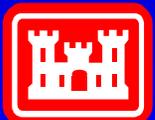


# **Methylmercury Speciation Study**

**Douglas Taggart, Denise MacMillan, Ted  
Shannon, Vic McFarland, and Charles Lutz  
Environmental Laboratory**

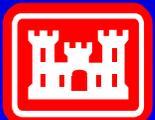


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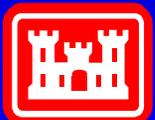
# Project Background

- **Mercury contamination of San Francisco Bay sediments from mercury mines and other sources**
- **Sediment study proposed as part of wetlands restoration**
- **Methylmercury and total mercury determinations requested**



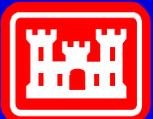
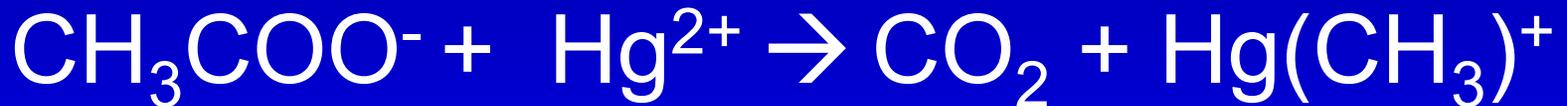
# **Methylmercury Method Selection**

- **Separation techniques: organic extraction, distillation, solid phase extraction, etc.**
- **Analysis: gas chromatography with ECD, AA, ICP, CVAF, FTIR**
- **ECB determined that distillation and CVAF would be required**



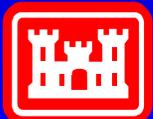
# Mercury Methylation

Bacteria in sediment reduce  $\text{Hg}^{2+}$  to  $\text{CH}_3\text{Hg}^+$  and oxidize  $\text{CH}_3\text{Hg}^+$  to  $\text{Hg}^{2+}$  under a variety of conditions



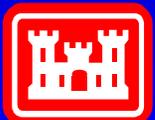
# Methylmercury Poisoning

- Minimata Bay, Japan
  - Preferential bioaccumulation and biomagnification
- Iraq
  - Fungicide-treated grain
- Wildlife
  - 2200 fish advisories in 2000
  - Loons, panthers, otters, oysters



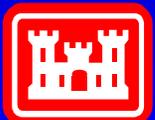
# Methylmercury Exposure Limits

- Reference Dose: 0.1 ng/g bw/day
- Est. Avg. Exposure: 0.027 ng/g/day from fish tissue
- WQ Criterion: 0.3 mg/kg fish



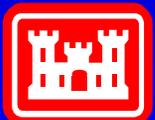
# Mercury Contamination of Bay Area Sediments

- **Mercury mines**
- **Particulates from Gold Rush areas**
- **Contamination in fish species regularly exceeds level of concern for consumption**



# Method Overview

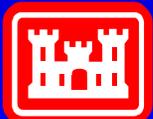
- **Sample distillation**
- **Sample ethylation**
- **Adsorb mercury species**
- **Desorb and chromatograph**
- **Pyrolize to elemental mercury**
- **Atomic fluorescence detection**



# EPA Method 1630

## Published QC Parameters

- LCS recovery: 69 -131%
- CRM recovery: 67-133%
- Matrix spike recovery: 65 – 135%; RPD = 35
- Water MDL: 0.02 ng/L
- Three distillation blanks per analytical batch
- Ethylation blank
- Calibration RSD < 15%
- Low standard recovery: 65 - 135

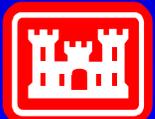


# Method Considerations

- **Safety**
  - **Personal protective equipment**
  - **Mid- to low-level standards**
  - **Laminar flow hood**
- **Contamination**
  - **Powder-free gloves**
  - **Restricted entry**
  - **Clean room environment**

