Trace Level Methyl Mercury Analysis by Method 1630

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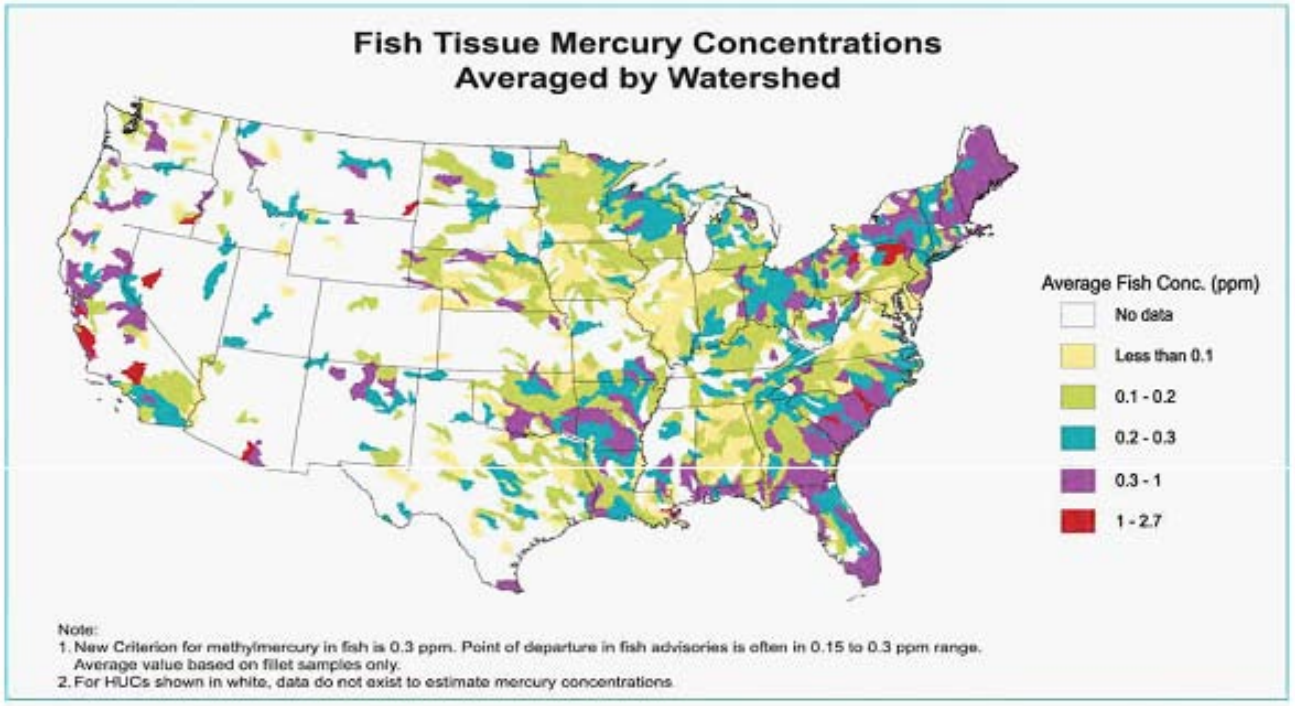
Why is Methylmercury a Concern?

