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# A noble approach for the trace analysis of monomethyl mercury using gas chromatography-time-of-flight mass spectrometry with thermal desorption (TD-GC-TOF MS)

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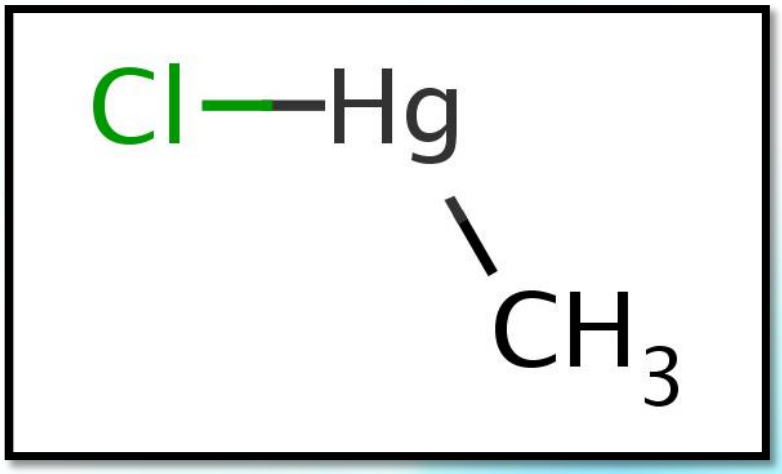
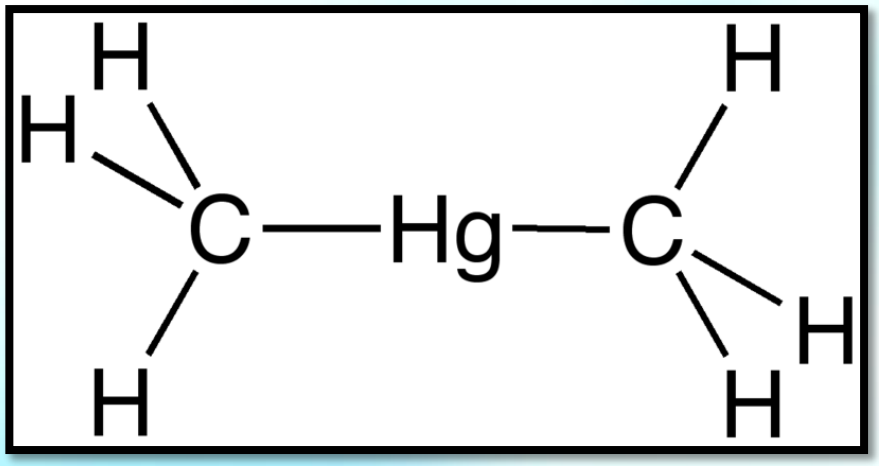
# 1. Introduction

# 1. Introduction

- Organic mercury species usually have the formula: (1) $HgR_2$: often volatile and (2) HgRX: often solids; here, R is alkyl and X is usually halide or acetate.




- methyl mercury chloride (MMC) and dimethyl mercury

http://www.molport.com/buy-chemicals/moleculelink/chloro-methyl-mercury/3930297

http://en.wikipedia.org/wiki/Dimethyl_mercury

# 2. General analysis of organic mercury

## 2. General analysis of organic mercury

- **Single detection system**

a. GC + Electron Capture Detector (ECD)

b. Gas (or Liquid) chromatography-Mass spectrometry (GC (LC)-MS)

c. GC-MS with derivatization

d. GC-MS with thermal desorption

- **Hypernated detection system**

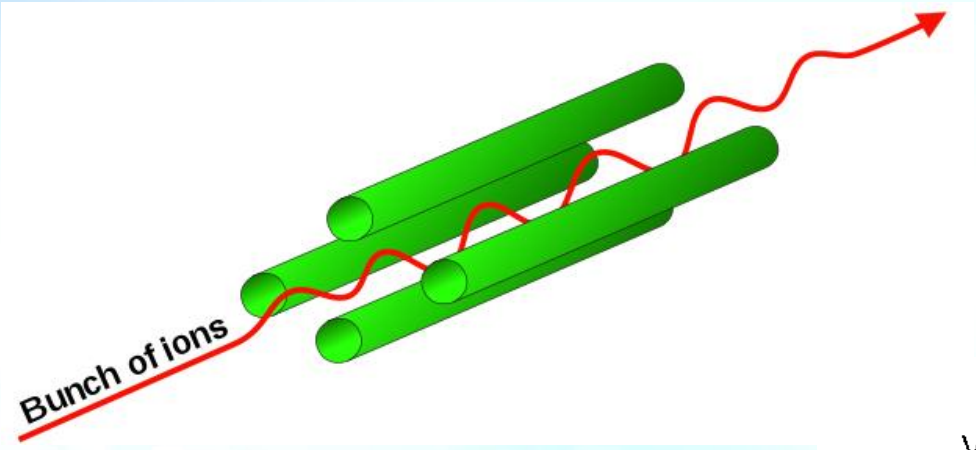
a. GC + Atomic Absorption Spectrometry (AAS)

b. GC + Atomic Fluorescence Spectrophotometer (AFS)

c. GC-MS + Inductively Coupled Plasma mass spectrometry (ICP-MS)

