Trace–Level Automated Mercury Speciation Analysis

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EPA 1630 Methyl Mercury in Water (and biological/sediment extracts) by Distillation, Aqueous Ethylation, Purge and Trap, and CVAFS (ICP-MS)

Brooks Rand Labs MERX® Automated Methylmercury System

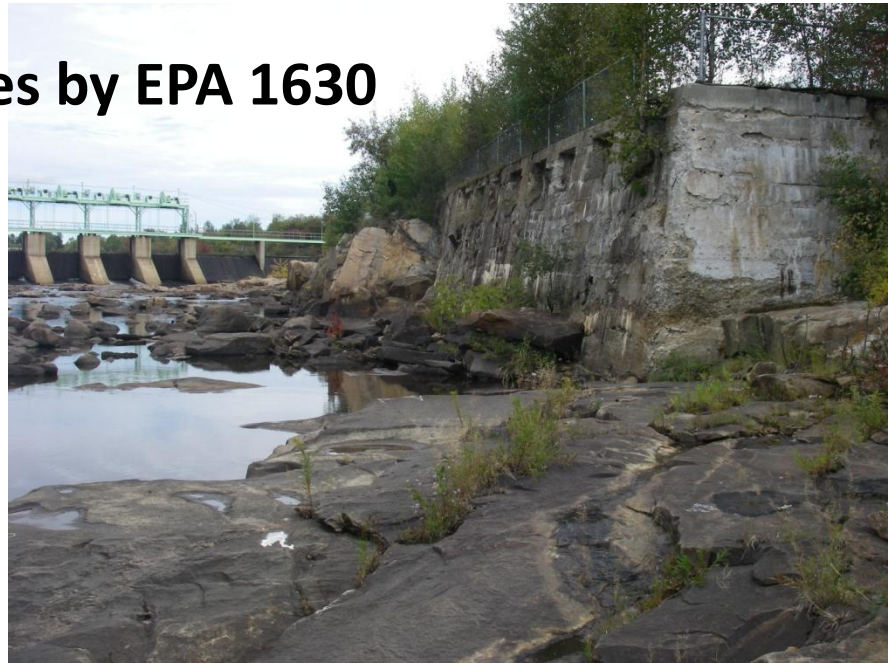
Aims:

1. Automated low-level methyl Hg determination
2. Coupling automated system with ICP-MS
3. Determination of higher MW Hg species

Methyl Hg in environmental samples by EPA 1630

Methyl Hg bioaccumulates – speciation in multiple compartments of the environment

- Hg methylation in sediment
- Methyl Hg in surface water is a predictor of fish Hg
- low trophic level organisms < 90% methyl Hg



Superfund site, Berlin NH

Surface water
Periphyton
Benthic organisms – mayfly, caddisfly, dragonfly, crayfish
Juvenile fish – minnows, bass
“Snack-size” fish – smallmouth bass, perch
Swallows, bats
Sediment
Porewater

Add buffer and derivatizing agent ($NaBEt_4$)

↓

Hg species to react with ethylating agent — t = 17 min

↓

Purge ethylated Hg species from solution and preconcentrate on Tenax trap — t = 17 min

↓

Dry Tenax trap — t = 7 min

↓

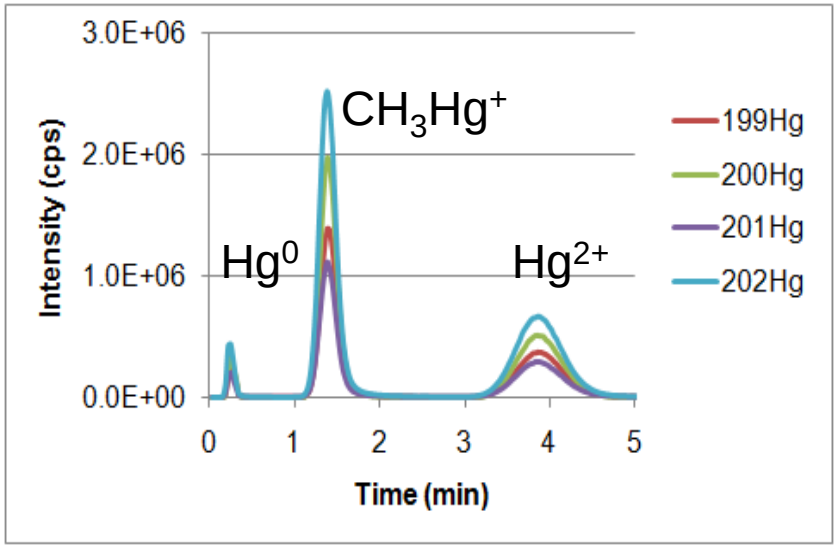
Thermal desorption and separation by packed column GC with detection by AFS — t = 6 min

Advancements to EPA 1630

Detection by ICP-MS: Species-specific isotope dilution:

Enriched isotope spike: $CH_3{}^{201}Hg$

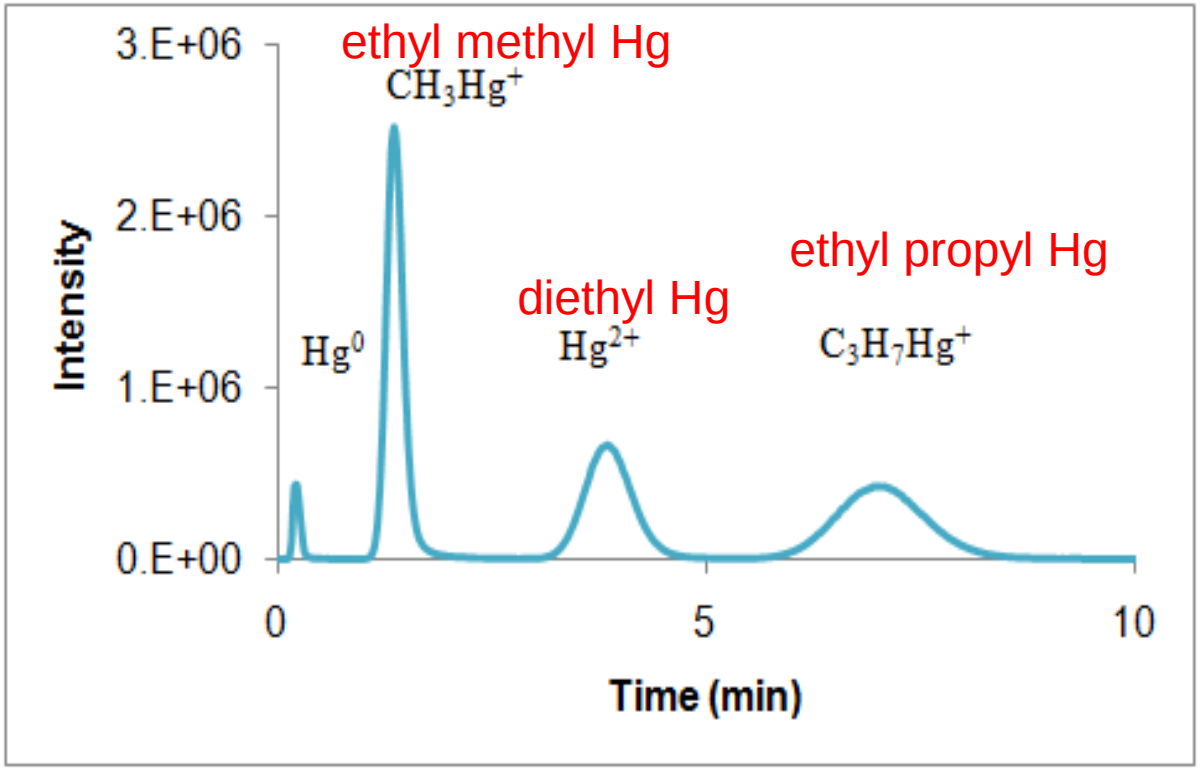
Correction for:
- √ matrix effects / ethylation efficiency
- √ species transformation
- √ inorganic Hg (^{199}Hg)



Advancements to EPA 1630

<u>High MW Hg species</u>
vaccines, pesticides, cosmetics, biological samples

Derivatizing agents – propylation, butylation, phenylation
Internal standards – spike with high MW Hg species



