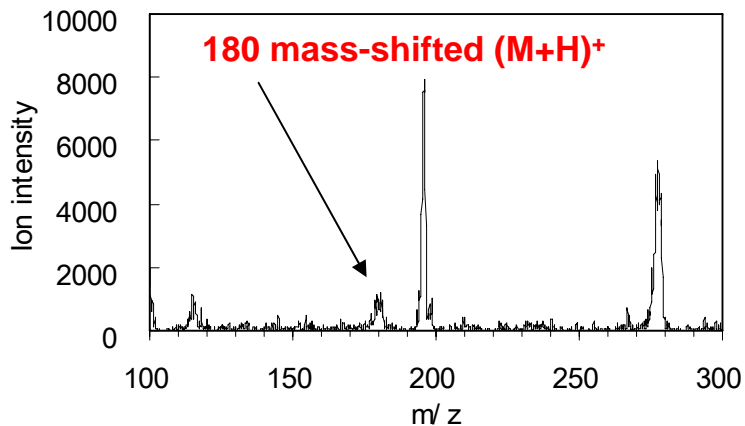
Mass Spectrum (GA, GB, GD, CN)

HITACHI
Inspire the Next

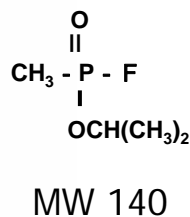
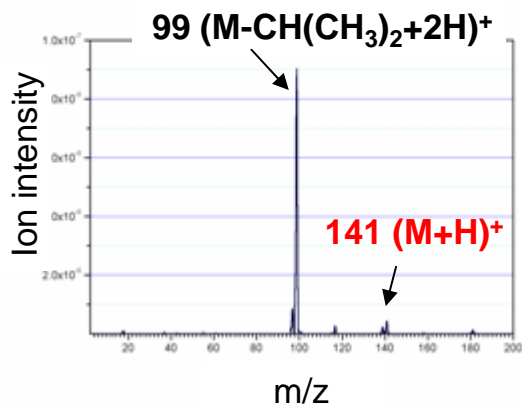
Tabun (GA)



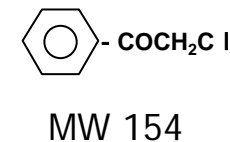
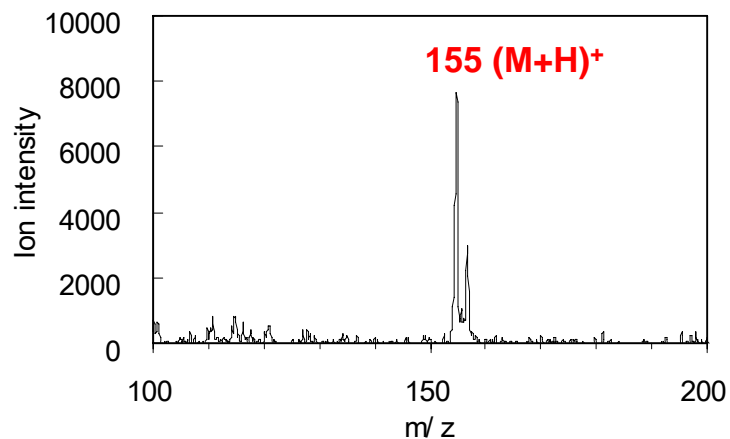
Soman (GD)



Sarin (GB)

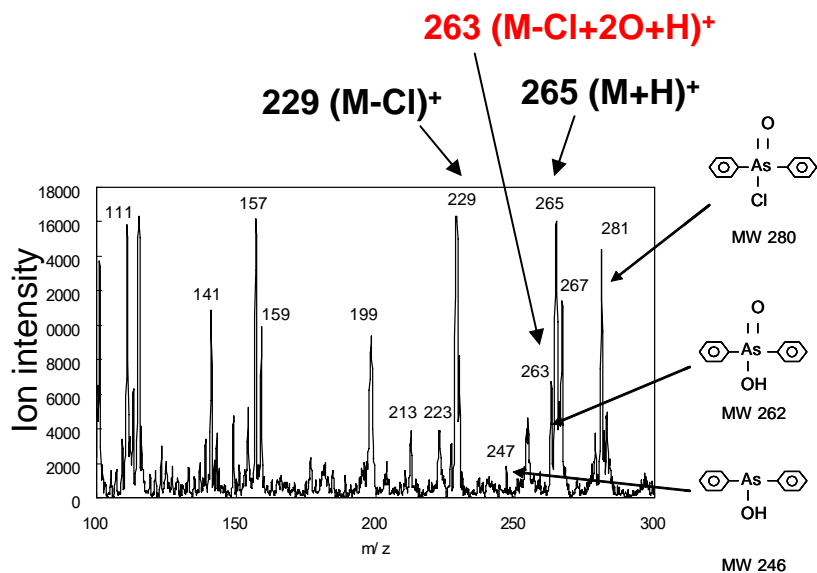
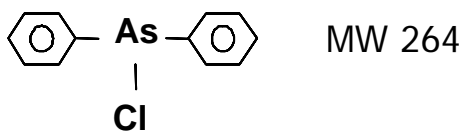