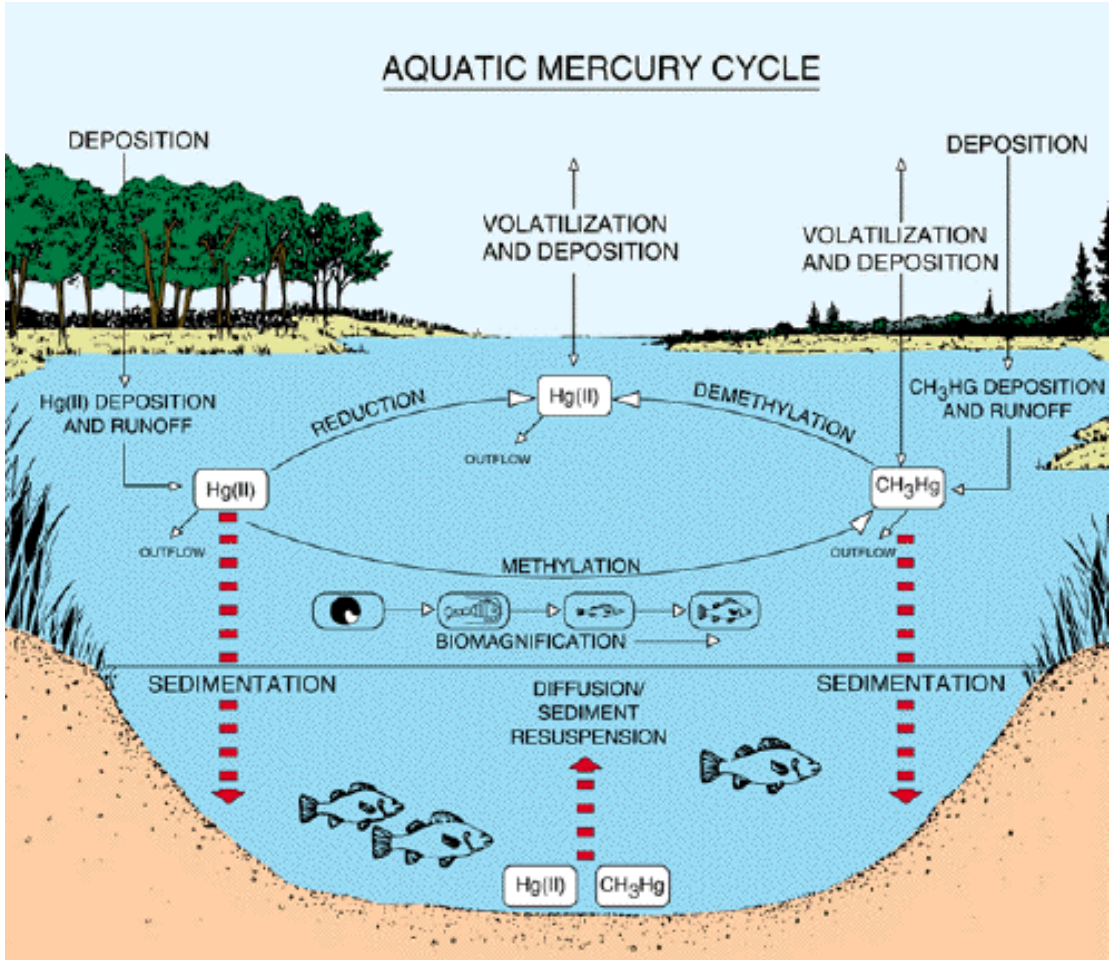
- Toxic Effects in Humans and Wildlife - Potent neurotoxin.
- Universally Present in Fish - Mercury hotspots in Florida Everglades.
- Highly Bioaccumulative - Bioconcentration factor between 1E4 to 1E5 (WHO,1990)



Sources and Distribution of Mercury

- Inorganic mercury transported through the atmosphere .
  - Sources – coal-fired power plants, municipal and medical incinerators, landfills and chlor-alkali plants.
- Conversion of inorganic Hg (II) to methylmercury by sulfate reducing bacteria in anoxic sediments – enters water colums.
- In the food web –
  - Bioaccumulation and Biomagnification.

Mercury Biogeochemical Cycling



Typical Levels of Total Mercury and Methylmercury

Sample Type	Total Hg (ppb)	Average MeHg Fraction (%)
Surface Water	0.0001 - 0.01	5% - 80%
Plants	0.5 - 1.0	2%
Shellfish, Crayfish	1.0 - 5.0	100%
Mosquito fish	5.0 - 200	80%
Large-mouth Bass	200 - 3000	100%
Mammalian Hair	500 - 20,000	90%
Bird Eggs	500 - 10,000	75%
Wading Bird Feathers	500 - 200,000	100%

