Mercury Emissions Monitoring by TXRF

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nanoXRF

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Outline

- Problem of Mercury Emissions
- MATS Standards
- Mercury Sensor Requirements
- Mercury Sensor/Standards fabrication
- TXRF Data on ng/cm^2 Standards
- Conclusions

Mercury Emissions from EGUs

- **The toxic effects of mercury in water and air are well known**
  - Mercury exposure at high levels can harm the brain, heart, kidneys, lungs, and immune system of people of all ages.
- **In Dec. 2011, EPA announced mercury and air toxics standards (MATS) which reduce mercury emissions from EGUs which will**
  - Have widespread benefits especially to minority and low-income populations who are disproportionately impacted by asthma and other debilitating health conditions.
  - And up to **540,000** missed work or "sick" days will be avoided each year, enhancing productivity and lowering health care costs for American families.
- **However, currently there are no instruments to continuously monitor Hg emissions from EGUs to enable enforcement of these new MATS standards .**
- **Hence there exists a need to develop new technologies to continuously monitor mercury emissions from EGUs.**

MATS Regulations

TABLE 3—EMISSION LIMITATIONS FOR COAL-FIRED AND SOLID OIL-DERIVED FUEL-FIRED EGUS

Subcategory	Filterable particulate matter	Hydrogen chloride	Mercury
Existing—Unit not low rank virgin coal	3.0E–2 lb/MMBtu. (3.0E–1 lb/MWh)	2.0E–3 lb/MMBtu. (2.0E–2 lb/MWh)	1.2E0 lb/TBtu. (1.3E–2 lb/GWh).
Existing—Unit designed low rank virgin coal	3.0E–2 lb/MMBtu. (3.0E–1 lb/MWh)	2.0E–3 lb/MMBtu. (2.0E–2 lb/MWh)	1.1E+1 lb/TBtu. (1.2E–1 lb/GWh). 4.0E0 lb/TBtu [a]. (4.0E–2 lb/GWh [a]).
Existing—IGCC	4.0E–2 lb/MMBtu. (4.0E–1 lb/MWh)	5.0E–4 lb/MMBtu. (5.0E–3 lb/MWh)	2.5E0 lb/TBtu. (3.0E–2 lb/GWh).
Existing—Solid oil-derived	8.0E–3 lb/MMBtu. (9.0E–2 lb/MWh)	5.0E–3 lb/MMBtu. (8.0E–2 lb/MWh)	2.0E–1 lb/TBtu. (2.0E–3 lb/GWh).
New—Unit not low rank virgin coal	7.0E–3 lb/MWh	4.0E–4 lb/MWh	2.0E–4 lb/GWh.
New—Unit designed for low rank virgin coal	7.0E–3 lb/MWh	4.0E–4 lb/MWh	4.0E–2 lb/GWh.
New—IGCC	7.0E–2 lb/MWh [b] 9.0E–2 lb/MWh [c]	2.0E–3 lb/MWh [d]	3.0E–3 lb/GWh [e].
New—Solid oil-derived	2.0E–2 lb/MWh	4.0E–4 lb/MWh	2.0E–3 lb/GWh.

Benefits of MATS

Estimated Annual Number of Adverse Health Effects Avoided Due to Implementing the MATS	
Health Effect	**Cases Avoided**
Premature death	4,200-11,000
Chronic bronchitis	2,800
Heart attacks	4,700
Asthma attacks	130,000
Hospital and emergency room visits	5,700
Restricted activity days	3,200,000

The value of the air quality improvements for people's health alone totals $37 billion to $90 billion each year. That means that for every dollar spent to reduce this pollution, Americans get $3-9 in health benefits.