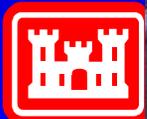
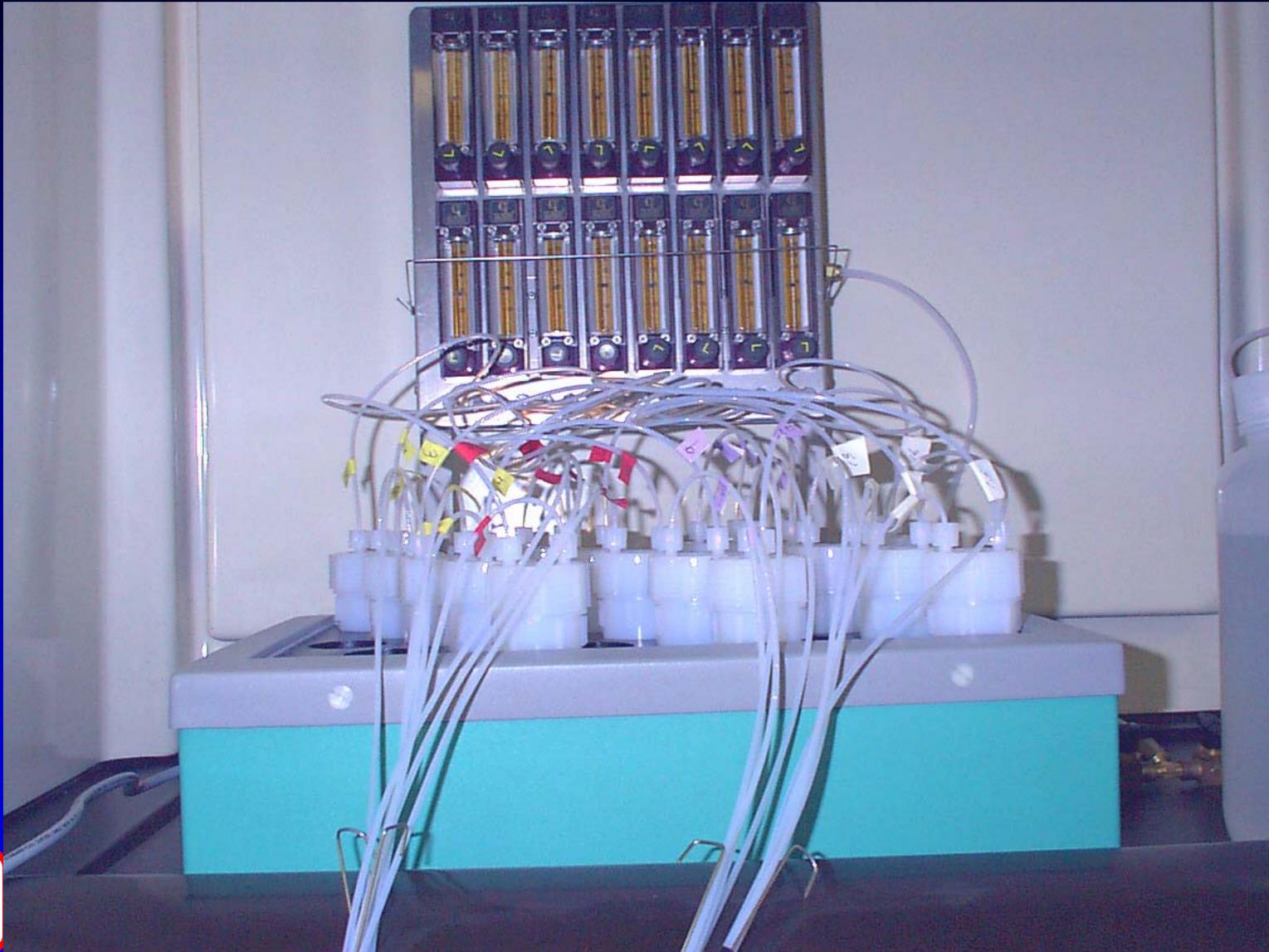