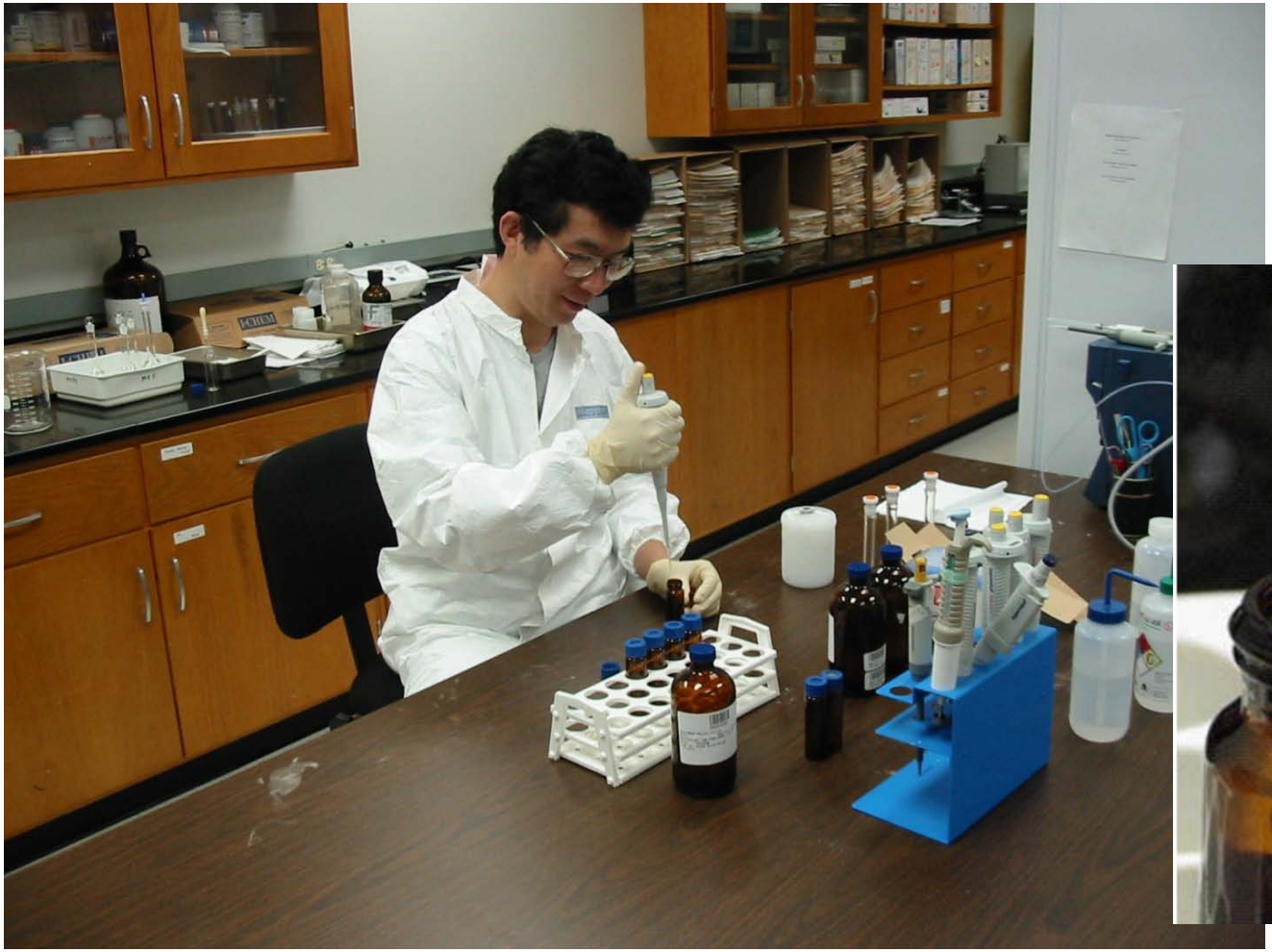
Draft EPA Method 1630

- Requires distillation of water samples to remove interferants .
- Uses an acetate buffer (pH 4-5).
- Ethylation using sodium tetraethylborate.
- Manually purged and trapped.
- Desorbed and injected into a packed isothermal column.
- GC separation of the methyl-ethylmercury and diethylmercury followed by pyrolysis at 800 Celsius.
- Detection using an atomic fluorescence (AF) detector with an MDL of 0.06 ng/L.

Florida D.E.P. Modified Method

- Direct ethylation of methylmercury to volatile methylethylmercury in a 40 mL VOC vial.
- Water Samples:
  - 40 ml of sample (no distillation required).
  - 4 ml citrate buffer (pH 4-4.5)
  - 25 µl 2% sodium tetraethylborate (in 2% KOH).
- Tissue Samples:
  - Digest 1 g tissue in 10 ml 25% KOH/methanol solution at 90 C.
  - Add 50 µl of extract to 100 ml water.
  - Add same reagents as above.

