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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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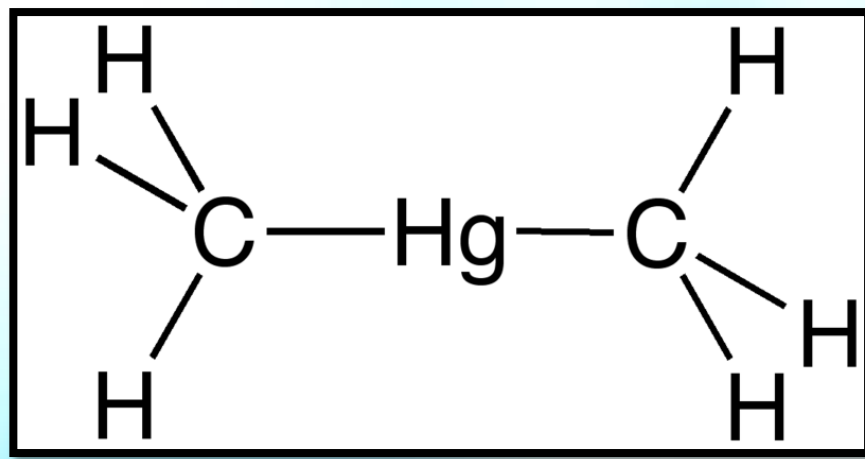
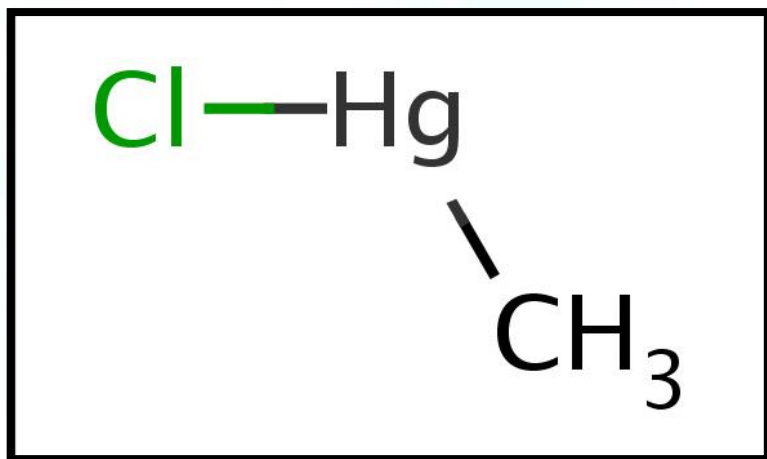


1. Introduction



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**

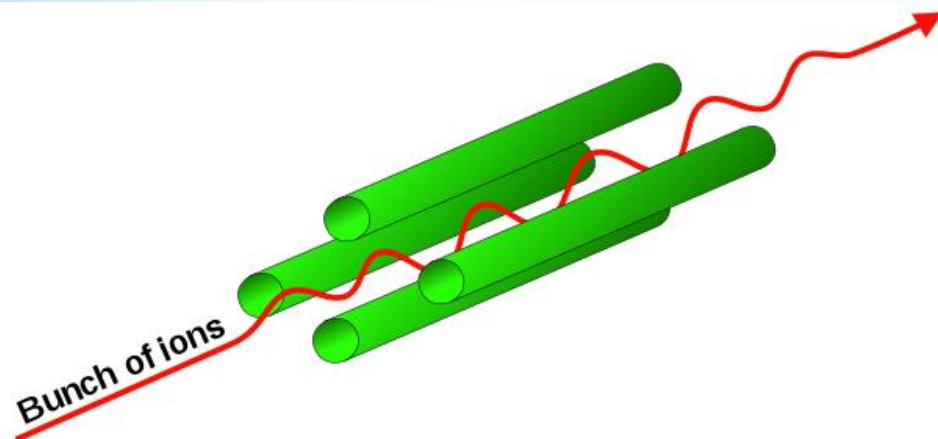
- a. GC + Atomic Absorption Spectrometry (AAS)
- b. GC + Atomic Fluorescence Spectrophotometer (AFS)
- c. GC-MS + Inductively Coupled Plasma mass spectrometry (ICP-MS)