# Hamilton Army Airfield



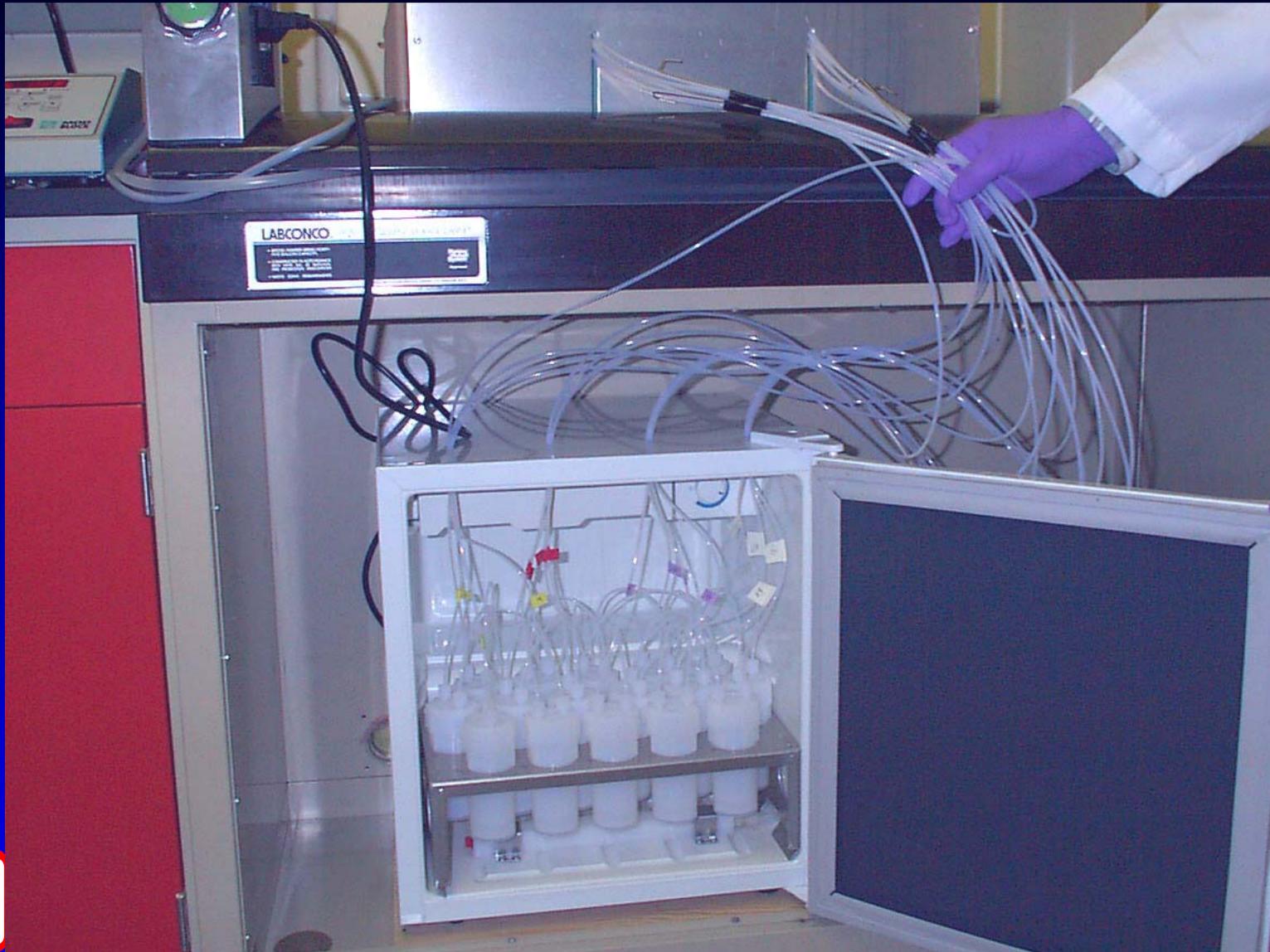
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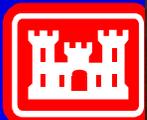
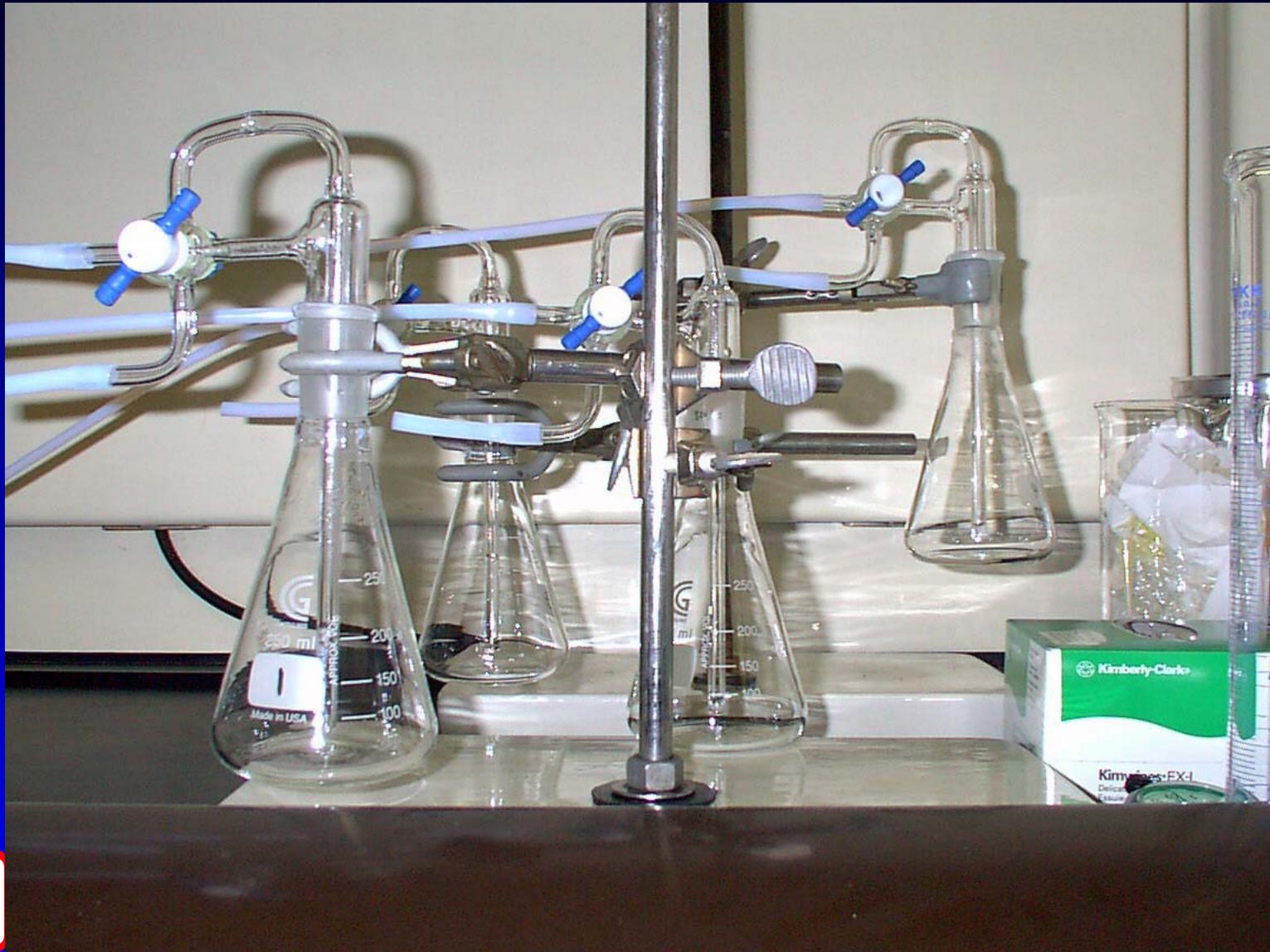
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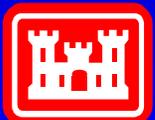
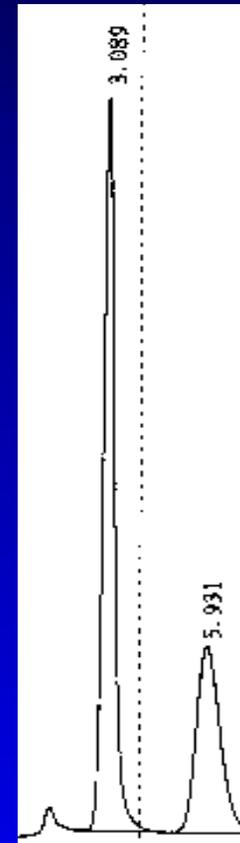