Sample Preparation



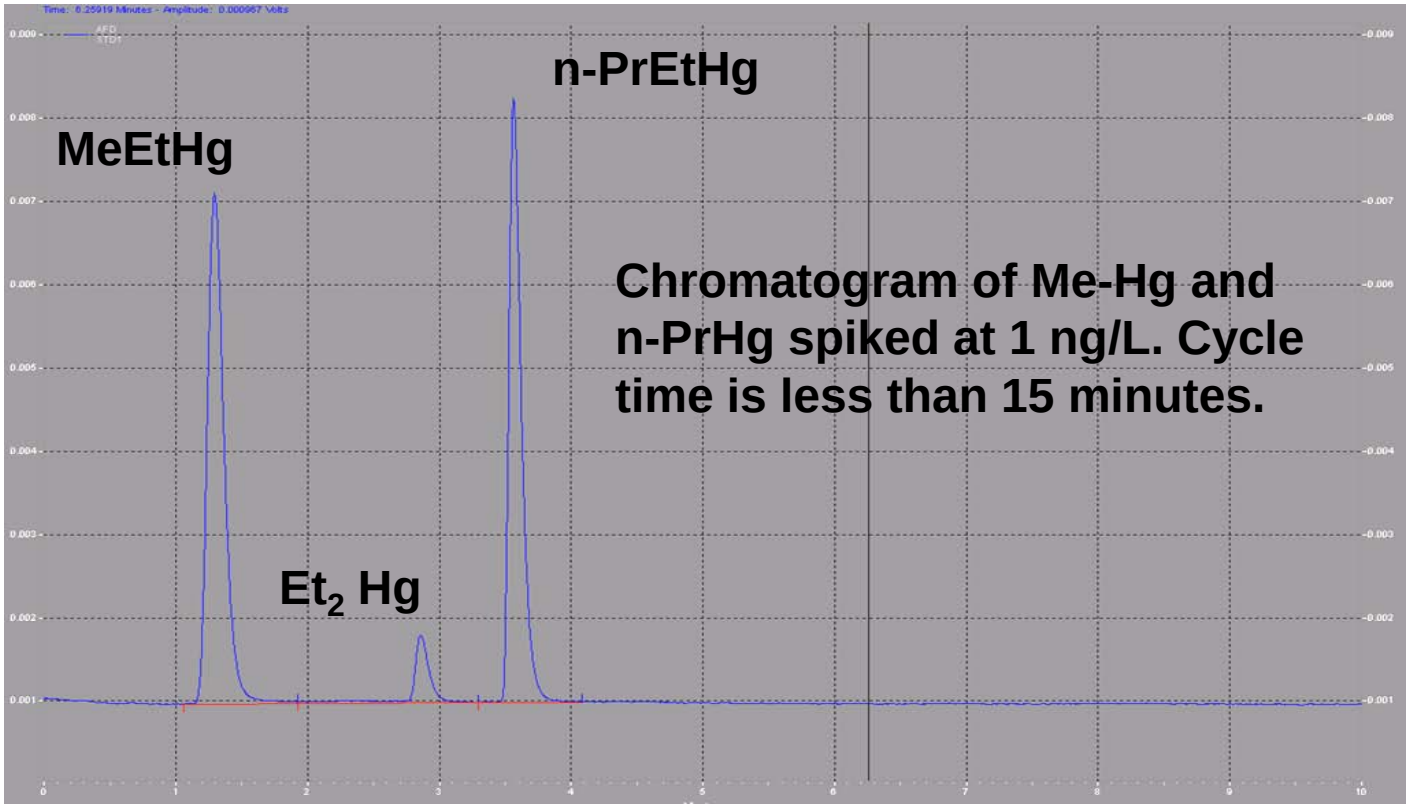
- **Add Buffer**
- **Derivatize**
- **Mix Well**

(Zero Headspace)

Instrumental Analysis

Derivatization	Ethylation by sodium tetraethylborate in 2% KOH.
Purge and Trap	Tekmar 3000 with Tenax trap - desorb at 180 Celsius.
GC Separation	HP-5890, He carrier gas, 15 m DB5, 0.32 mm ID.
Pyrolysis	Alumina tube furnace, 850 Celsius.
AF Detection	Tekran 2500 AF detector, argon makeup gas, MDL = 0.02 ng/L.