Chloroacetophenone (CN)

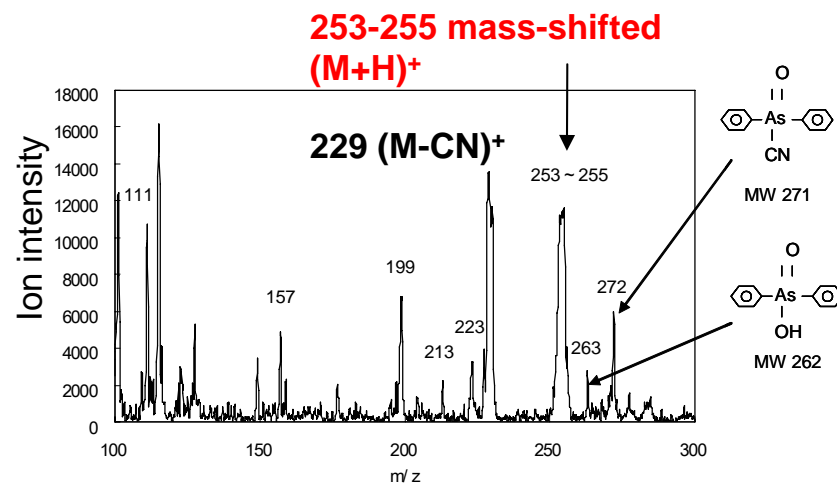
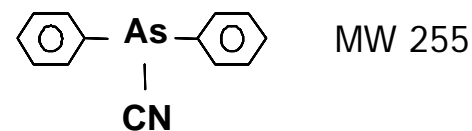


Mass Spectrum (DA, DC)

Diphenylchloroarsine (DA)



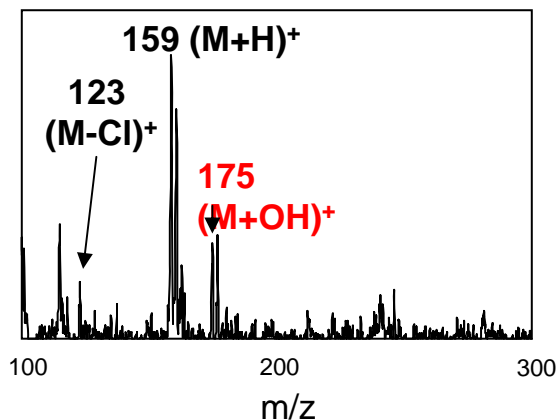
Diphenylcyanoarsine (DC)



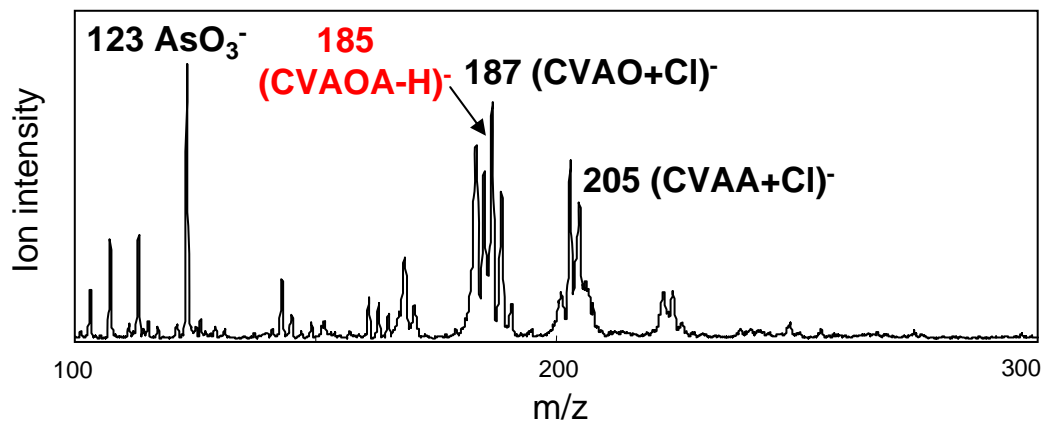
Mass Spectrum (HD, L1)