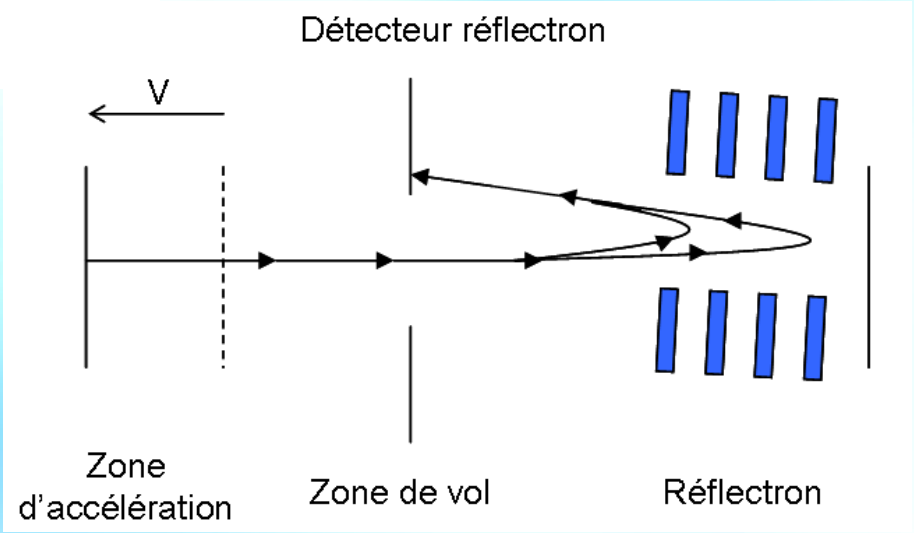
- **High sensitivity of TOF MS**

**(comparison of mass spectrometry between quadrupole and time-of-flight)**




← Quadrupole mass spectrometry

Time-of-flight mass spectrometry →



# Ultra-sensitivity of TOF-GC-MS

Table. Detectability of VOC by TD-TOF-GC-MS

Kim Y.-H., Kim K.-H.* (2012) Ultimate detectability of volatile organic compounds: How much further can we reduce their ambient air sample volumes for analysis? Analytical Chemistry. In Press

US EPA TO-17: Recommended Typical Sampling Volume of 1 to 4 L

Actual detection mass (ADM) from real ambient air

| Order | Compounds | Minimum detection volume (mL) | | Actual detection mass (Concentration) (pg (ppb))[b] | | ADM/MDL (pg/pg) | |
|---|---|---|---|---|---|---|---|
| | | TOF MS | Q MS | TOF MS[c] | Q MS | TOF MS | Q MS |
| 1 | AA | 2 | ND | 21.2 (6.02) | ND | 0.49 | - |
| 2 | PA | 0.5 | ND | 1.60 (1.37) | ND | 0.32 | - |
| 3 | BA | ND | ND | ND | ND | - | - |
| 4 | IA | ND | ND | ND | ND | - | - |
| 5 | VA | 2 | ND | 5.32 (0.77) | ND | 1.91 | - |
| 6 | B | 1 | 50 | 1.94 (0.62) | 128 (0.82) | 0.46 | 0.63 |
| 7 | T | 0.5 | 20 | 4.14 (2.25) | 383 (5.19) | 1.56 | 2.43 |
| 8 | S | 1 | ND | 1.08 (0.26) | ND | 0.26 | - |
| 9 | p-X | 0.5 | 200 | 0.41 (0.19) | 287 (0.34) | 0.26 | 1.97 |
| 10 | m-X | 0.5 | 100 | 0.75 (0.35) | 318 (0.75) | 0.15 | 2.28 |
| 11 | o-X | 0.5 | 100 | 0.23 (0.11) | 110 (0.26) | 0.15 | 0.79 |
| 12 | MEK | ND | ND | ND | ND | - | - |
| 13 | MIBK | ND | ND | ND | ND | - | - |
| 14 | i-BuAl | ND | ND | ND | ND | - | - |
| 15 | BuAc | 2 | ND | 2.41 (1.57) | ND | 2.37 | - |
| 16 | PPA | ND | ND | ND | ND | - | - |
| 17 | BTA | ND | ND | ND | ND | - | - |
| 18 | IVA | ND | ND | ND | ND | - | - |
| 19 | VLA | ND | ND | ND | ND | - | - |
| | **Mean** | **1.05** | **94.0** | **3.91 (1.35)** | **245 (1.47)** | **0.79** | **1.62** |
| | SD | 0.69 | 68.4 | 6.29 (1.78) | 120 (2.10) | 0.82 | 0.85 |
| | Min | | | o-X: 0.23 (0.11) | o-X: 110 (0.26) | m-X: 0.15 | B: 0.63 |
| | Max | | | AA: 21.2 (6.02) | T: 383 (5.19) | BuAc: 2.37 | T: 2.43 |