Chromatogram



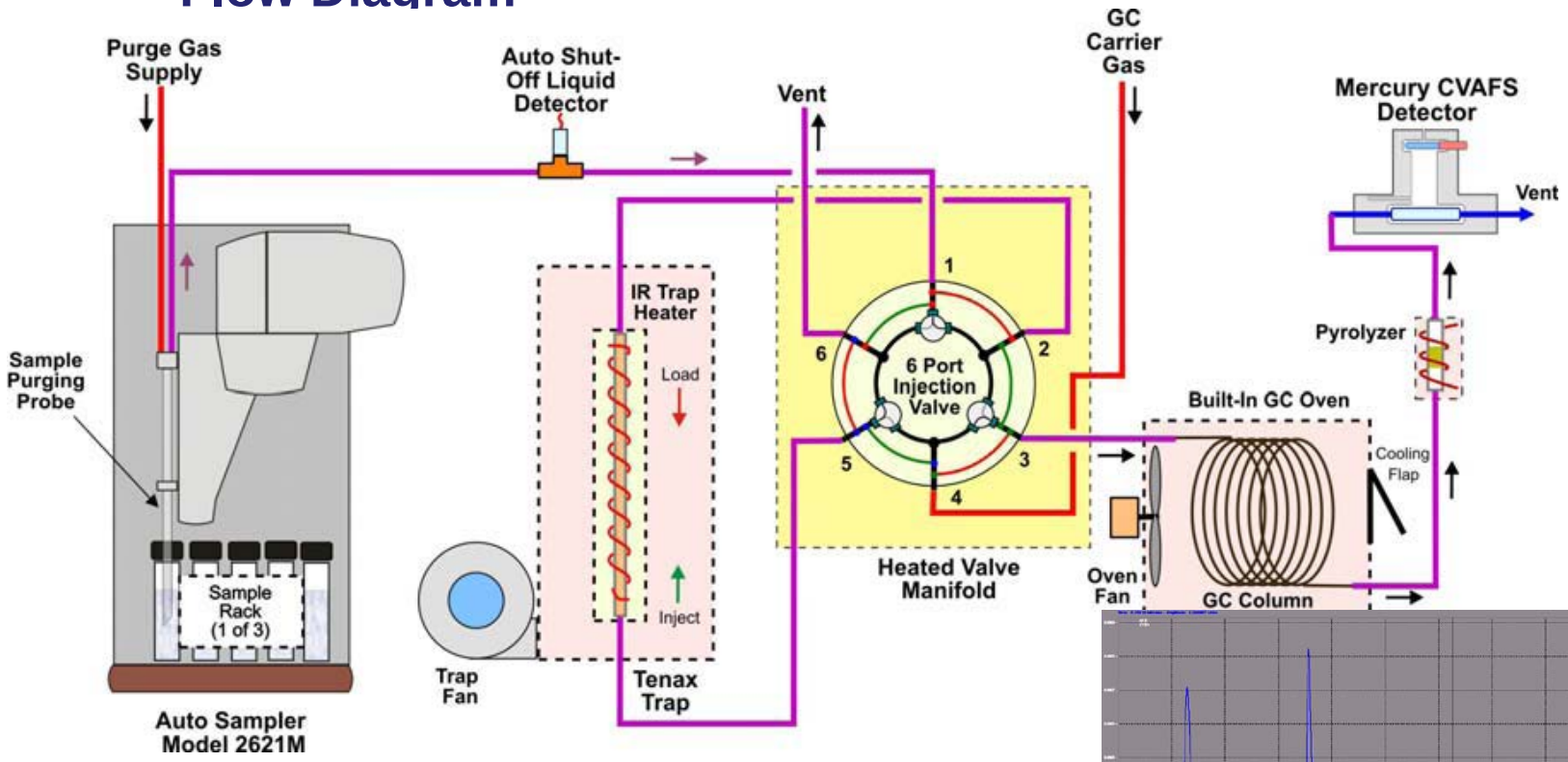
Instrument

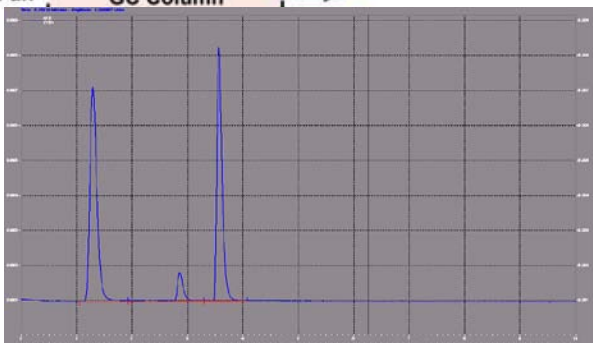
Instrument

New In-Vial Purge Configuration for the Tekran 2700 Methyl Mercury Analysis System