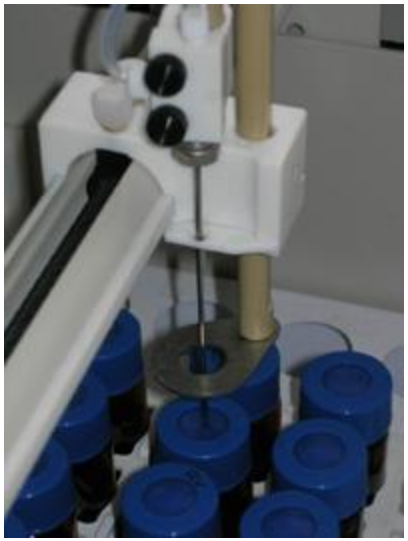
MERX-M Automated Methylmercury System

Brooks Rand Labs

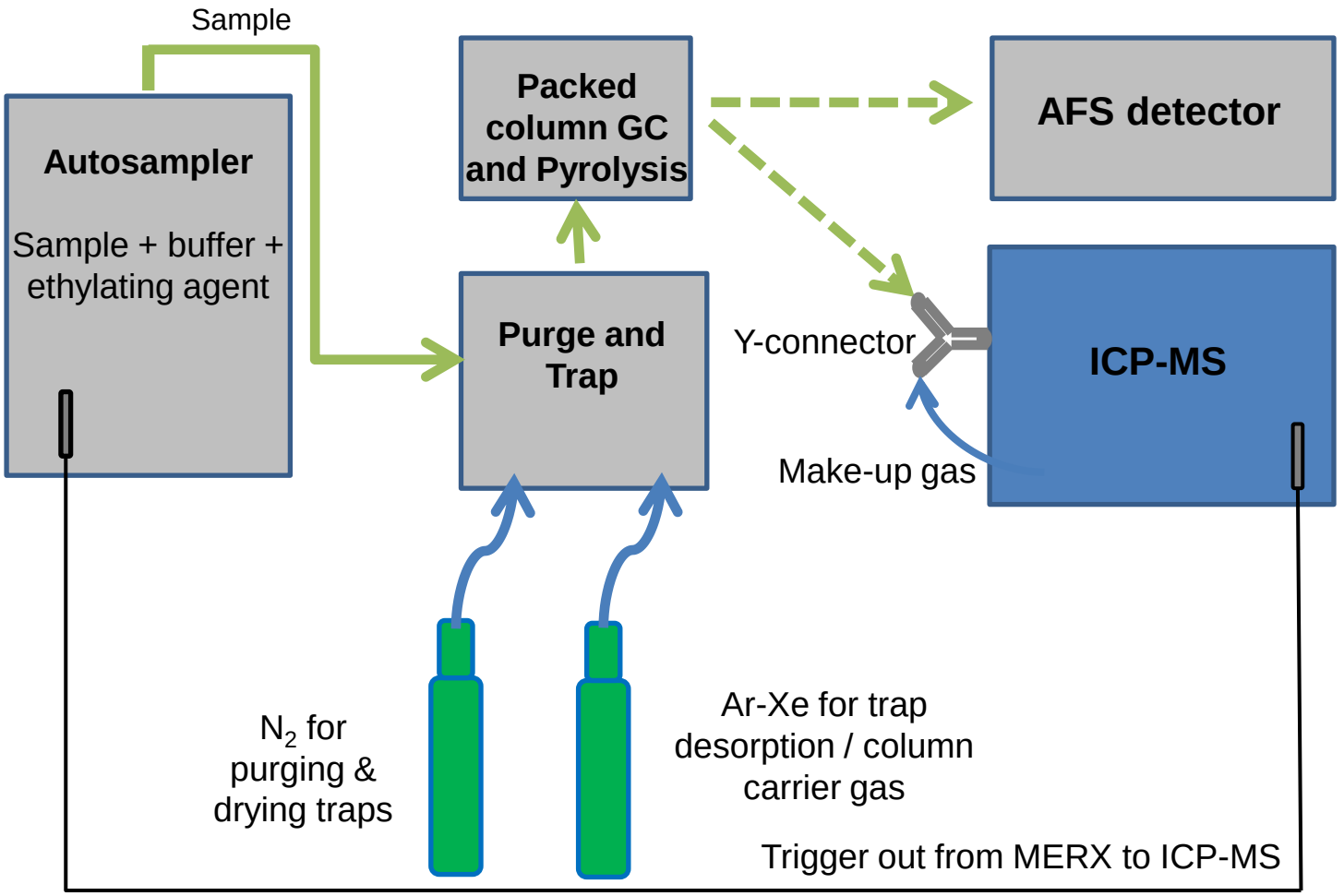
- Autosampler for 72 40mL vials
- Gas pressurized liquid transfer to purge vessel for aspiration of volatile Hg species
- Three Tenax traps rotate between loading, heating and drying, enabling a 6.5 min. sample time.
- IR heating to volatilize Hg from trap
- Packed column gas chromatography and pyrolysis
- Atomic fluorescence detection