Mustard gas (HD)

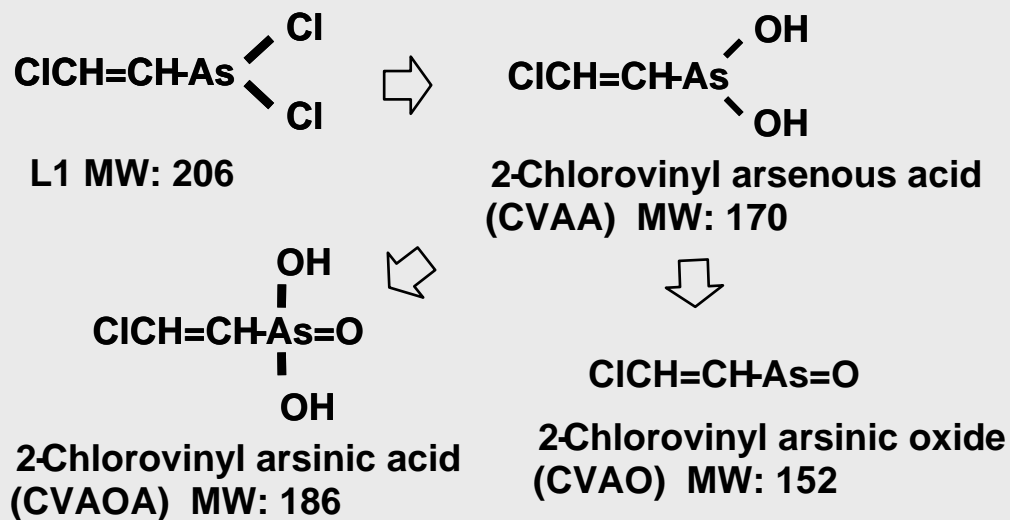
$S(CH_2-CH_2-Cl)_2$ MW 158



Lewisite 1 (L1)

