REINHOLD ENVIRONMENTAL Ltd.

2019 REINHOLD Round Table Presentation

June 24 & 25, 2019, in Birmingham, Alabama / Hosted by Southern Company

Technology Update -Measurement and Monitoring of Mercury, Arsenic and Selenium in Flue Gas

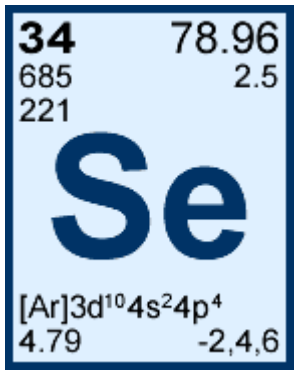
2019 REINHOLD/PCUG Conference

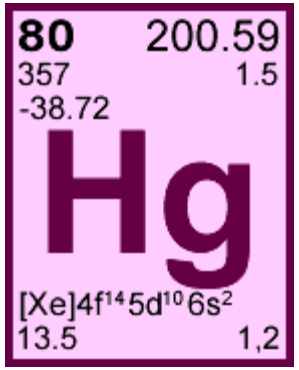
June 24, 2019

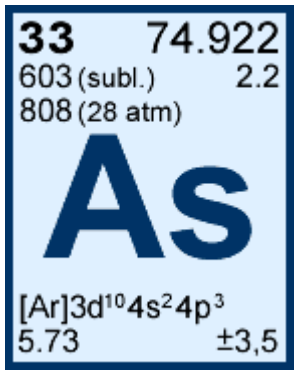
Presented By

Rob Doran

New reasons to measure or monitor Hg, As, or Se?







Effluent Limitations Guidelines and standards for the steam electric power generating category - Clean Water Act
or
ELG Rule - 2015

What are ELGs?

- Effluent Guidelines are national regulatory standards for wastewater discharged to surface waters and municipal sewage treatment plants. EPA issues these regulations for industrial categories, based on the performance of treatment and control technologies.

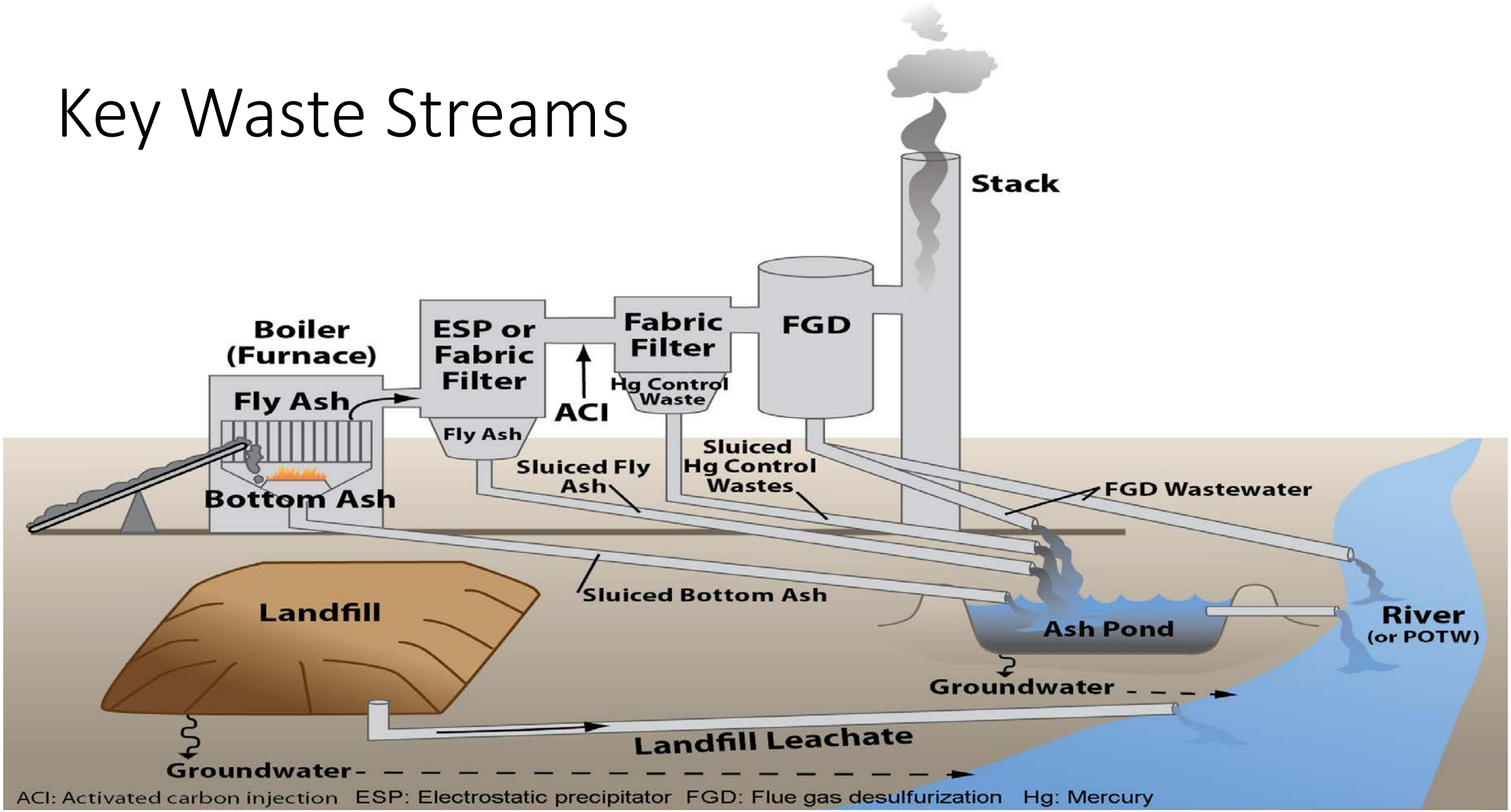
This ELG?