What Do MATS Mean

MATS Limit: **2×10^{-4} lbs/GWhr**

For a 100MW EGU,

The allowed Hg emissions per hour are : 2×10^{-5} lbs ~ **9 mg of Hg in Flue**

Assuming 0.1% Collection gives **9 ug of Hg on the sensor per hour**

However, this is the UPPER LIMIT. We must be able to measure 0.1 % of this upper limit on a ~1cm^2 sensor accurately giving a sensitivity of

9 ng/cm^2 or 90 pg/mm^2

Hence TXRF

TXRF Solution

Total Reflection X-Ray Fluorescence (TXRF) to measure mercury concentrations using silver-mercury amalgamation technique

FACTS:

1. In 2001-06, Dr. Cooper showed that he can measure 1 ug/cm^2 mercury by ED-XRF
2. TXRF technique has been shown to have sensitivity in the 0.1-1ng/cm^2 range

HOWEVER:

1. Need to develop sensors (substrates) to accurately and consistently collect mercury emissions from the flue
2. Calibration Standards and Relative Accuracy compared to EPA Standard Methods

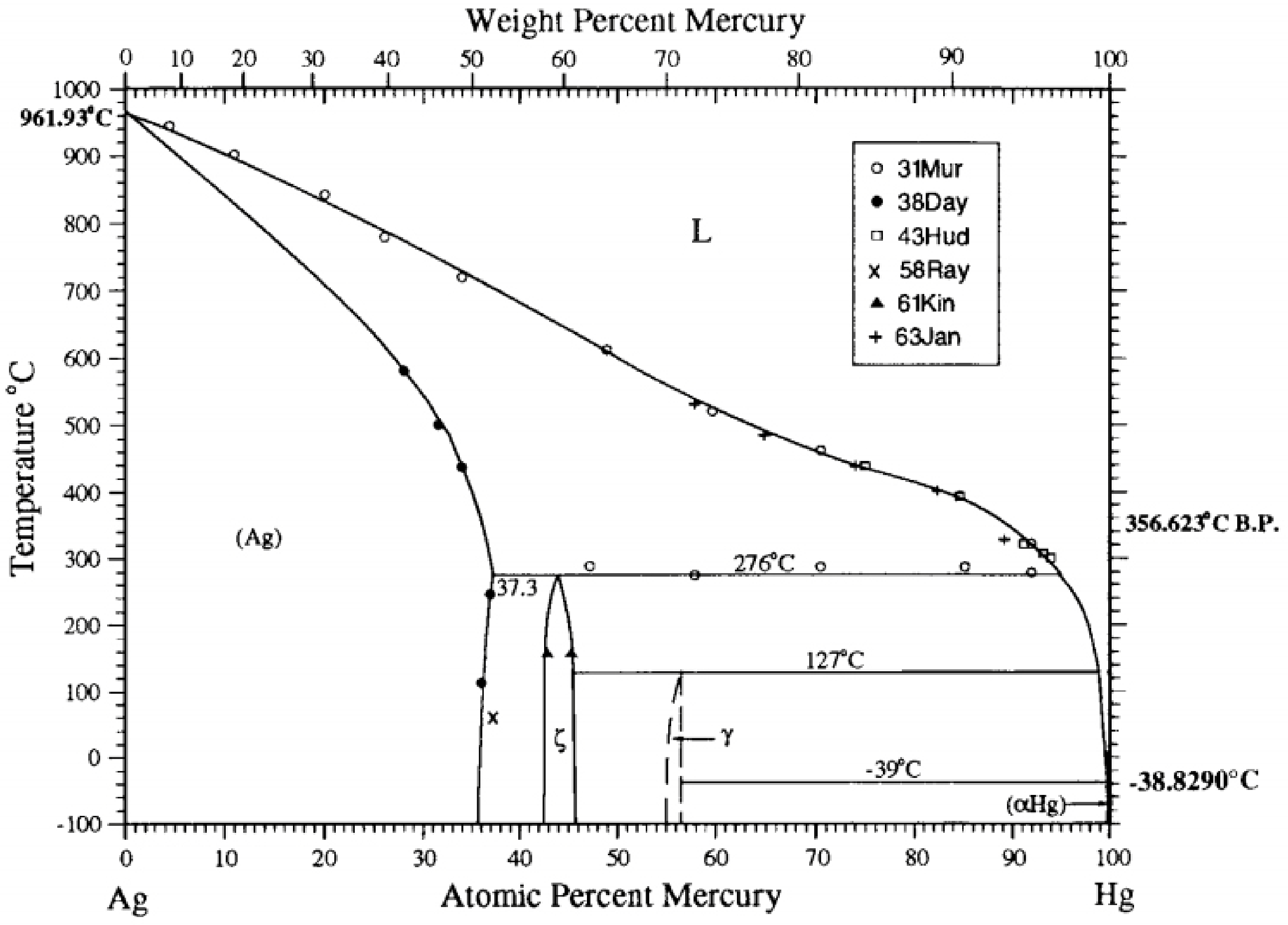
Mercury Collection Problems

- Hg is in vapor phase in the flue
- Temperature is several hundred degree C
- Various species-TGM-Total Gaseous Mercury
- Mercury must be collected at high temperature because it condenses un-evenly when cooled from Flue temperature
- Amalgam formation with Au, Ag, Pd are commonly used

Amalgam Selection for TXRF

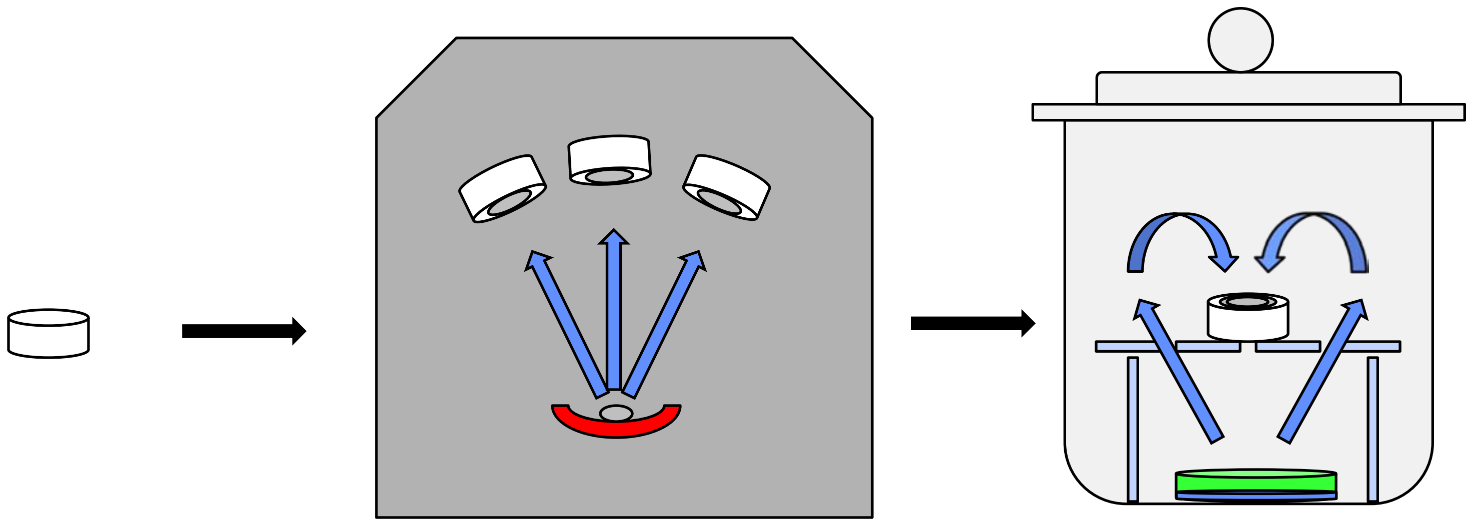
Z	Elem	$K\alpha_1$	$K\beta_1$	$L\alpha_1$	$L\beta_1$	$L\beta_2$	$L\gamma_1$	$M\alpha$	$M\beta$
80	Hg			9.987	11.821	11.922	13.828	2.195	2.282
79	Au			9.712	11.440	11.583	13.379	2.123	2.204
47	Ag	22.159	24.938	2.984	3.150	3.347	3.519		