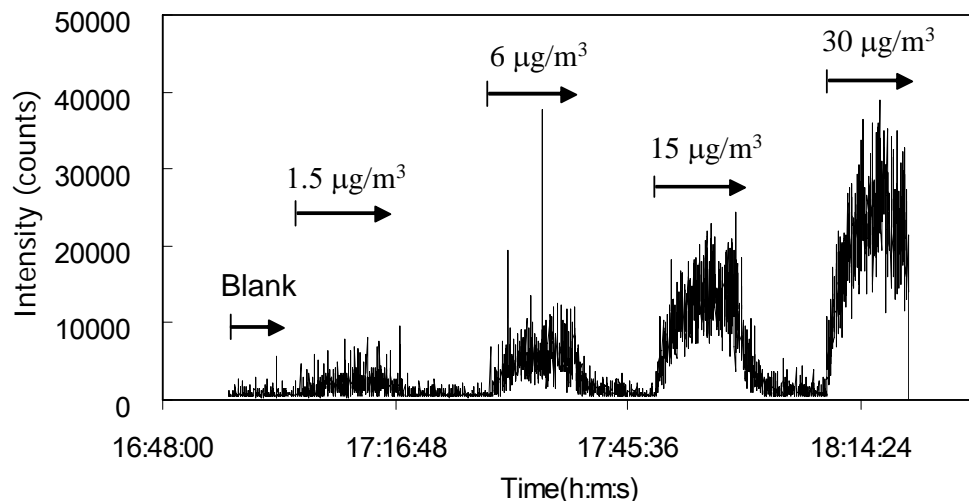


Decomposition of L1 in environment

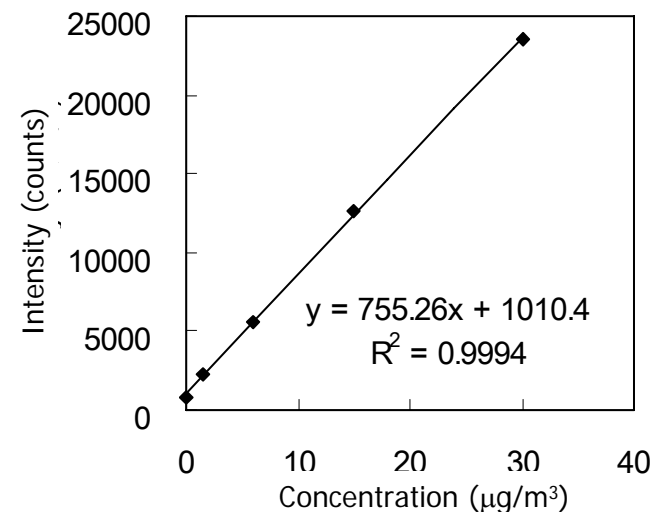


Detection limit (HD) by Tandem MS

Signal profile (m/z175→77) for various conc. of HD in 10-L container

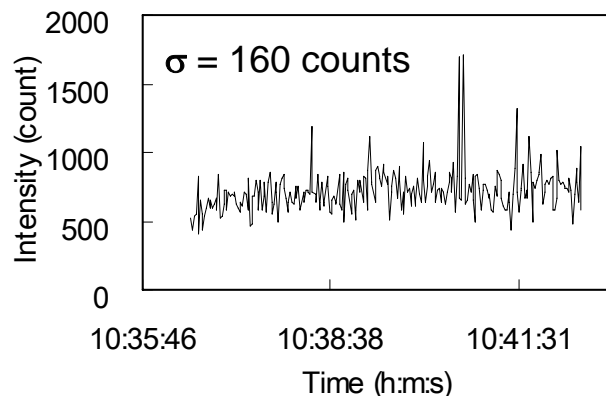


Calibration curve



Sensitivity
= 760 counts/($\mu\text{g}/\text{m}^3$)

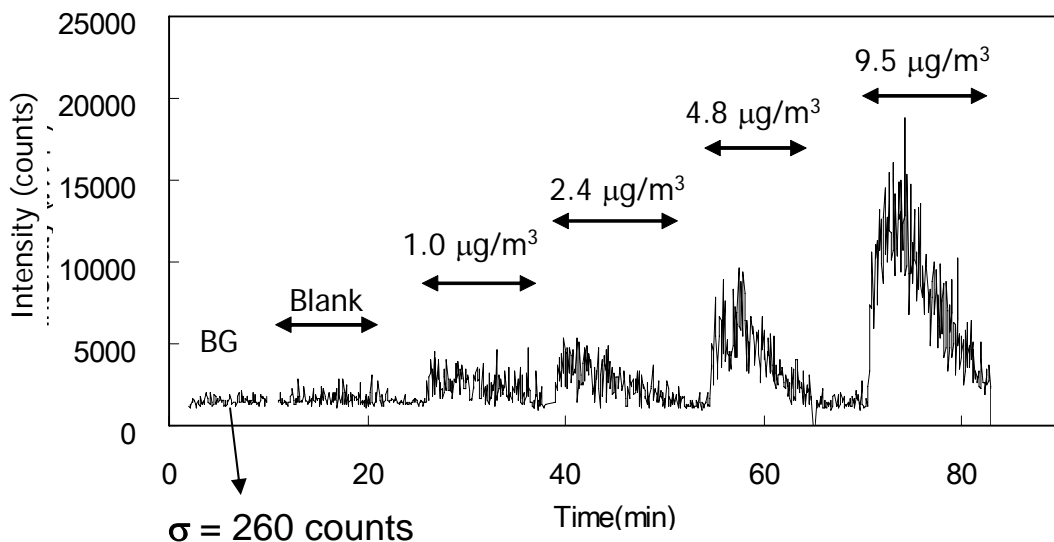
Background deviation (Lab. air)