2. General analysis of organic mercury

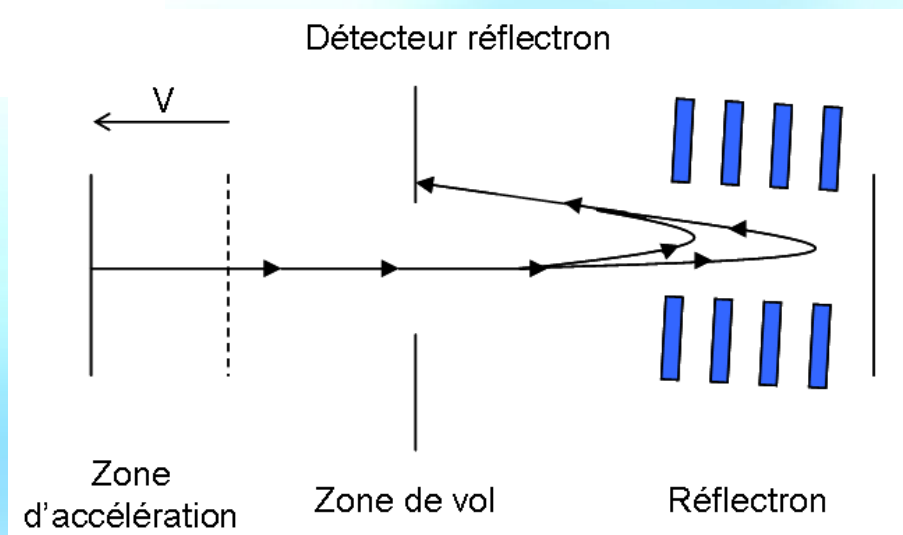
- High sensitivity of TOF MS

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



← Quadrupole mass spectrometry

Time-of-flight mass spectrometry →





3. Analysis of MMHg using TOF MS



3. Results and discussion

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

[B] Actual detection mass (ADM) from real ambient air

Order	Compounds	Minimum detection volume		Actual detection mass (Concentration)		ADM/MDL	
		(mL)		(pg (ppb)) ^b		(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

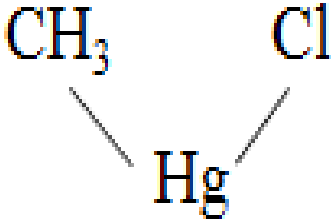
^b For the derivation of molar ratio (ppb), the minimum sample volume for the first detection was used (e.g., 2 mL for VA by TOF MS)



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 (°C):	170	
Formula:	CH ₃ HgCl	
CAS number:	115-09-3	



3. Analysis of MMHg using TOF MS

● 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 μL ⁻¹)		1,492
1st WS ^b		Methanol	MMC
	Volume (μL)	19,880	120
	Concentration (ng μL ⁻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 ($\text{ng } \mu\text{L}^{-1}$)
	1st WS	Methanol	
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 °C (5 min)	TIC scan range:	35~260 m z^{-1}
Oven rate:	20 °C min^{-1}	EIC range:	198~202, 213~217
Max oven temp:	210 °C (9.5 min)	(m z^{-1})	233~237, 248~254
Total time:	20 min	Ion source temp.:	230 °C
Carrier gas:	He (99.999%)	Interface temp.:	230 °C

B. Thermal desorber (Unity, Markes, UK)

Cold trap:	Carbopack B+ Tenax TA	Trap low:	- 10 °C
Split mode:	Splitless	Trap high:	320 °C
Trap hold time:	20 min	Flow path temp:	150 °C