Ag-Hg Phase Diagram



Solubility of Hg in pure Ag is 35-37%

Hg Standard Fabrication Process



1. Clean Substrate

2. Ultra Precise Proprietary Thin Film Vacuum Deposition of Silver onto Quartz Substrate

3. Ultra Precise Proprietary Room Temperature Vapor Phase Deposition of Mercury

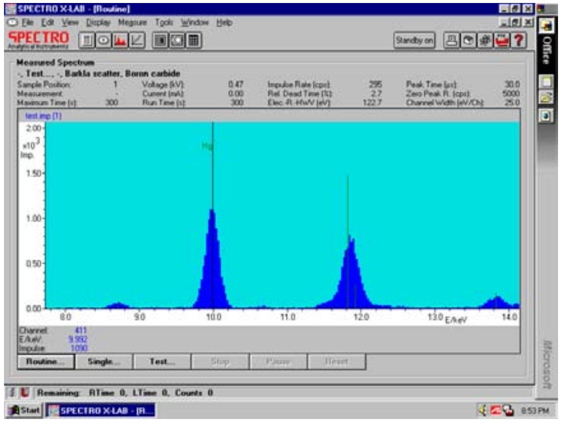
ng Standard Fabrication Steps

- Step 1: Fabricate 1-100 ug/cm^2 NIST Traceable Calibration Standards by Hg-Ag Amalgam Process and Certify them by weighing the deposits (nanoXRF Process)
- Step 2: Confirm the Low End 0.3-3 ug/cm^2 Standards Accuracy by Drawing XRF Calibration Curve
- Step 3: Use these Standards to determine the TXRF Calibration Curve for Hg-Ag Standards
- Step 4: Fabricate a series of nanoGram Standards and determine their concentration using the TXRF Calibration Curve
- Step 5: Correlation with ICP and AAS

nanoXRF Standard Certification Process

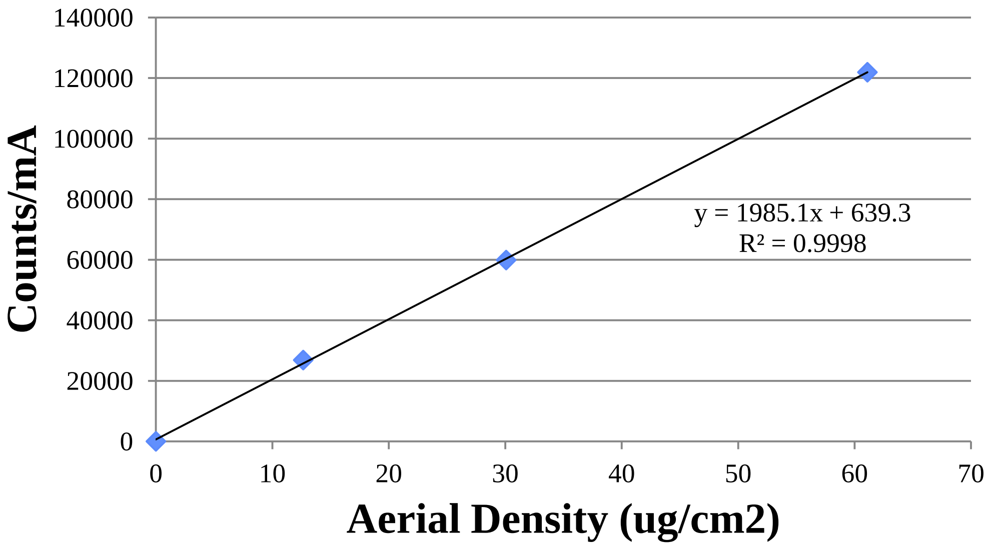
- Each standard is measured *in-situ* during manufacturing with a resolution of 1 nanogram.
- Each standard is measured with a high precision balance with a resolution of 100 nanograms.
- Each standard is measured with a XRF instrument to confirm the standard accuracy.
- Each standard is measured by XRF to guarantee absence of contamination.
- Each standard is compared against other XRF standards to >95% agreement