Manual method: ~30 samples in 8 hrs., 8 hrs. of analyst time

Automated method: 72 samples in 10 hrs., 2 hrs. of analyst time



Configuring MERX-M to AFS/ICP-MS detection



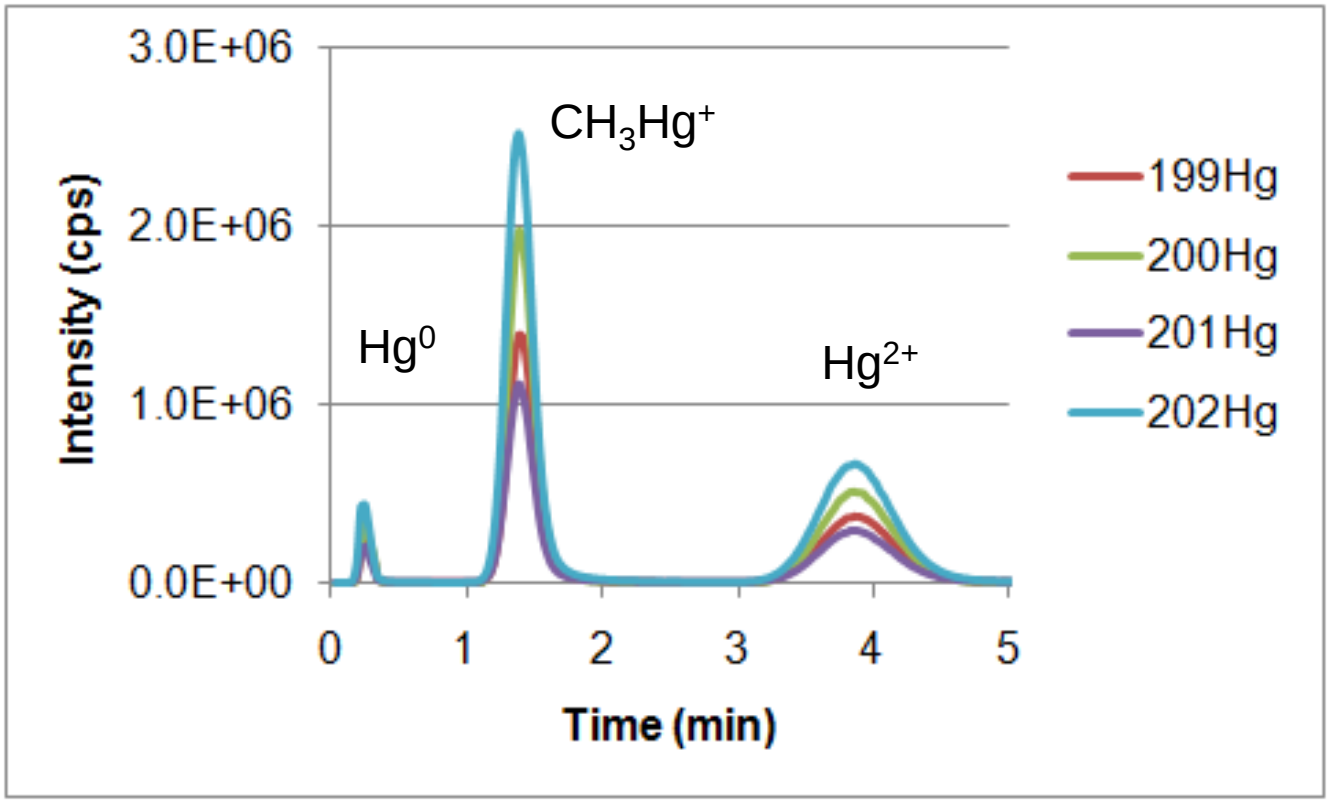
Atomic Fluorescence Detection :

Brooks Rand Model III CVAFS

ICP-MS detection :

Thermo Element 2 magnetic sector ICP-MS

Agilent 7500 quadrupole ICP-MS


3.0E+06
2.0E+06
1.0E+06
0.0E+00
Intensity (cps)
CH_3Hg^+
Hg^0
Hg^{2+}
0
1
2
3
4
5
Time (min)
199Hg
200Hg
201Hg
202Hg

Method detection limit

7 calibration standards

LOD: Limit of Detection – 3 times σ_{blank} (n=9)
LOQ: Limit of Quantitation – 10 times σ_{blank} (n=9)

MDL: Method Detection Limit - 3 times $\sigma_{std\ at\ LOQ}$(n=8) 0.5pg (12.5 pg/L)

Methyl Hg determination

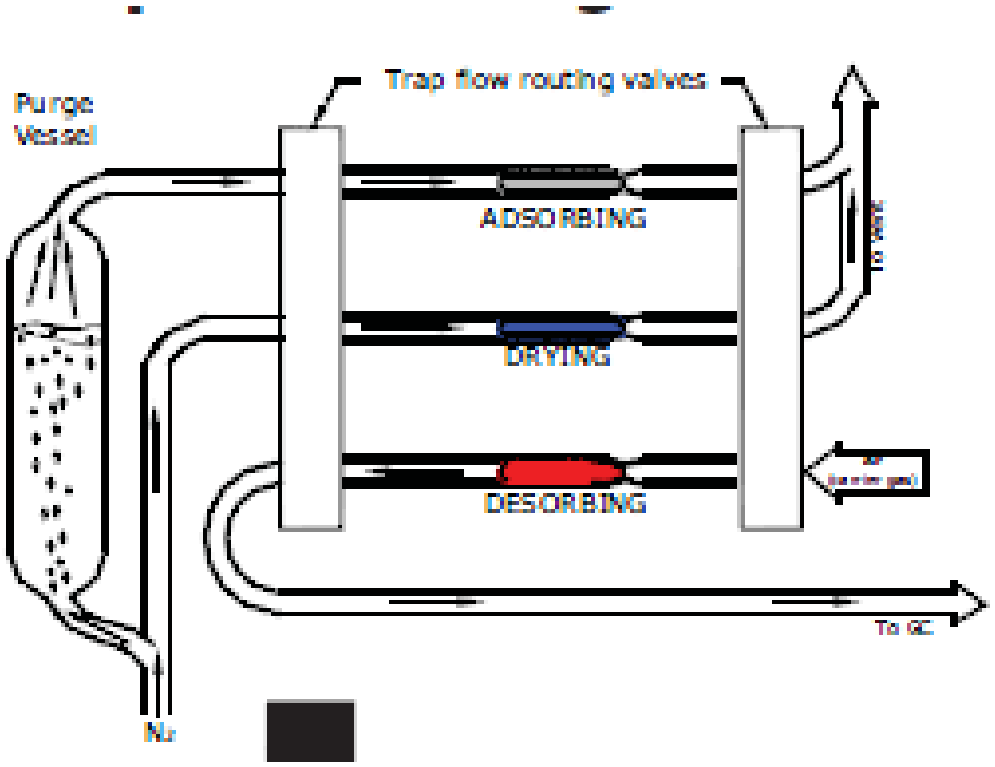
EPA recommends MDL of 20 pg/L

	CH_3Hg^+			
	AFS	**ICP-MS** Element 2	**ICP-MS** Agilent	**ID-ICP-MS** Element 2
MDL (pg/L)	1.1	0.7	3.8	1.5