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 °C

3. Analysis of MMHg using TOF MS

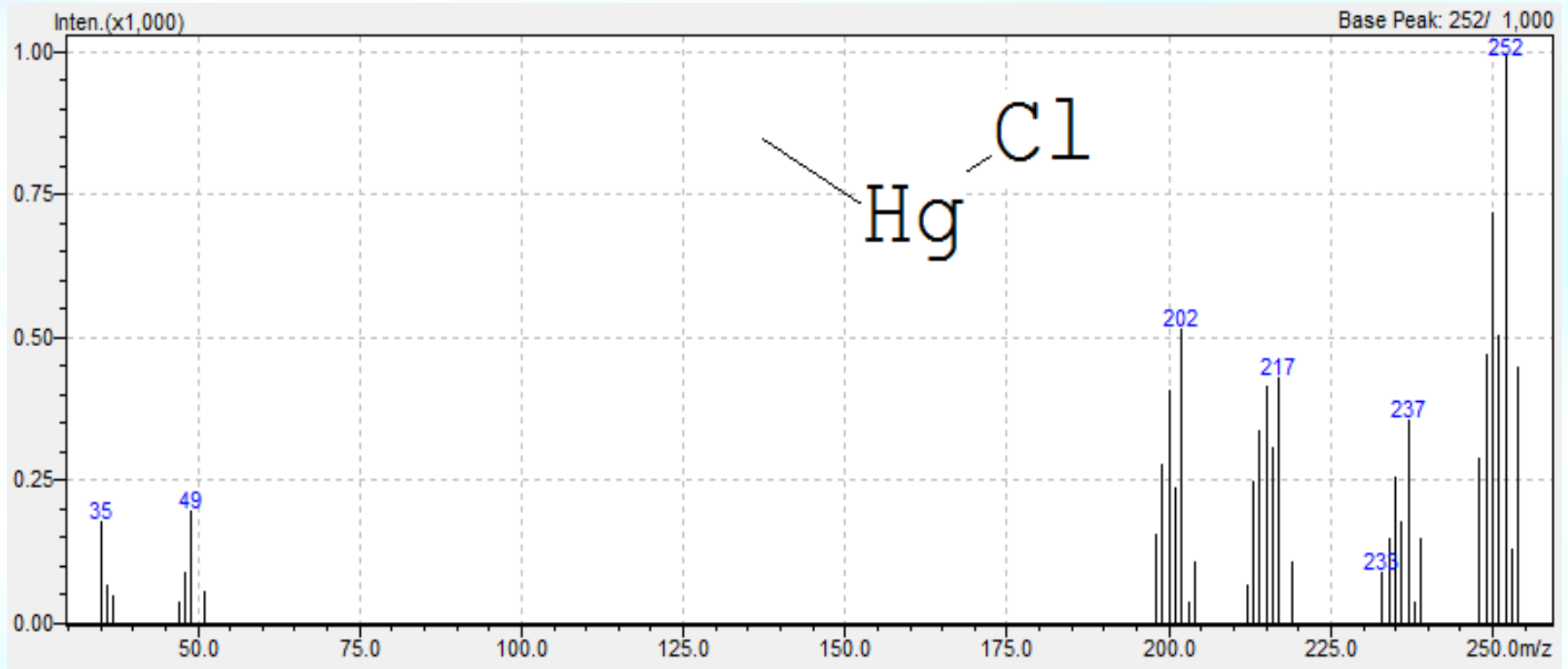
- Sorbent tube (Tenax TA + Carboxen B + Carboxen 1000)