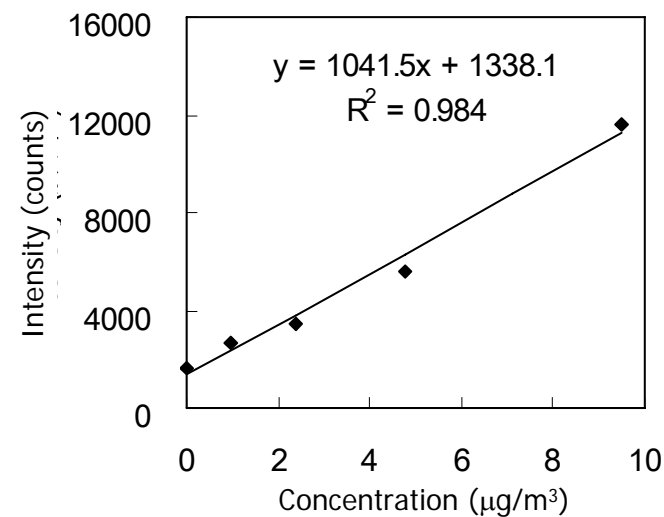
3σ Detection limit:
 $0.63 \mu\text{g}/\text{m}^3$ (1s)

Detection limit (L1) by Tandem MS

Signal profile (m/z185→123) for various conc. of L1 in 10-L container



Calibration curve

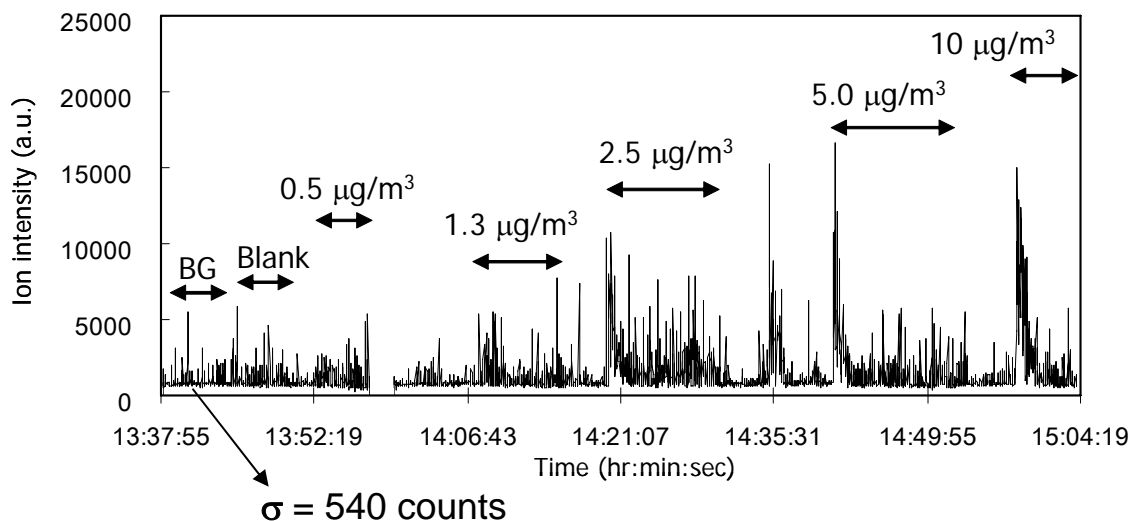


Sensitivity
= 1000 counts/ $(\mu\text{g}/\text{m}^3)$

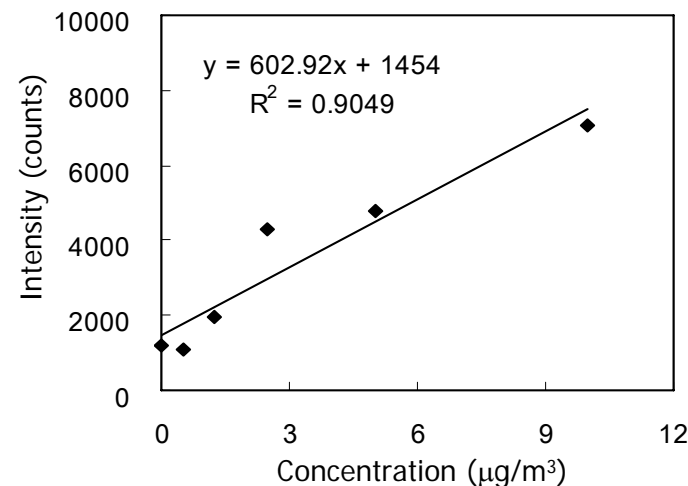
3σ Detection limit:
0.63 $\mu\text{g}/\text{m}^3$ (1s)