Carryover

pg CH_3Hg blank / 1000 pg std

AFS	ICP-MS
0.17 %	0.18%

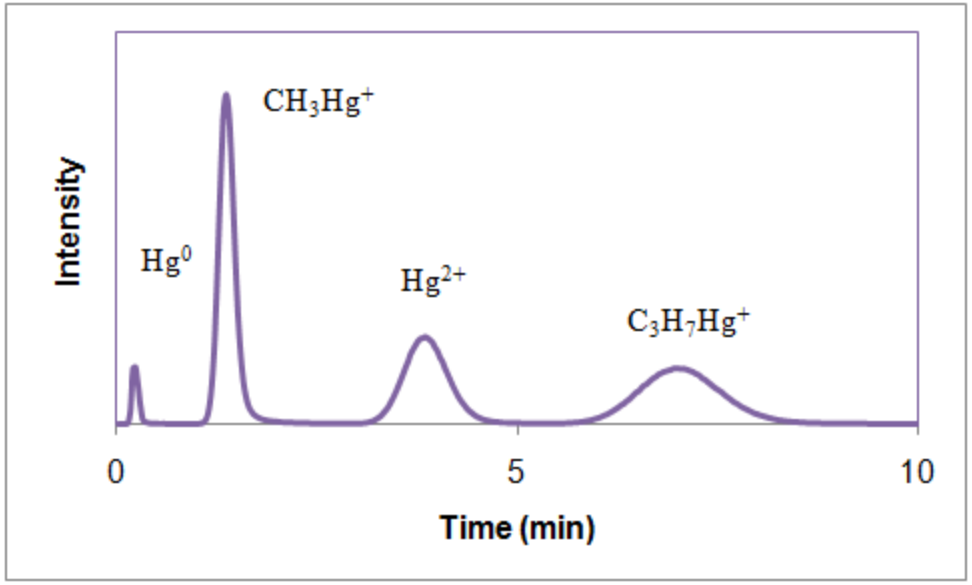


Methyl Hg in Standard Reference Materials

	Certified Value (µg/g)	**AFS (µg/g)**	**ICP-MS (µg/g)**
TORT -2	0.152 ± 0.013	0.143 ± 0.007	0.152 ± 0.003
DOLT-4	1.33 ± 0.12	1.21 ± 0.01	1.34 ± 0.017
DORM-2	4.47 ± 0.32	4.04 ± 0.05	4.23 ± 0.063