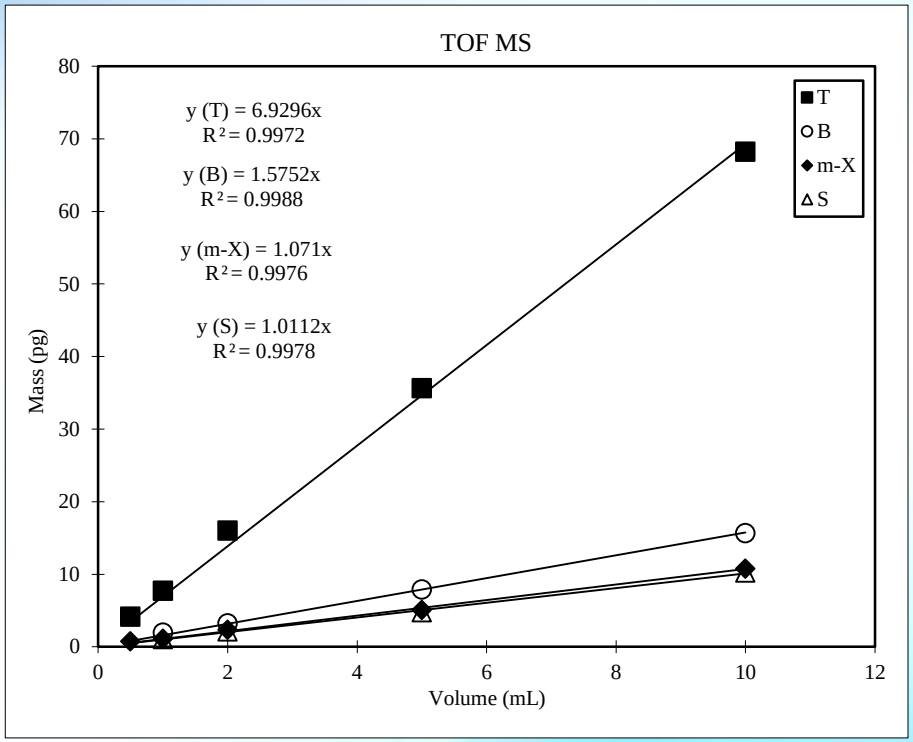
[a] Test based on the analysis of VOC in ambient air

sample volume: (1) TOF MS = 0.5, 1, 2, 5 and 10 mL; and (2) Q MS = 10, 20, 50, 100, and 200 mL

[b] For the derivation of molar ratio (ppb), the minimum sample volume for the first detection was used (e.g., 2 mL for VA by TOF MS)

# Ultra-sensitivity of TOF-GC-MS

- Results of actual ambient VOC (BTSX) sample analysis -



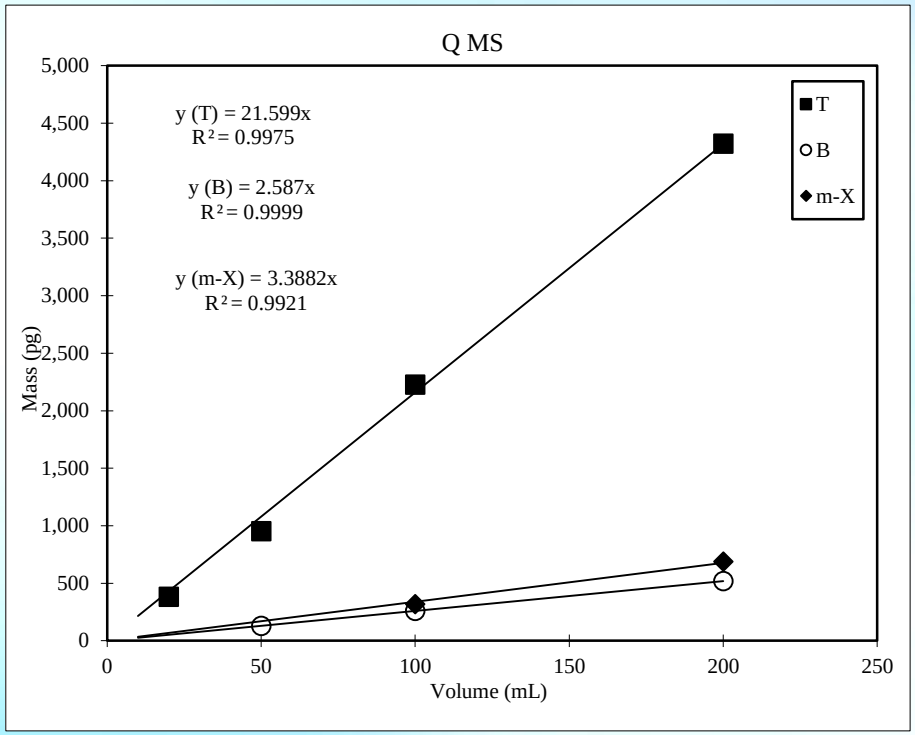
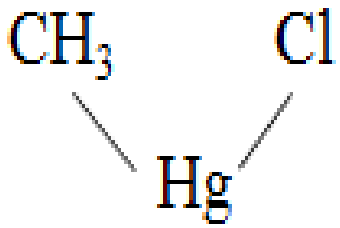




Fig. 5. The stability of quantifiable components in ambient air sample with decreasing sample volume from 10 mL (TOF MS: left) and 200 mL (Q MS: right): relationship between sample volume and quantified mass of target compounds.