- EPA promulgated the Steam Electric Power Generating Effluent Guidelines and Standards (40 CFR Part 423) in 1974, and amended these in 1977, 1978, 1980, 1982 and 2015.
- This covers wastewater discharges from power plants operating as utilities.
- These regulations are incorporated into the National Pollutant Discharge Elimination System (NPDES) permits.

New or Additional Requirements For Certain Wastewater Streams

- Flue gas desulfurization (FGD) scrubber blowdown
- Fly ash sluicing
- Bottom ash sluicing
- Flue gas mercury control wastewater
- Fuel Gasification waste streams (coal and petroleum coke)

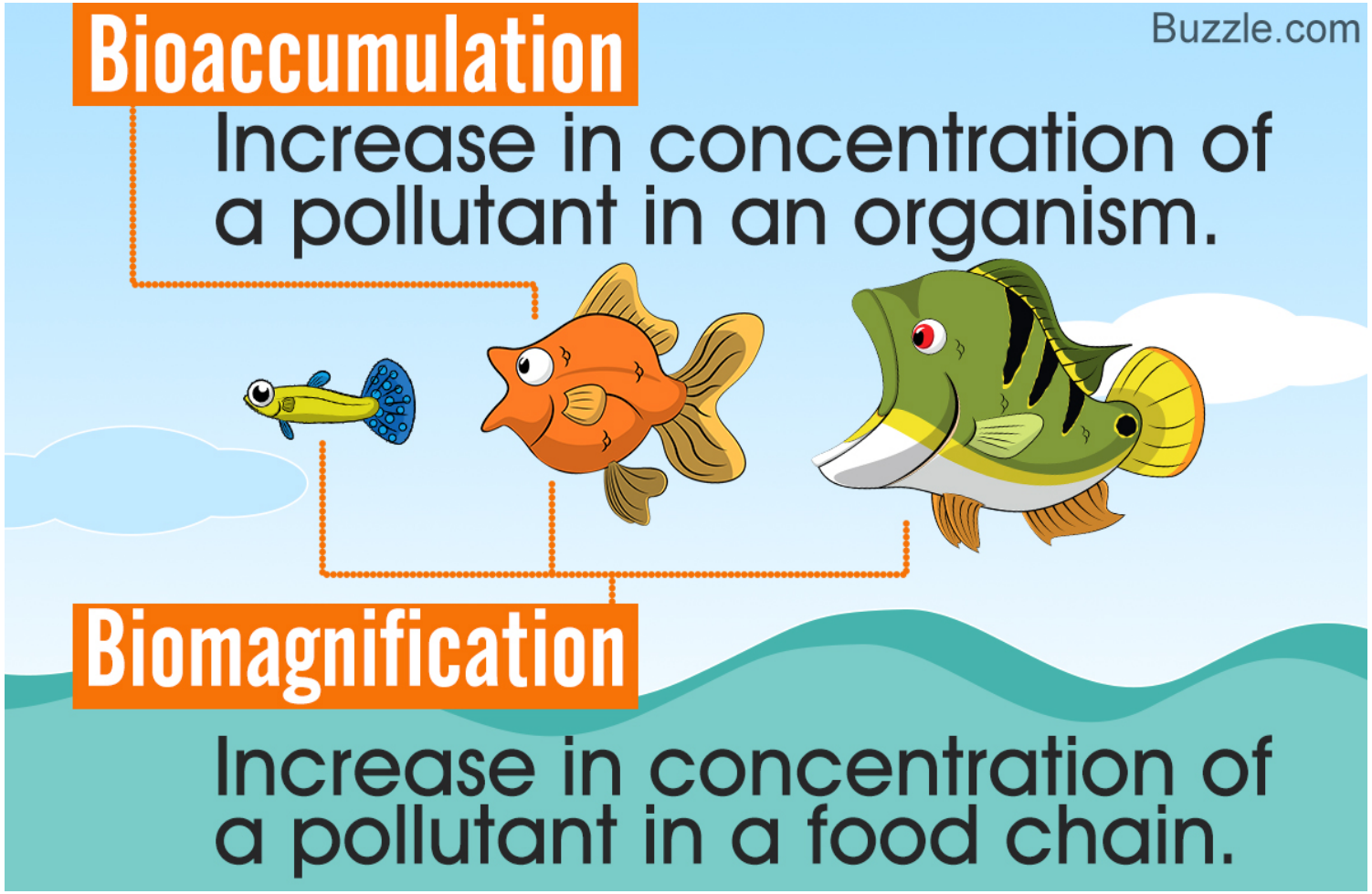
Key Waste Streams



What is the current enforcement status of this rule, pending litigation, changes since 2015 or reconsideration under the current Administration?

Why did the EPA pick out Hg, Se and As?

- These toxins have bioaccumulation - biomagnification properties



Selenium frequently observed at high concentrations in coal combustion wastewater; readily bioaccumulates; elevated concentrations have caused fish kills and numerous sublethal effects (e.g., increased metabolic rates, decreased growth rates, reproductive failure) to aquatic and terrestrial organisms. Short term exposure at levels above the MCL can cause hair and fingernail changes; damage to the peripheral nervous system; fatigue and irritability in humans. Long term exposure can result in damage to the kidney, liver, and nervous and circulatory systems.

Arsenic Frequently observed in high concentrations in coal combustion wastewater; causes poisoning of the liver in fish and developmental abnormalities; is associated with an increased risk of cancer in humans in the liver and bladder.

Mercury Biota with elevated levels have exhibited sublethal effects including metabolic changes and abnormalities of the liver and kidneys; can convert into methylmercury, increasing the potential for bioaccumulation; human exposure at levels above the MCL for relatively short periods of time can result in kidney damage.

Drivers for air measurements?

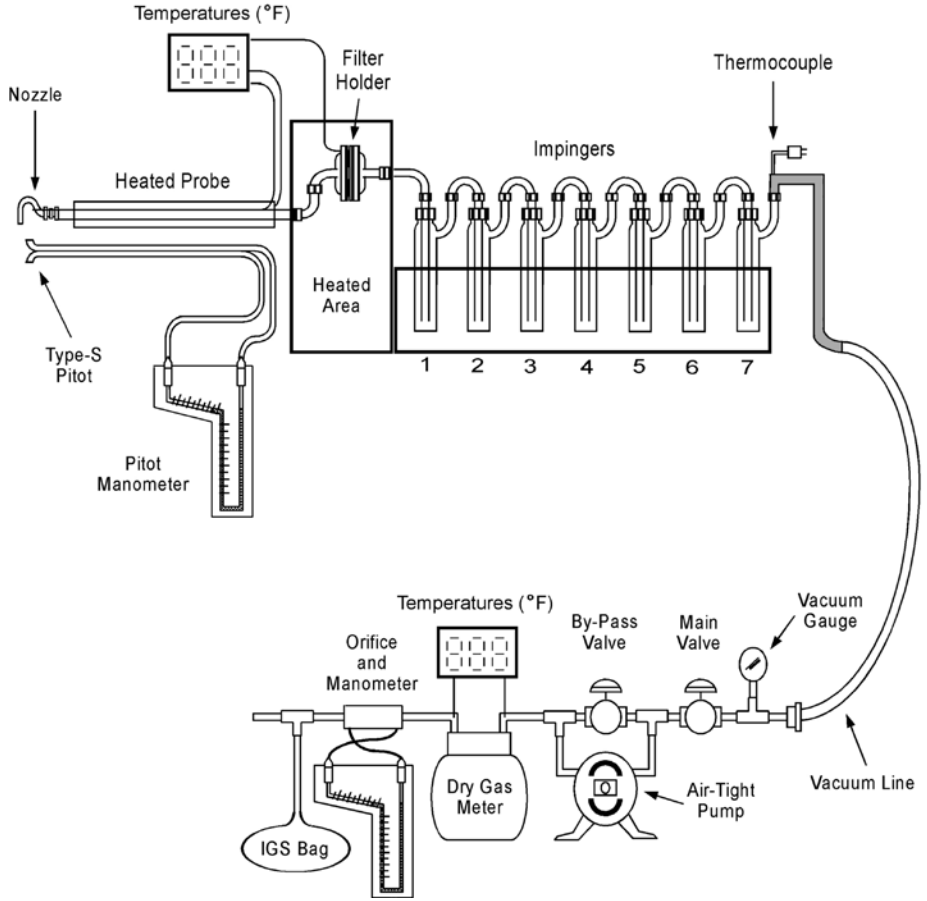
- Speciation determinations of the metal
- Mass balance and fate analysis
- Air Pollution Control design