n-propyl Hg

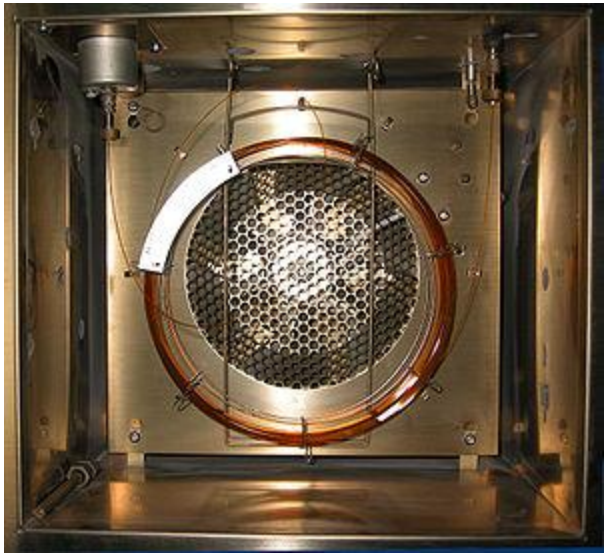
Packed column GC



1 ng CH_3Hg, C_3H_7Hg

Capillary GC: ↑ resolution and ↓ retention time

√ Gradient heating
√ Higher theoretical plates

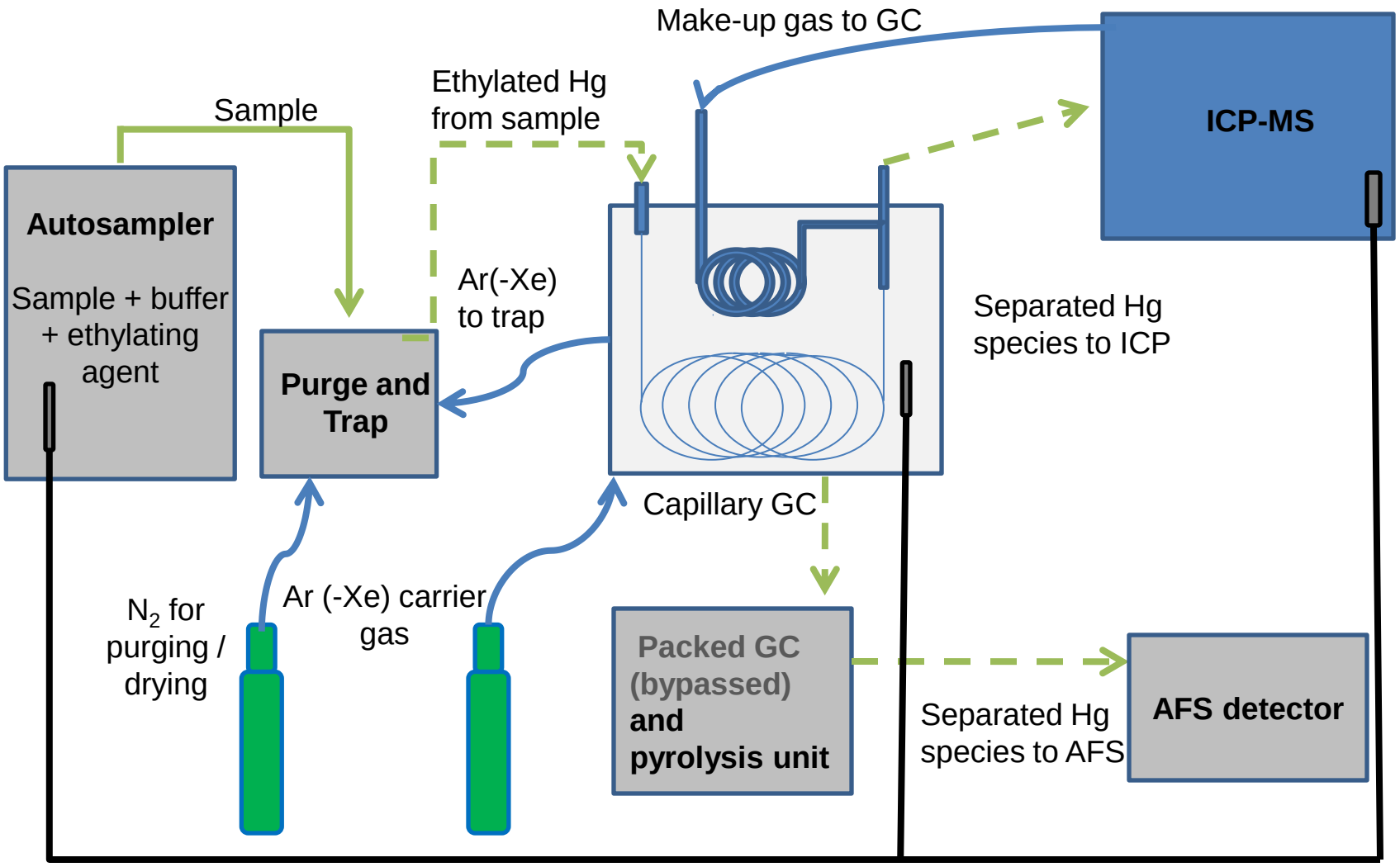


GC parameters

Agilent 6890N GC

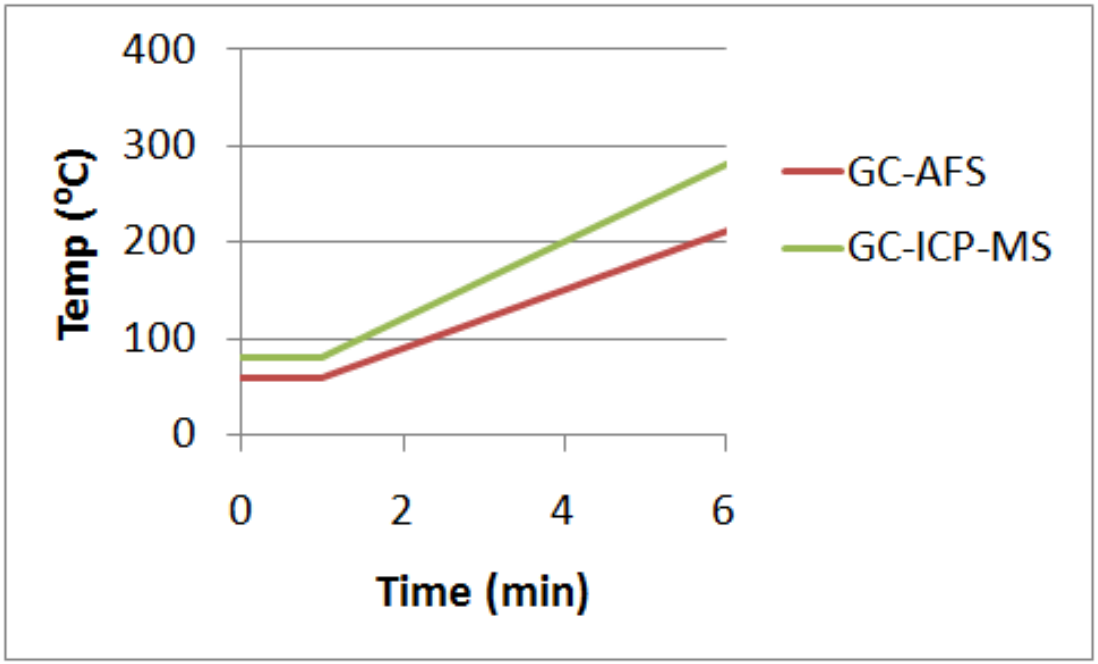
Inlet mode	Splitless
Column	Agilent HP-1Megabore 0.53mm ID
GC flowrate	15 mL/min