XRF Calibration Curve for Hg-Ag



Spectro X-Lab 2000 XRF

Mercury Calibration Curve



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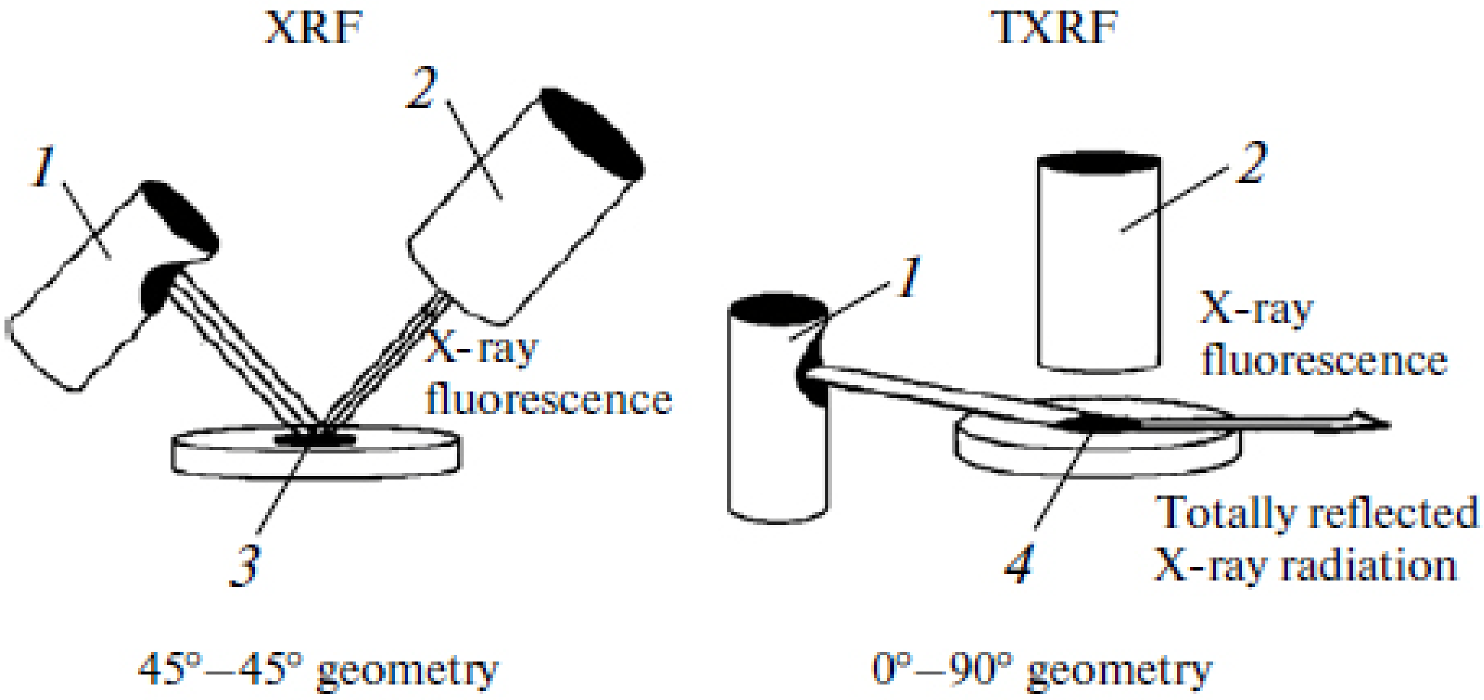
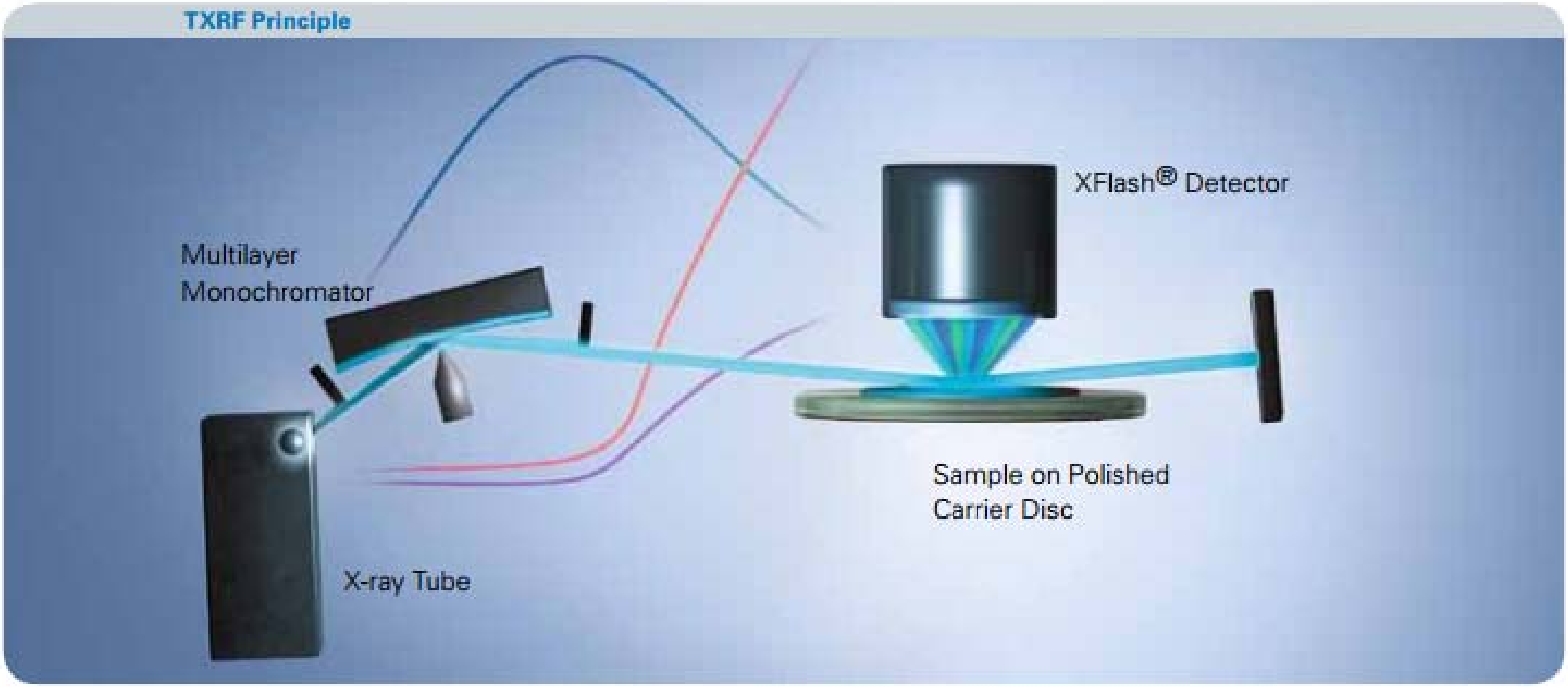
ED-XRF vs TXRF