3. Analysis of MMHg using TOF MS

- Mass spectrum of MMC





3. Analysis of MMHg using TOF MS

● Chromatogram

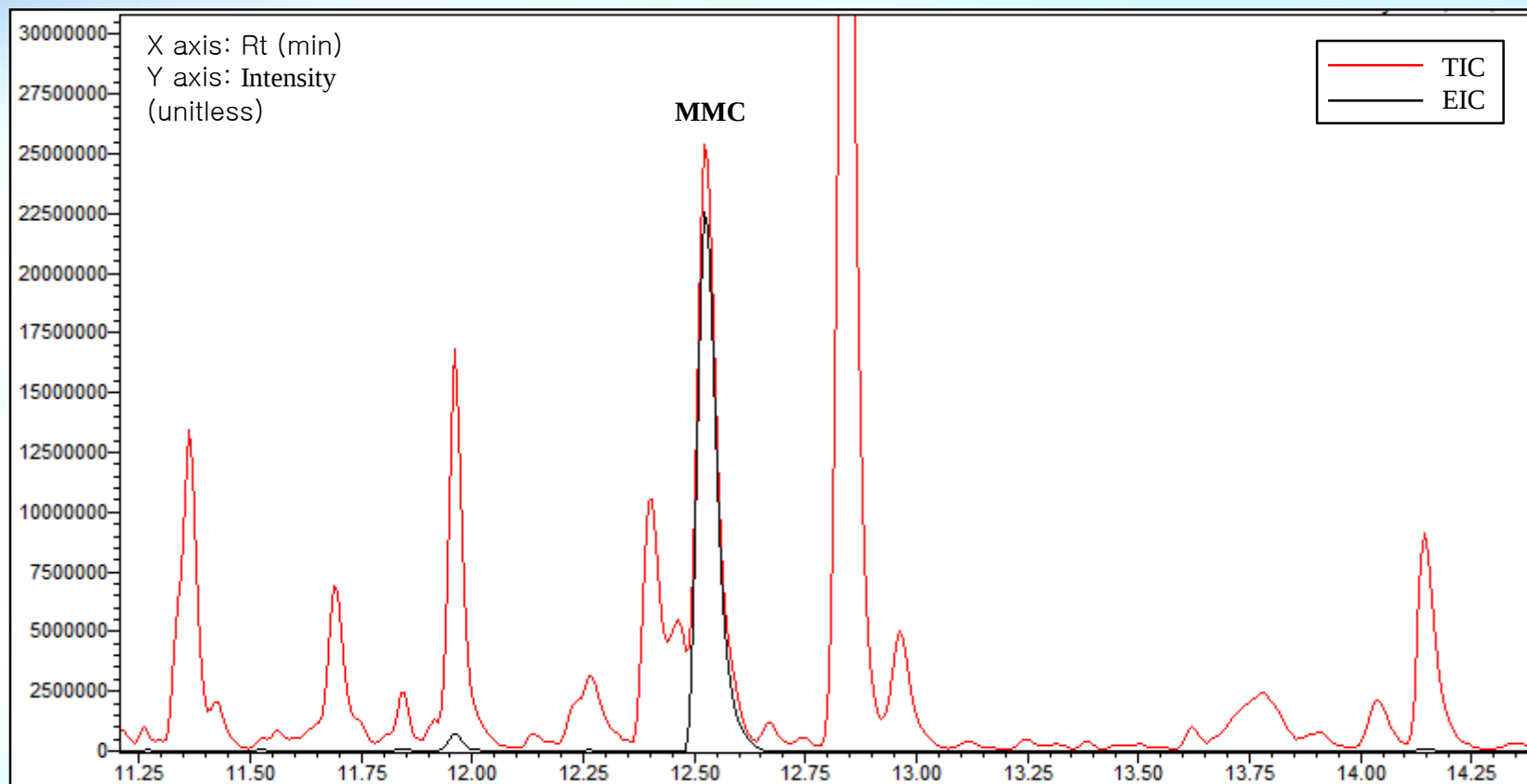


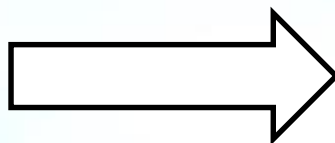
Figure 1. Chromatogram of 4.48 ng μL^{-1} of F-WS determined by the two scan modes (TIC vs. EIC)



3. Analysis of MMHg using TOF MS

- Experimental scheme

F-WS of MMC

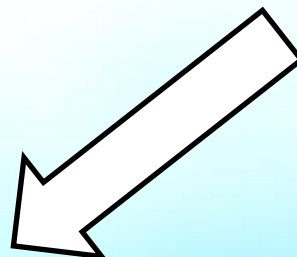


Back-up gas
(N₂ ; 99.999%)