# 3. Analysis of MMHg using TOF MS

- **Target compound**

Table 1. Information of methyl mercury chloride

| | | |
|---|---|---|
| Compounds: | Methyl mercury chloride | Chemical structure |
| Short name: | MMC |  |
| MW (g $mol^{-1}$): | 251.08 | |
| Density (g $mL^{-3}$): | 4.063 | |
| Melting point (℃): | 170 | |
| Formula: | $CH_3HgCl$ | |
| CAS number: | 115-09-3 | |

## Preparation of liquid phase MMC standard

Table 2. Preparation of MMC standard for the analysis by the TD-GC-MS system

a. Preparation of liquid phase MMC standard

| | Compounds | 6N HCl | MMC |
|---|---|---|---|
| Primary grade chemical | Concentration (%) | 100 | 95.0 |
| | Density (g $mL^{-1}$) | 1.10 | 4.06 |
| PS[a] | Bulk mass (mg) | 220,400 | 316 |
| | Real mass (mg) | 220,400 | 300 |
| | Volume (mL) | 201 | 0.08 |
| | Concentration (ng $\mu L^{-1}$) | | 1,492 |
| | | Methanol | MMC |
| 1st WS[b] | Volume (μL) | 19,880 | 120 |
| | Concentration (ng $\mu L^{-1}$) | | 8.95 |

[a] PS: Dilution of pure chemical (primary grade chemical)

[b] 1st WS: Dilution of PS to make in 20 mL solution

# 3. Analysis of MMHg using TOF MS

b. Preparation of final working standard (F-WS) for 8 point calibration: absolute mass (ng) of MMC loaded on the sorbent tube (ST) sampler

| Order | Mixing volume (μL) | | Concentration[c] (ng μL$^{-1}$) |
|---|---|---|---|
| | 1st WS | Methanol | MMC |
| 1 | 40 | 19,960 | 0.018 |
| 2 | 100 | 19,900 | 0.045 |
| 3 | 200 | 19,800 | 0.090 |
| 4 | 2,000 | 18,000 | 0.895 |
| | PS | Methanol | MMC |
| 5 | 60 | 19,940 | 4.48 |
| 6 | 120 | 19,880 | 8.95 |
| 7 | 240 | 19,760 | 17.9 |
| 8 | 600 | 19,400 | 44.8 |