Configuring MERX-M to capillary GC with AFS/ICP-MS detection



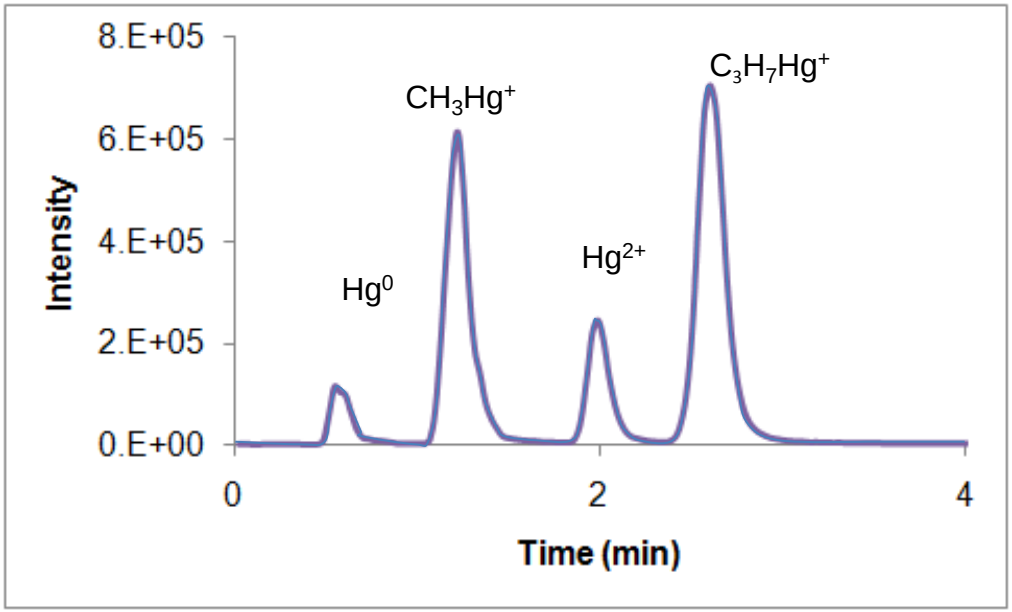
Trigger out from MERX to capillary GC and ICP-MS