Detection limit (DA) by Tandem MS

Signal profile (m/z263→245) for various conc. of DA in 10-L container



Calibration curve

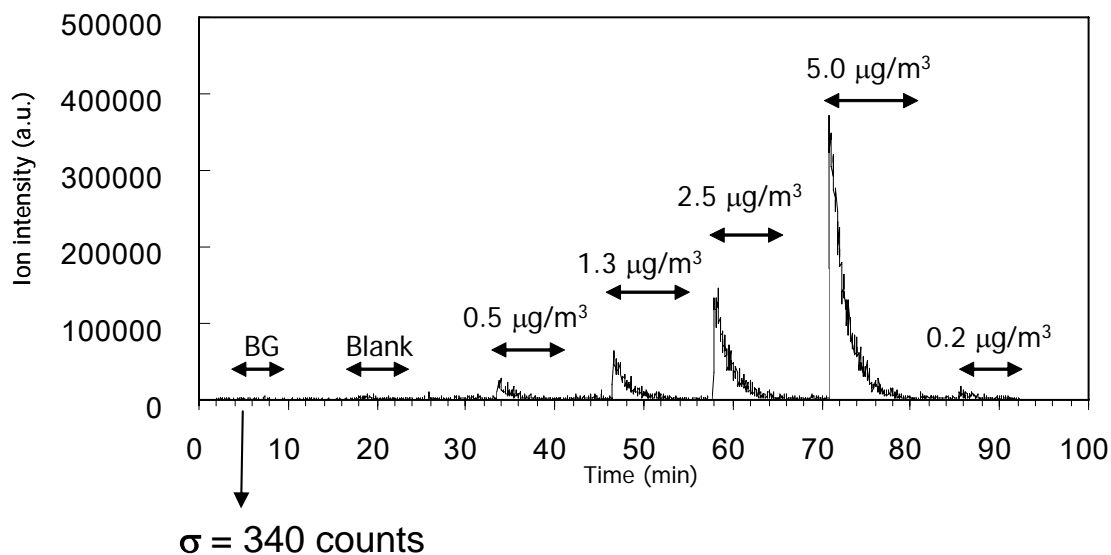


Sensitivity
= 600 counts/ $(\mu\text{g}/\text{m}^3)$

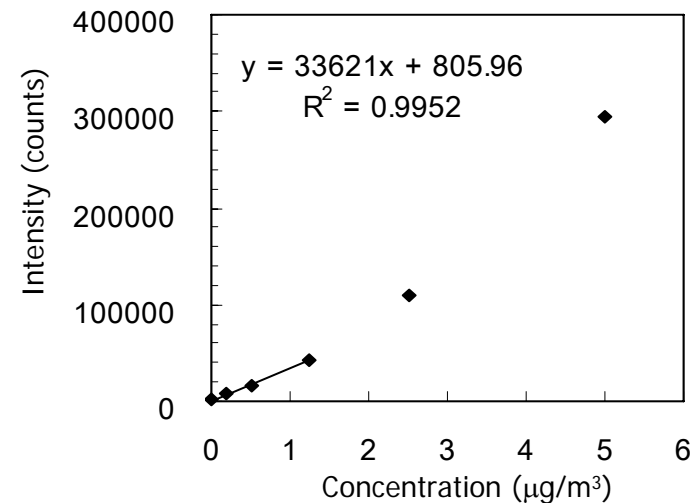
**3σ Detection limit:
2.7 $\mu\text{g}/\text{m}^3$ (1s)**