Drivers for air monitoring?

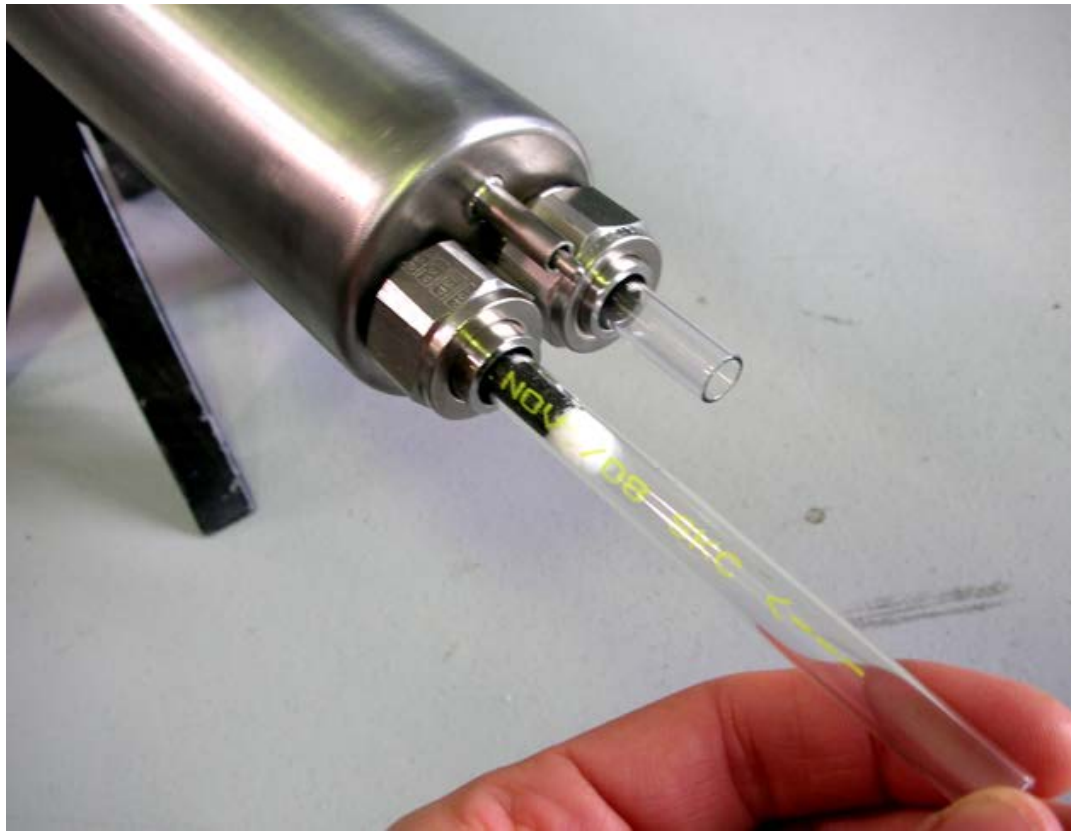
- Regulatory
- Air Permit Requirements

Reference Method Measurements

- “Wet Methods”
- US EPA Method 29



- Sorbent Traps
- US EPA Method 30B



Evaluated Continuous Emissions Monitoring Technologies

- Cold Vapor Atomic Fluorescence (CVAF)
- Thermal Atomic Absorption (AA)
- X-ray Fluorescence (XRF)
- Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)
- Laser Induced Breakdown Spectroscopy (LIBS) & Laser Spark
- Sorbent Traps