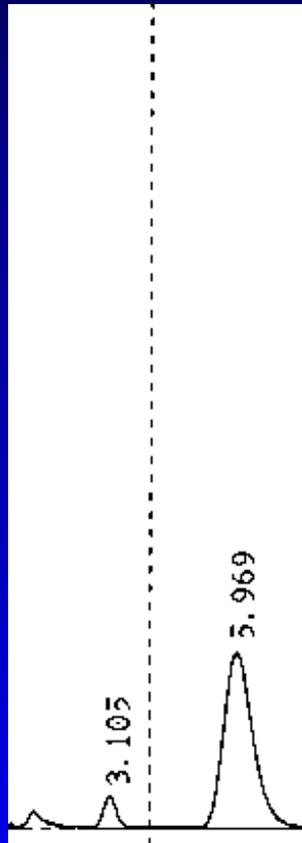
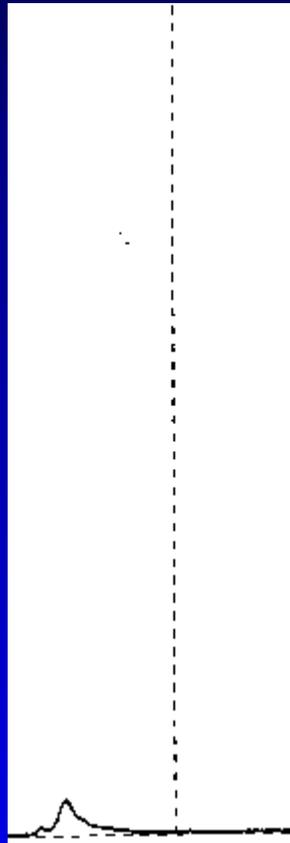
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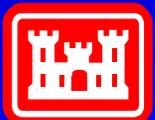
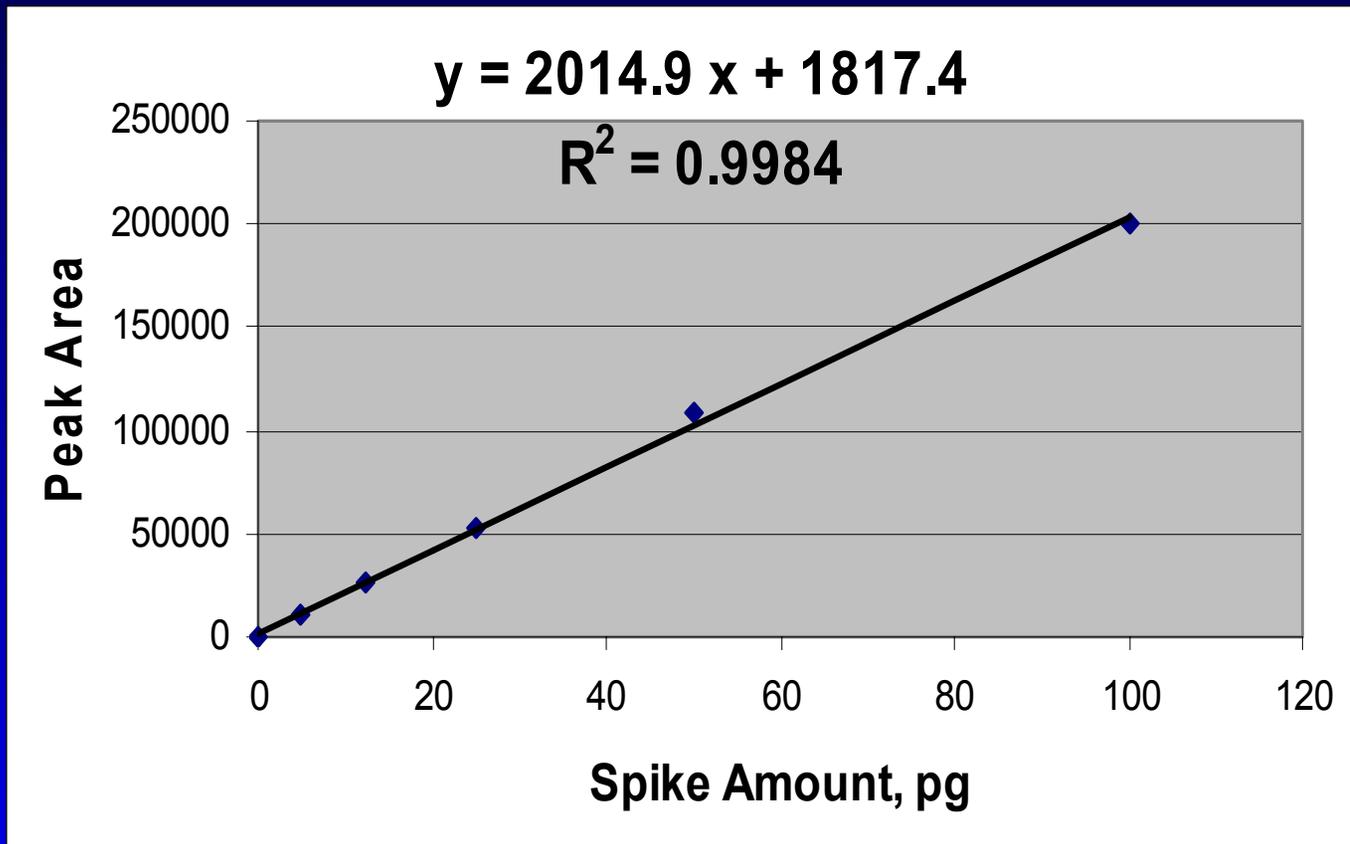
# Methylmercury Chromatograms



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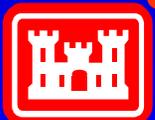
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# Typical Calibration Curve



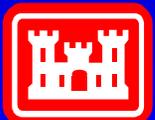
# Study Results

- Methylmercury found in sediment at  $<0.050\text{ug/kg}$ - $10\text{ug/kg}$
- Mercury found in sediment at 30-740  $\text{ug/kg}$
- Low calibration standard equivalent to  $0.05\text{ ng/L}$  in water or  $50\text{ ng/kg}$
- Method blanks  $< 0.02\text{ ng/L}$  ;
- MDL  $0.02\text{ ng/L}$  or  $10\text{ ng/kg}$



# Conclusions

- Sensitive and precise
- Labor intensive
- Expensive



# Other New Methods

- **Arsenic speciation**
- **Perchlorate**
- **Metals by ICP/MS**
- **PCB congeners**
- **RDX, TNT breakdown products**