Detection limit (DC) by Tandem MS

Signal profile (m/z255→229) for various conc. of DC
in 10-L container



Calibration curve

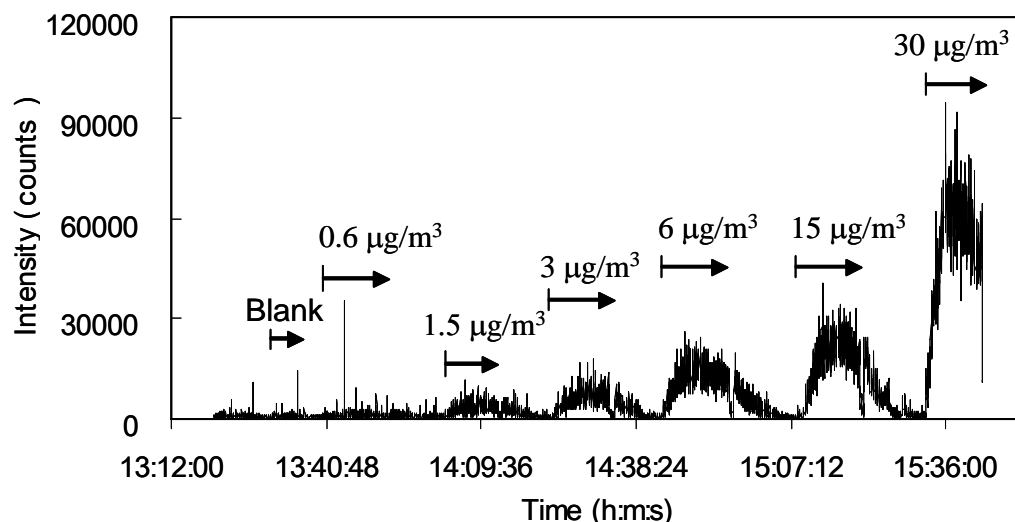


Sensitivity
= 34000 counts/ $(\mu\text{g}/\text{m}^3)$

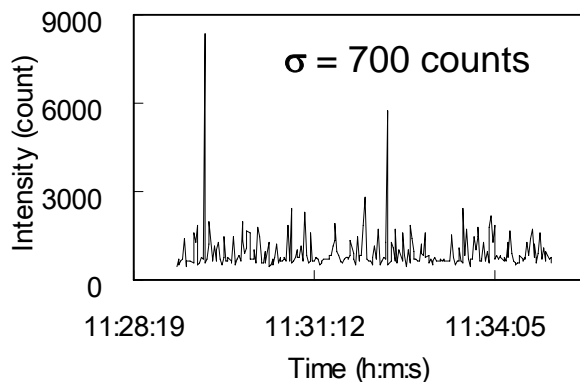
**3σ Detection limit:
0.03 $\mu\text{g}/\text{m}^3$ (1s)**

Detection limit (HD): 35-m tube

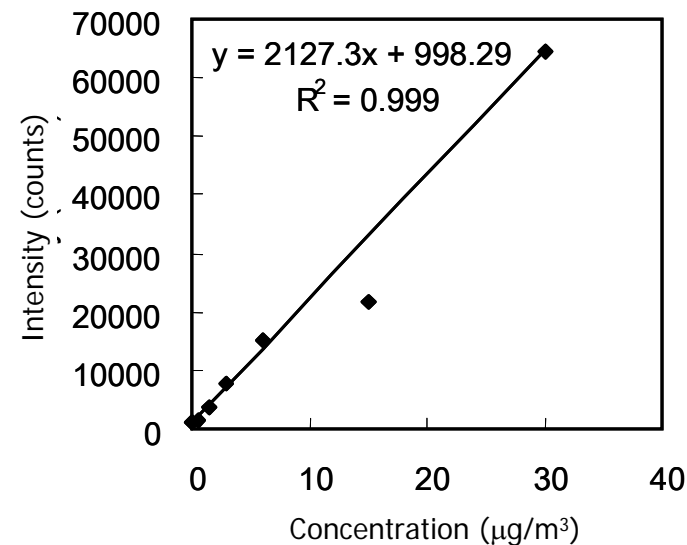
Signal profile (m/z175→77) for various conc. of HD in 10-L container



Background deviation (Lab. air)