Capillary GC heating program



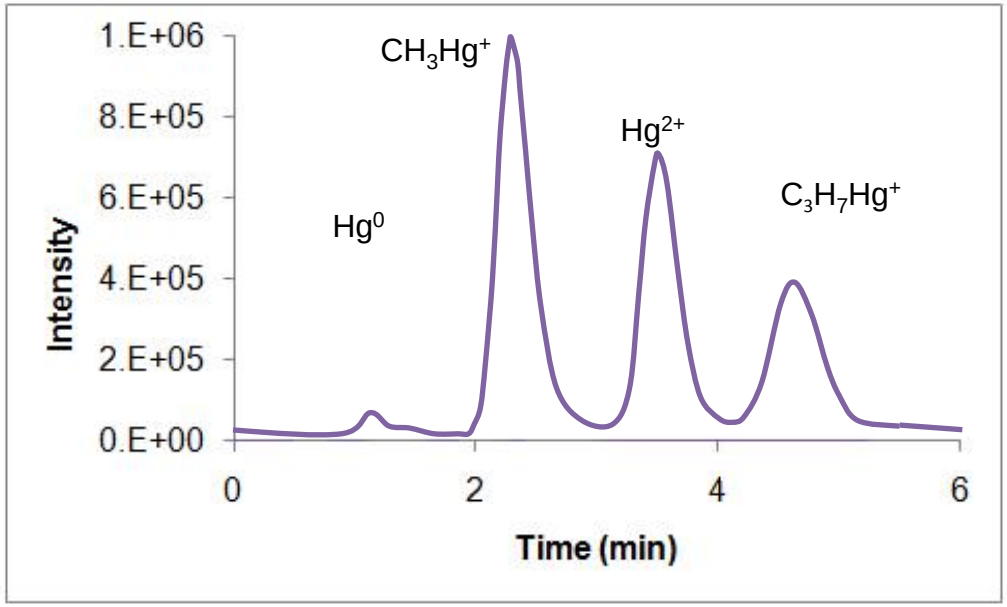
Capillary GC

GC coupled with ICP-MS



Run time < 4 min

GC coupled with AFS



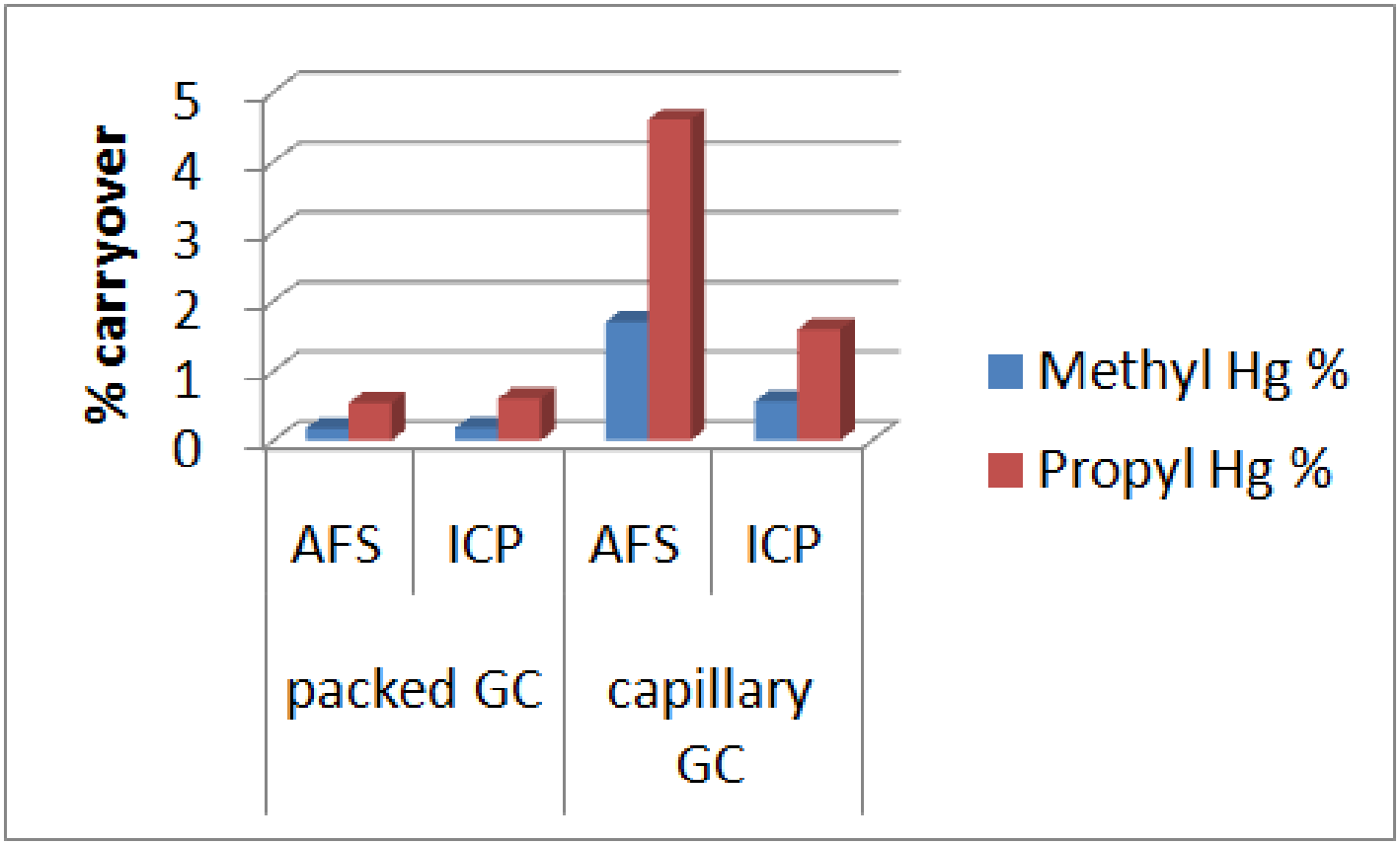
Run time 6min

Method Detection Limits

EPA recommends MDL of 20 pg/L

		Methyl Hg pg/L	**Propyl Hg** pg/L
packed GC	AFS	1	6
	ICP	1	6
capillary GC	AFS	6	13
	ICP	1	2

Carryover


% carryover
5
4
3
2
1
0
AFS
ICP
AFS
ICP
packed GC
capillary GC
Methyl Hg %
Propyl Hg %

Summary:

1. Automated system achieved MDL of < 2 pg/L, reducing analyst time from 8 hrs. for a 30 sample run to 2 hrs. for a 72 sample run.

2. Connection to ICP-MS achieved similar MDL as AFS, and enabled the use of isotope dilution.

3. Capillary GC decreased run time (4 min) relative to packed GC (10 min) for high MW weight Hg species (propyl Hg).

Taylor et al., Analytical Methods 2011

Thanks!

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