Instrument

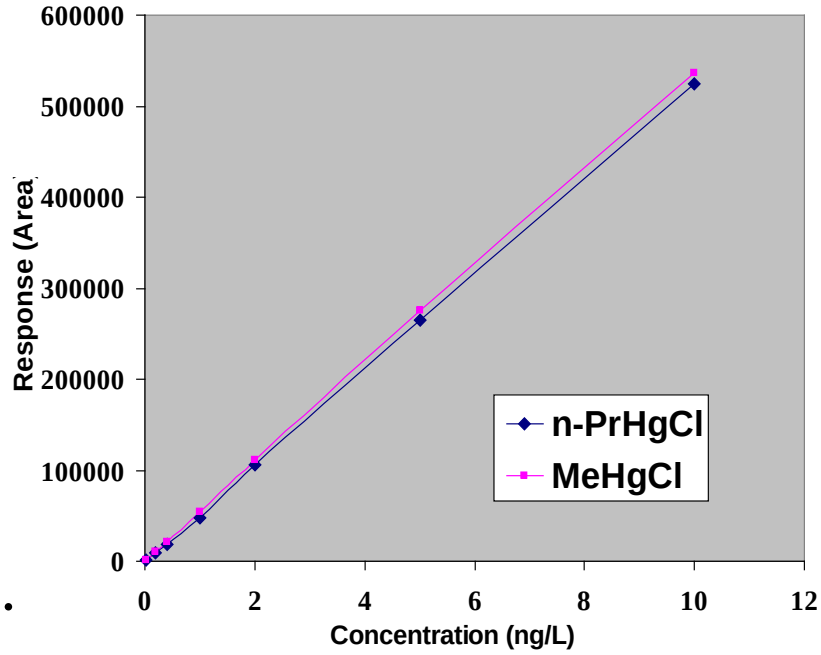
Flow Diagram



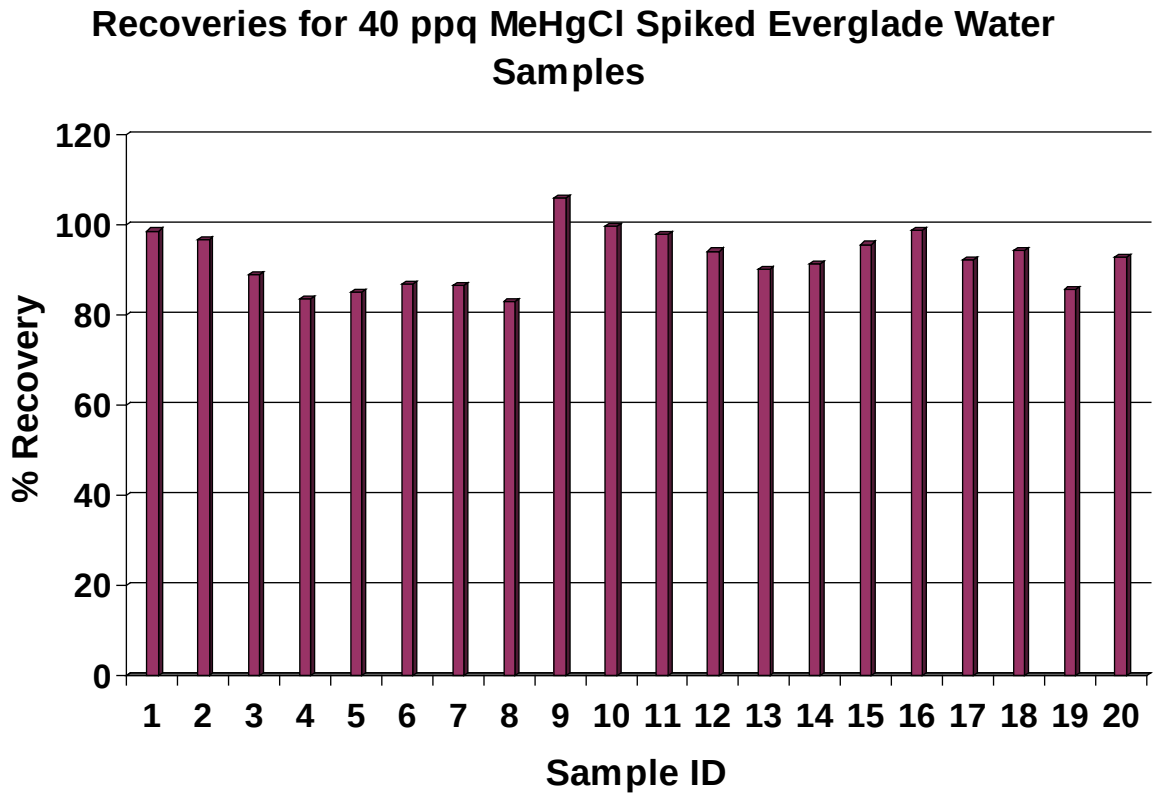


Method Performance

- Excellent linearity
- MeHgCl and n-PrHgCl have almost identical response.