[c] Analysis volume: 1 μL

# 3. Analysis of MMHg using TOF MS

## TD-GC-TOF MS system

Table 3. Operational conditions of TD-GC-MS system for the analysis of MMC

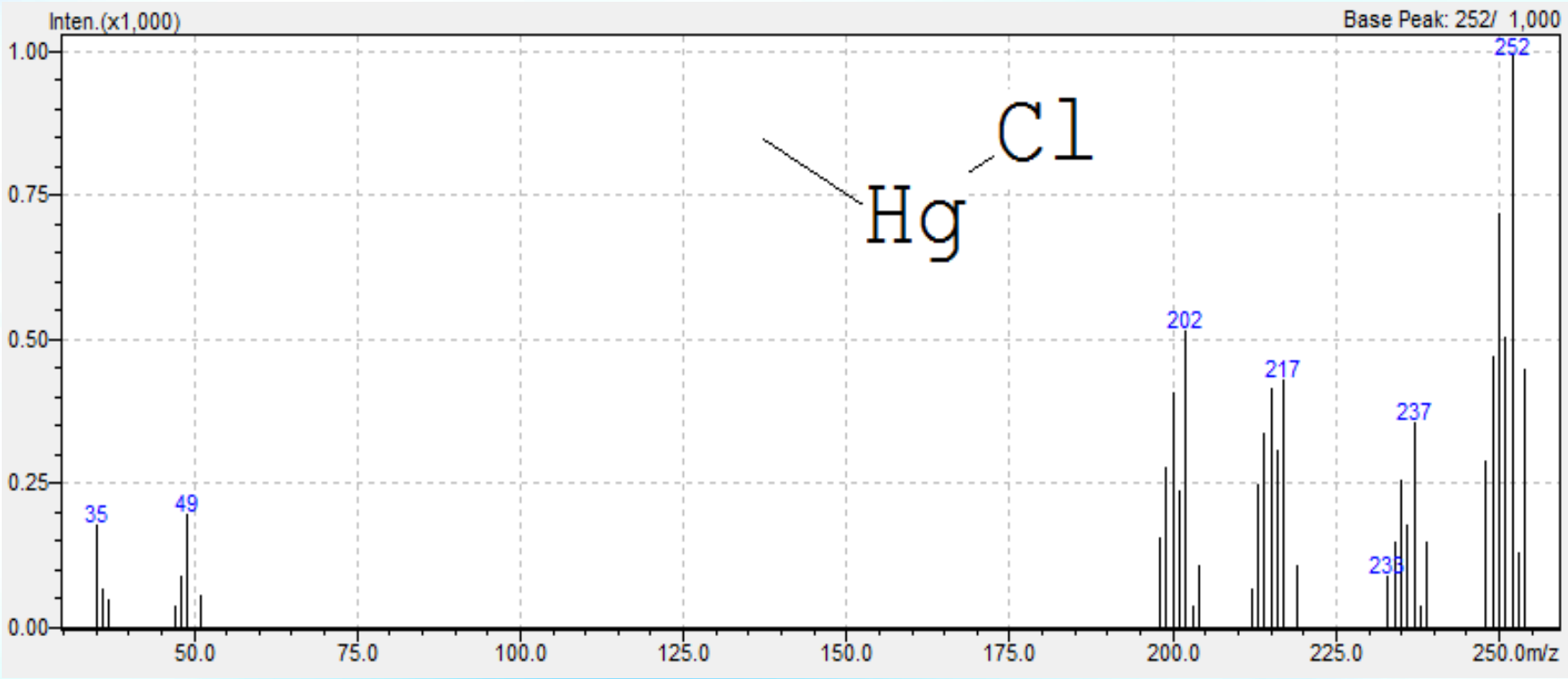
| | | | |
|---|---|---|---|
| **A. GC (Agilent GC 7890A, USA) and TOF MS (Almsco Bench TOF-dx, UK)** | | | |
| Column: CP Wax (diameter: 0.25 mm, length: 30 m, and film thickness: 0.25 µm) | | | |
| Oven setting | | Detector setting | |
| Oven temp: | 100 ℃ (5 min) | TIC scan range: | 35~260 m $z^{-1}$ |
| Oven rate: | 20 ℃ $min^{-1}$ | EIC range: | 198~202, 213~217 |
| Max oven temp: | 210℃ (9.5 min) | (m $z^{-1}$) | 233~237, 248~254 |
| Total time: | 20 min | Ion source temp.: | 230 ℃ |
| Carrier gas: | He (99.999%) | Interface temp.: | 230 ℃ |
| **B. Thermal desorber (Unity, Markes, UK)** | | | |
| Cold trap: | Carbopack B+ Tenax TA | Trap low: | - 10 ℃ |
| Split mode: | Splitless | Trap high: | 320 ℃ |
| Trap hold time: | 20 min | Flow path temp: | 150 ℃ |
| **C. Sorbent (Sampling) Tube** | | | |
| Sorbent material: | Tenax TA + Carbopack B + Carboxen 1000 (mass ratio=1:1:1) | | |
| Desorption flow: | 50 mL $min^{-1}$ | | |
| Desorption time: | 5 min | Temp.: | 300 ℃ |