Calibration curve

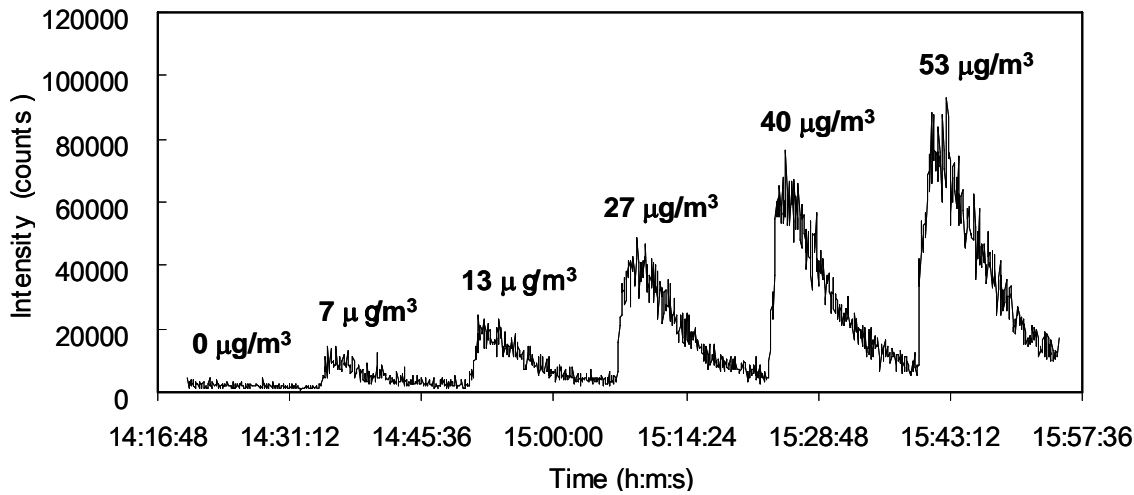


Sensitivity
= 2100 counts/ $(\mu\text{g}/\text{m}^3)$

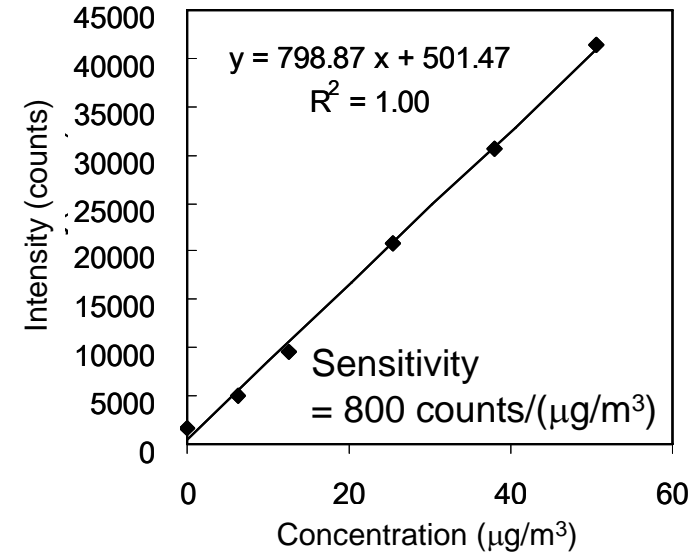
3 σ Detection limit:
1.0 $\mu\text{g}/\text{m}^3$ (1s)

Detection limit (L1): 35-m tube

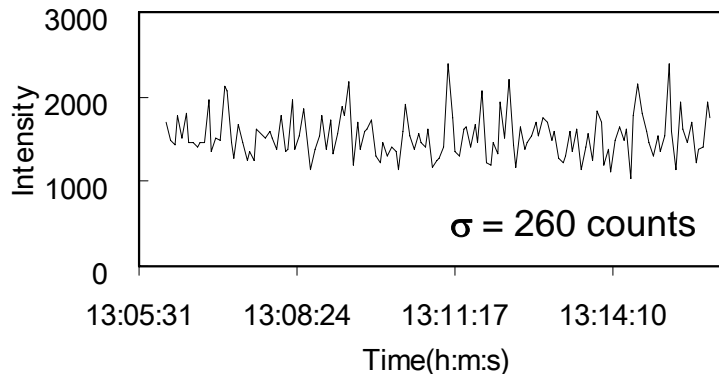
Signal profile (m/z185→123→107) for various conc. of L1 at MS inlet



Calibration curve



Background deviation (Lab. air)



3 σ Detection limit:
0.98 µg/m³ (1s)

Detection limits for vaporized CWAs with APCI-MS

Type	Agent	Detection marker	3 σ detection limit [$\mu\text{g}/\text{m}^3$]	
			Single MS (3min)	Tandem MS (1s)
Nerve gas	Tabun (GA)	(M+H) ⁺	0.16	n/a
	Sarin (GB)	(M+H) ⁺	0.07	n/a
	Soman (GD)	(M+H) ⁺	0.30	n/a
Blister agent	Mustard gas (HD)	(M+OH) ⁺	0.12	0.6 (1*)
	Lewisite 1 (L1)	(M-2Cl+3O+H) ⁻	0.70	0.6 (1*)
Vomit agent	Diphenylchloroarsine (DA)	(M-Cl+2O+H) ⁺	n/a	3
	Diphenylcyanoarsine (DC)	(M+H) ⁺	n/a	0.03
Tear gas	Chloroacetophenone (CN)	(M+H) ⁺	0.10	n/a

* through 35-m Tube