Currently used for Hg monitoring

- Cold Vapor Atomic Fluorescence (CVAF)
- Thermal Atomic Absorption (AA)
- Sorbent Traps

X-ray Fluorescence (XRF)

- Only technology that made it to commercial application as a multi-metals (MMX) CEMS - e.g., Cooper Environmental Xact system
- reel-to-reel (RTR) filter tape sampling technology followed by X-ray fluorescence (XRF) analysis of metals in the deposit.
- Limited use since no regulatory requirement. Accepted for MATS but PM CEMS being used as alternative.
- Multiple systems used for a short time at several army munitions incinerators
- One system was used extensively at the Ely Lilly Tippecanoe Incinerator; Lafayette IN from 2005-2010. Evonik Degussa purchased the site and shortly there after shuttered the MMX because of repair needs an dno regulatory requirement to keep it running.

MMX CEMS Performance Specifications

- Performance Specification 10 (PS-10 - 1996) - because the measurement technology had not been fully developed and demonstrated, the specification was not promulgated
- Performance Specification 12A (Hg CEMS) – was promulgated but lack of oxidized Hg standards for calibrating

MMX CEMS Other Test Methods (OTM)

- **OTM-16** Performance Specification YY: Specifications and Test Procedures for X-Ray Fluorescence Based Multi-Metals Continuous Emission Monitoring Systems at Stationary Sources
- **OTM-17** Candidate Conditional Method ZZ: Determination of Metal Concentration in CES' Xact CEMS Stilling Chamber Using Filters and Solid Sorbents with X-Ray Fluorescence Analysis
- **OTM-18** Performance Specification XX: Performance Specifications for a Quantitative Reference Aerosol Generator

MMX CEMS Other Test Methods (OTM)

- **OTM-19** Method X: Determination of Metal Concentrations in Emissions from Stationary Sources (Instrumental Analyzer Procedure)
- **OTM-20** Procedure Z: Quality Assurance Requirements for X-Ray-Fluorescence Based Multi-Metals Continuous Emission Monitoring Systems at Stationary Sources
- **OTM-21** Standard Operating Procedure for Generating a Quantitative Multi-Metals Reference Aerosol with the CES QAG

MMX CEMS Other Test Methods (OTM)

- These OTMs were mainly developed in response to the Ely Lilly install (2005).
- EPA states - “Since there is no federal requirement for multi-metals CEMS at this time, there has been no additional research since OTM 16-20 were drafted”.

Multi-Metals sampling and monitoring with sorbent traps

- EPA Method 30B
- Modified EPA Method 30B (speciated Hg)
- Performance Specification 12B (Monitoring Total Vapor Phase Mercury Emissions from Stationary Sources Using a Sorbent Trap Monitoring System)
- EERC Subtask 4.27 (2014 report discussing an evaluation of a Multi-Element Sorbent Trap (MEST) Method

EERC Subtask 4.27 (2014 evaluation of a Multi-Element Sorbent Trap (MEST) Method

- Sampled for antimony (Sb), arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), cobalt (Co), lead (Pb), manganese (Mn), nickel (Ni), and selenium (Se).
- Compared to EPA Method 29
- for Sb, As, Be, and Co show general agreement
- High blanks from trap materials

EERC Subtask 4.27 (2014 evaluation of a Multi-Element Sorbent Trap (MEST) Method

- Continue to refine the sampling and analysis process to improve (lower) detection
- Evaluate a synthetic sorbent trap material to obtain lower background contributions of metals
- Evaluate longer sampling times (6–8 hour) - improve the accuracy and provide a greater sample mass compared to the blank levels.

More recent trap sampling improvements

- Sorbent traps are now being used for As and Se sampling of flue gases
- Uses same equipment and general methodology as EPA Method 30B

- Could it be adapted for monitoring with current 40 CFR 75 Appendix K systems if needed?

Rob Doran| 724-227-0118 | cell:412-897-6589 | rdoran@cleanair.com