# 3. Analysis of MMHg using TOF MS

- **Sorbent tube (Tenax TA + Carbopack B + Carboxen 1000)**

# 3. Analysis of MMHg using TOF MS

- **Mass spectrum of MMC**



# 3. Analysis of MMHg using TOF MS

- **Chromatogram**

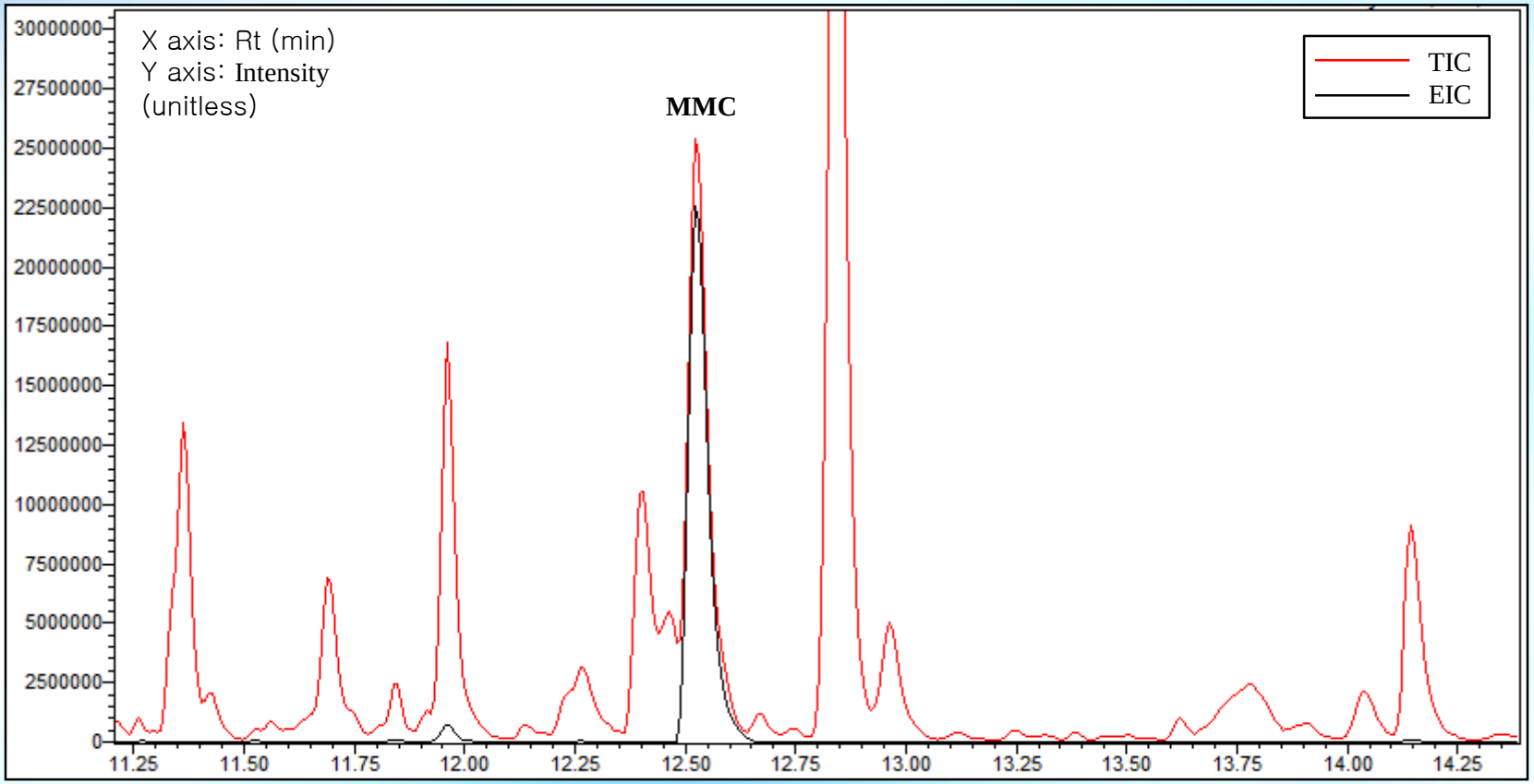
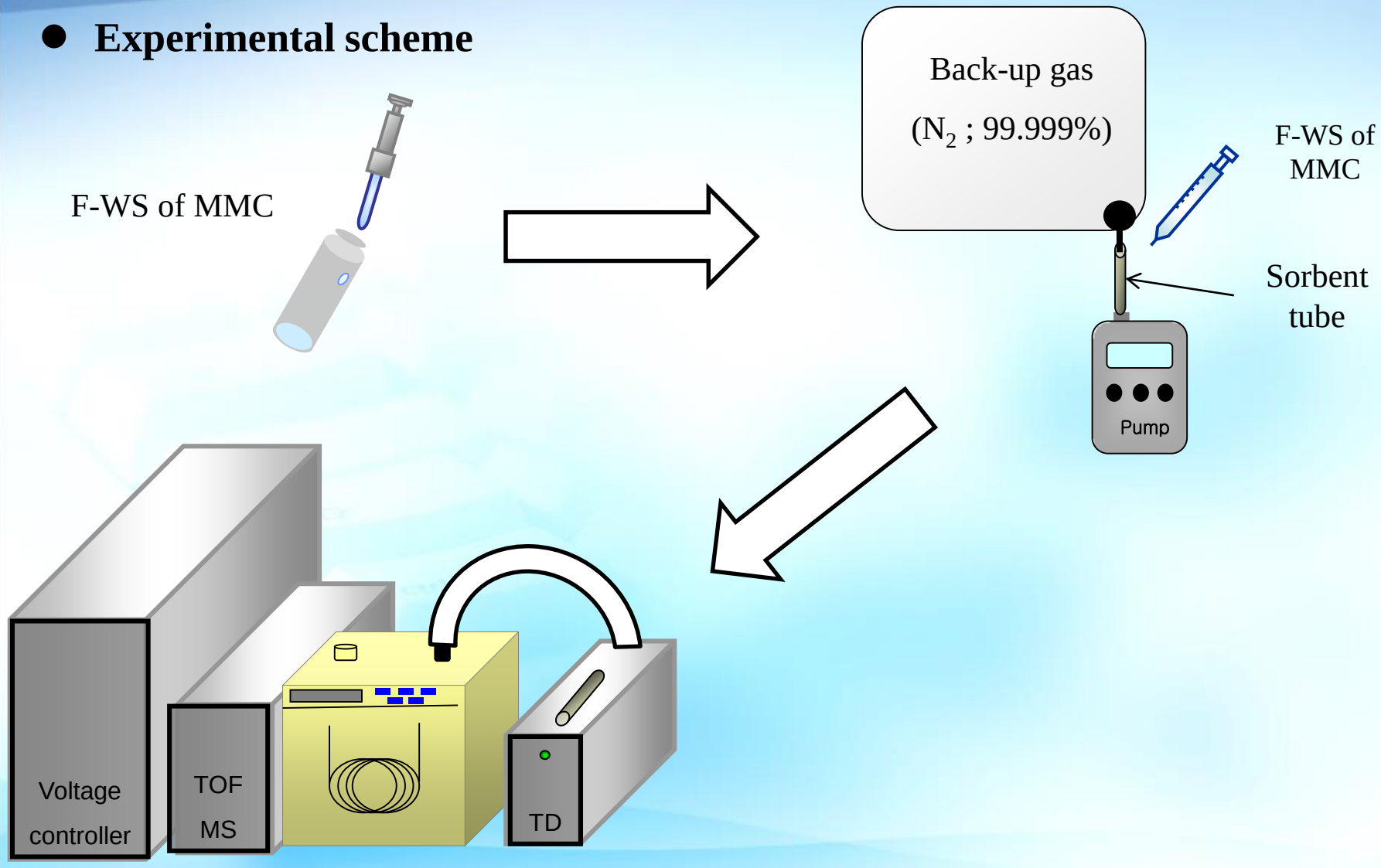