- No blank subtraction needed.
- Prone to carryover above 5 ng/L.



Method Performance



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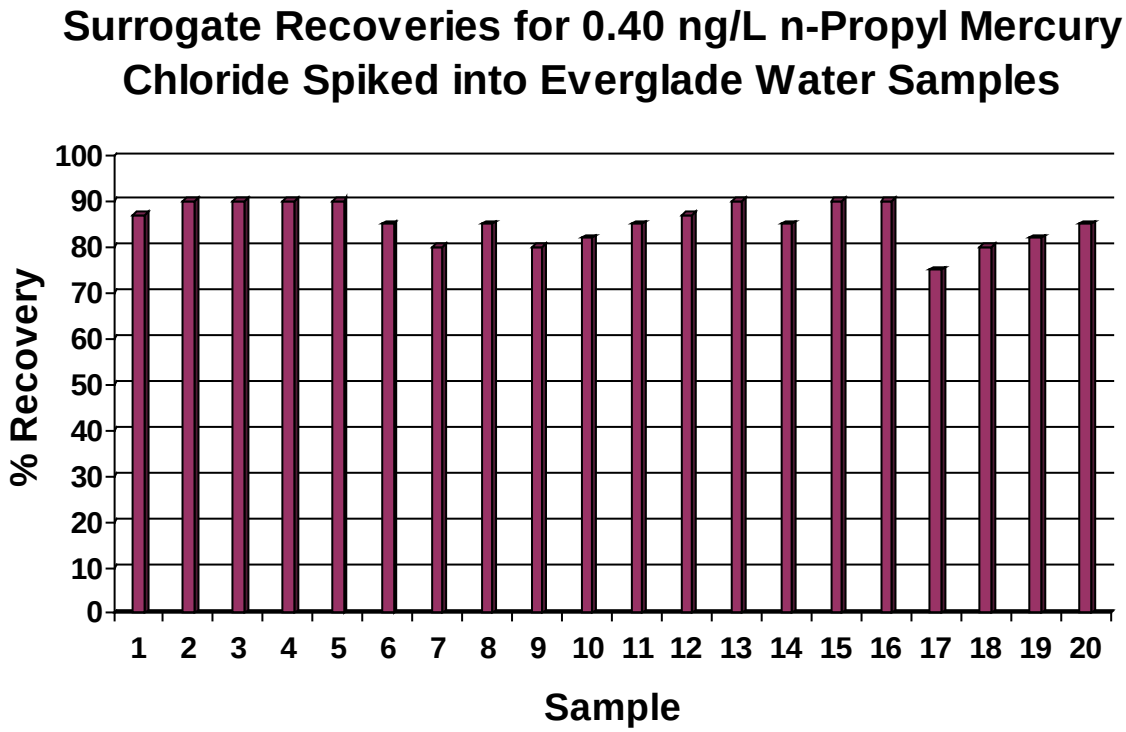