F-WS of
MMC

Sorbent
tube



Voltage
controller

TOF
MS

TD



4. Results of this study



4. Results of this study

● Calibration curve

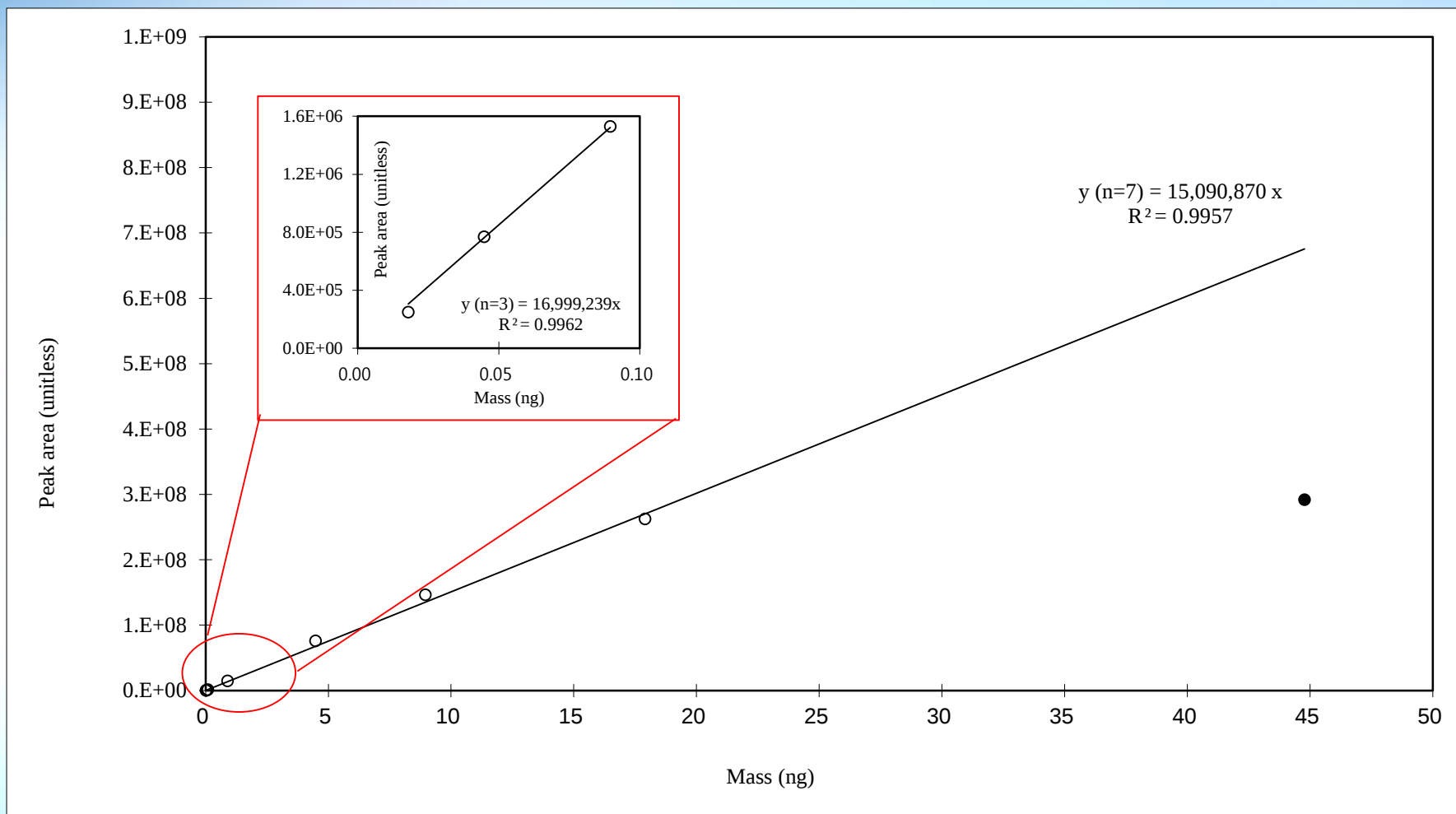


Figure 2. Calibration curves ($n=7$) of MMC (17.9 pg - 44.8 ng) in TD-GC-TOF MS system: Note that the linearity is no longer maintained above 20 ng



4. Results of this study

● Basic QA parameters for MMC analysis

A. Precision (n=3)

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

^a1 μL Injection of 0.895 ng μL^{-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	208,129	9,732	30,557	2.02
2	213,896				
3	190,504				
4	216,289				
5	216,520				
6	204,046				
7	201,887				
[B] Lower limit of detection (LOD) (n=7)					
1	1,874	2,006	171	513	0.034
2	1,804				
3	2,221				
4	2,036				
5	1,857				
6	2,224				
7	2,028				

^b 1 μ L Injection of 17.9 pg μ 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 spectrometry

^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)**



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