Figure 1.Chromatogram of 4.48 ng µL-1of F-WS determined by the two scan modes (TIC vs. EIC)

# 3. Analysis of MMHg using TOF MS

- **Experimental scheme**



# 4. Results of this study

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- **Calibration curve**

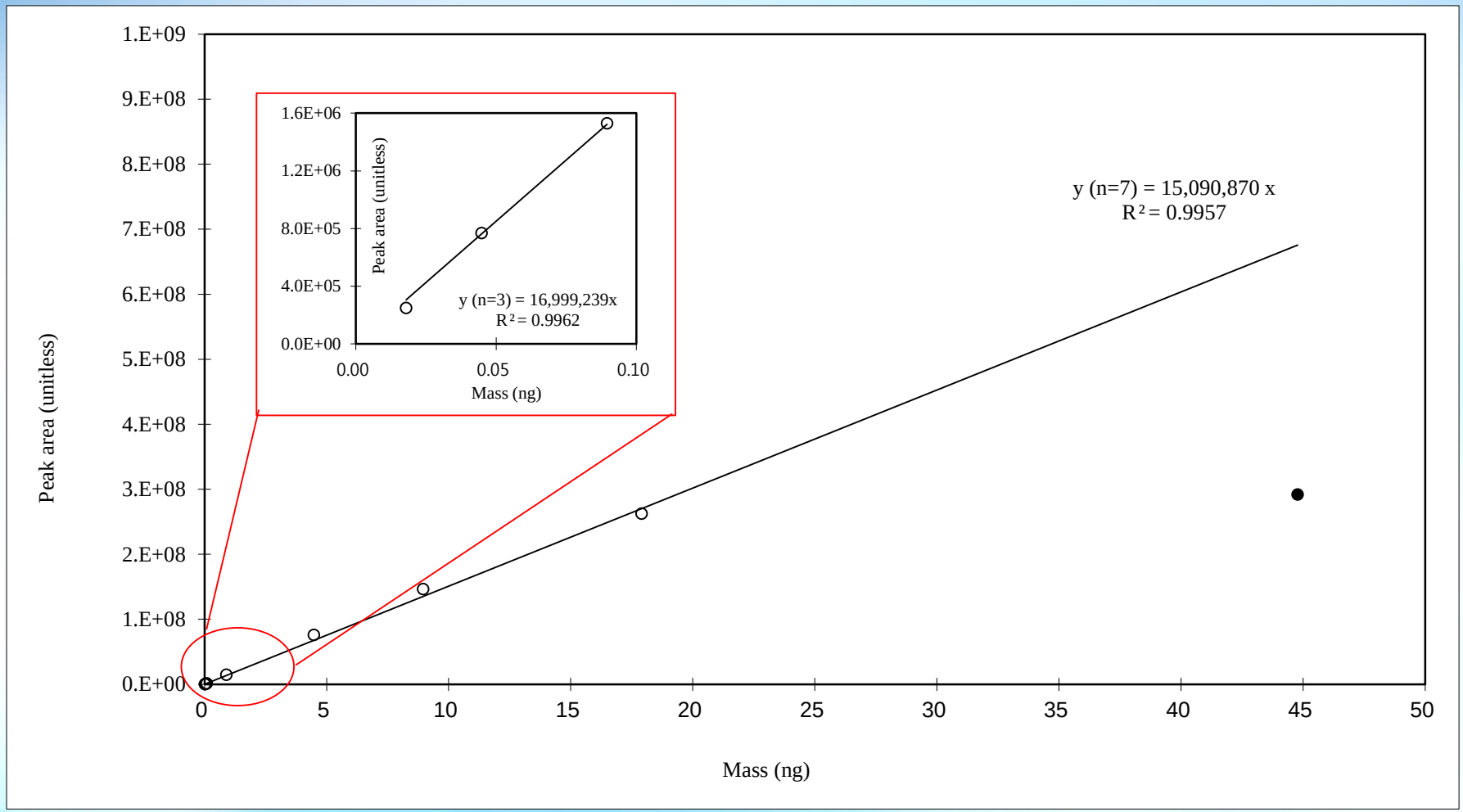


Figure 2. Calibration curves (n=7) of MMC (17.9 pg - 44.8 ng) in TD-GC-TOF MS system: Note that the linearity is no longer maintained above 20 ng