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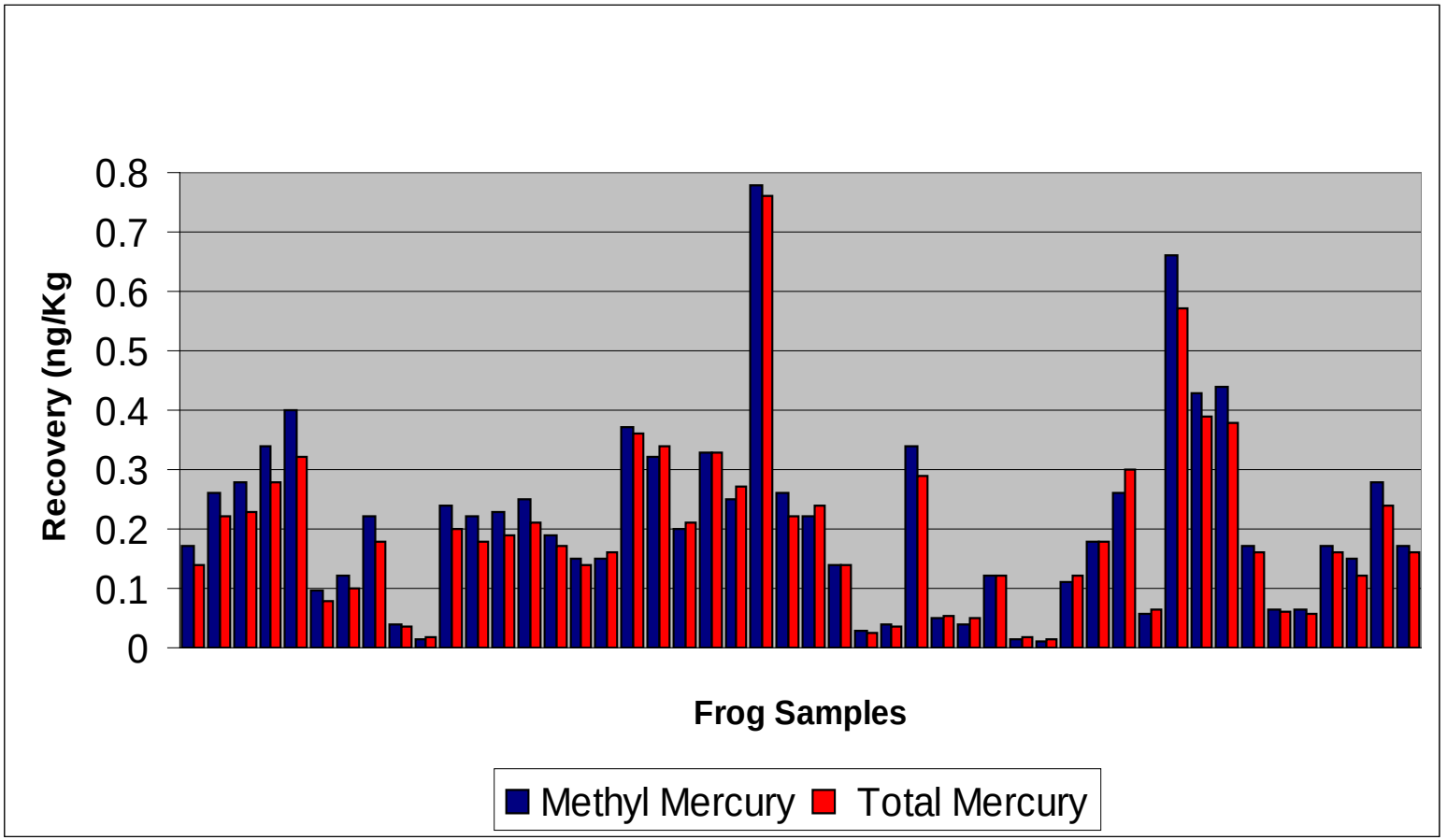

Contrasts Between 1630 and Modified Method.

1630 Draft	FDEP Modified Method
Requires distillation of water samples – 3 to 5 hours.	No distillation required – significant time savings.
Uses as acetate buffer. MDL = 0.06 ng/L.	Uses a cleaner citrate buffer. MDL = 0.02 ng/L.
Packed column, isothermal GC separation.	Capillary GC with temperature program – shorter run times, better resolution.
Uses some custom components - lower initial cost.	Uses commercial off-the–shelf technology – higher initial cost.
Manual method – long term operational costs are high, more labor intensive.	Automated method – significantly lower long term costs, requires less labor.
Greater system variability, low sample throughput.	Lower system variability, high sample throughput resulting in high ROI.

Conclusions

- Modified Sample Preparation - using direct ethylation is significantly faster due to the elimination of distillation.
- Instrument Automation - results in better system reproducibility and higher throughput.
- Large savings in time, labor and operational costs.
- Performance parameters (MDL, spike recoveries, precision) exceed those obtained using the manual method.
- Addition of a surrogate significantly improves monitoring for matrix effects or processing errors.