- **Basic QA parameters for MMC analysis**

A. Precision (n=3)

| Order | Peak area[a] | Mean | SD | SE | RSE (%) |
|---|---|---|---|---|---|
| 1 | 13,493,376 | | | | |
| 2 | 13,244,570 | 13,606,287 | 429,453 | 247,945 | **1.82** |
| 3 | 14,080,915 | | | | |

[a]1 μL Injection of 0.895 ng $\mu L^{-1}$ F-WS

# 4. Results of this study

B. Detection limit

| Order | Peak area[b] | Mean | SD | DL | |
|---|---|---|---|---|---|
| | | | | Peak area | mass[c] (pg) |
| [A] Method detection limit (MDL) (n=7) | | | | | |
| 1 | 213,759 | | | | |
| 2 | 213,896 | | | | |
| 3 | 190,504 | | | | |
| 4 | 216,289 | 208,129 | 9,732 | 30,557 | **2.02** |
| 5 | 216,520 | | | | |
| 6 | 204,046 | | | | |
| 7 | 201,887 | | | | |
| [B] Lower limit of detection (LOD) (n=7) | | | | | |
| 1 | 1,874 | | | | |
| 2 | 1,804 | | | | |
| 3 | 2,221 | | | | |
| 4 | 2,036 | 2,006 | 171 | 513 | **0.034** |
| 5 | 1,857 | | | | |
| 6 | 2,224 | | | | |
| 7 | 2,028 | | | | |

[b] 1 μL Injection of 17.9 pg $\mu L^{-1}$ F-WS

[c] [Peak area (MDL or LOD) / RF (calibration)] * 1,000

[d] peak area of background noise

# 4. Results of this study

## ● Comparison with previous studies for analysis of MMHg

Table 5. Overview of detection limits for methyl mercury between single and joint detection methods

| Order | Analytical system | | | DL (pg) | | Reference | |
|---|---|---|---|---|---|---|---|
| | Detector[a] | Pretreatment | Medium/Derivatizer | LOD | MDL | | |
| [A] Single detection system by gas chromatographic (GC) method | | | | | | | |
| 1 | Q MS | SPME[b] | sodium tetraethylborate | 20 | NA[e] | Mishra et al. | 2005 |
| 2 | Q MS | SPME | sodium tetraethylborate | 10 | NA | Cai and Bayona | 1995 |
| 3 | Q MS | Thermal desorption | sorbent tube | 6.85 | 201 | This study | |
| **4** | **TOF MS** | **Thermal desorption** | **sorbent tube** | **0.034** | **2.02** | **This study** | |
| [B] Joint detection system by GC plus spectrometric method | | | | | | | |
| 4 | AAS | SPME | sodium tetraethylborate | 26,000 | NA | Bin et al. | 1998 |
| 5 | AAS | microbeads | acidic potassium bromide | 200 | NA | Salih et al. | 1998 |
| 6 | QF-AAS | DI[c] | sodium tetraethylborate | 167 | NA | Craig et al. | 1999 |
| 7 | CV[e]-AFS | steam distillation | sodium tetraethylborate | 1.2 | NA | Bowles and Apte | 1998 |
| 8 | CV-AFS | DI | acidic potassium bromide | 1.2 | NA | Qrtiz et al. | 2002 |
| 9 | AFS | SCF[d] adsorbent | acidic potassium bromide | 0.2 | NA | Cai et al. | 1996 |
| 10 | ICP MS | DI | diethyl dithiocarbamate | 0.1-0.2 | NA | Fernández et al. | 2000 |
| 11 | ICP MS | DI | sodium tetraethylborate | 0.08 | NA | Slaets et al. | 1999 |
| 12 | ICP MS | DI | sodium tetraethylborate | 0.028 | NA | Martín-Doimeadios et al. | 2002 |

[a] Acronyms for detection systems: AAS=atomic absorption spectrometry; AFS=atomic fluorescence spectrometry; CV=cold vapour ICP MS=inductively coupled plasma mass spectrometry; QF=quartz furnace; Q MS=quadrupole mass spectrometry; and TOF MS=time-of-flight mass spectrometr

[b] solid-phase microextraction; [c] direct injection; [d] sulfhydryl cotton fiber; [e] Not available

# 5. Conclusions

# 5. conclusions

- MMHg was analyzed using single stage instrumental setup (GC-TOF MS) to replace complex joint system (GC or LC + inorganic detector)

- Thermal desorption was only used for pretreatment of MMHg without derivative process

- A fairly good linearity ($R^2$=0.9957) and reproducibility (RSE=1.82%) of MMHg were obtained using TD-GC-TOF MS system

- The DL of MMHg were very low(MDL=2.02 pg and LOD=0.034 pg)

# Thanks