Bruker S2 Picofox

S2 Picofox Hardware



S2 Picofox Specifications

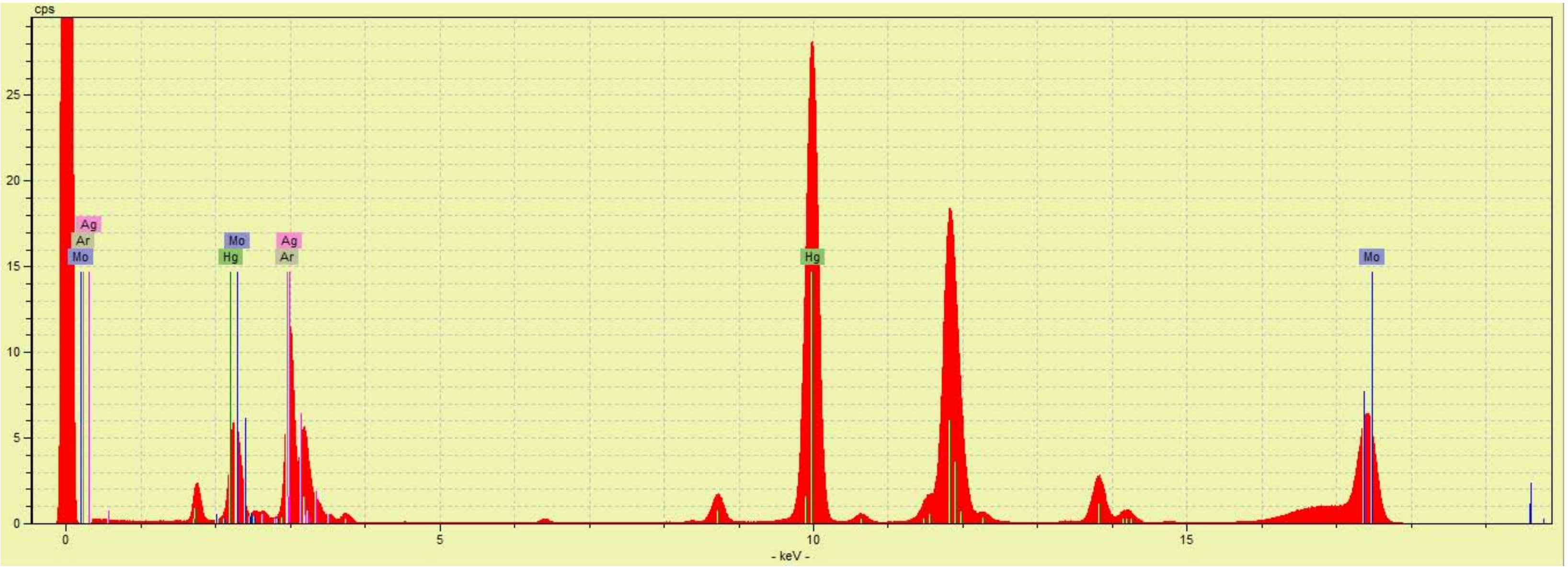
Element range	Mo excitation: Al to U (with exception of Nb to Ru) W excitation: K to U
Concentration	ppb to 100 %
Detection limit	< 3 pg Nickel (Mo excitation with High Efficiency Module)
Sample types	Liquids, suspensions, powders, particles, metals, thin layers, tissues, wipes, filters etc.
Sample volume	Liquids and suspensions from 1 to 50 µl Particles up to 100 µm in diameter, powders up to 10 µg
Sample carrier	25 quartz and 100 acrylic glass carriers (30 mm diameter) included in delivery
Sample changer	Manual version for single samples Automatic version with cassette for up to 25 samples
X-ray tube	30 W or 40 W metal-ceramic, max. 50 kV, 1 mA air-cooled, Mo or W target
X-ray optics	Multilayer monochromator
Detector	Peltier-cooled XFlash® Silicon Drift Detector No need for liquid nitrogen 30 mm² active area Energy resolution < 150 eV at 100 kcps (Mn Kα)
Interface	Data exchange by RS232 serial interface Sample changer with RS232 (automatic version)
Mains	100/240 V, 50/60 Hz, max. power consumption 180 W
Size	300 x 590 x 450 mm (height x width x depth)
Weight	37 kg
Options	Gas purge option for improved detection of Ag and Pd
Accessories	Washing cassette for sample carriers Sample cassette for 25 carriers Starter Set for TXRF (pipettes, tips, racks, tubes, mortar , spatula)

XFlash® is a trademark of Bruker Nano GmbH

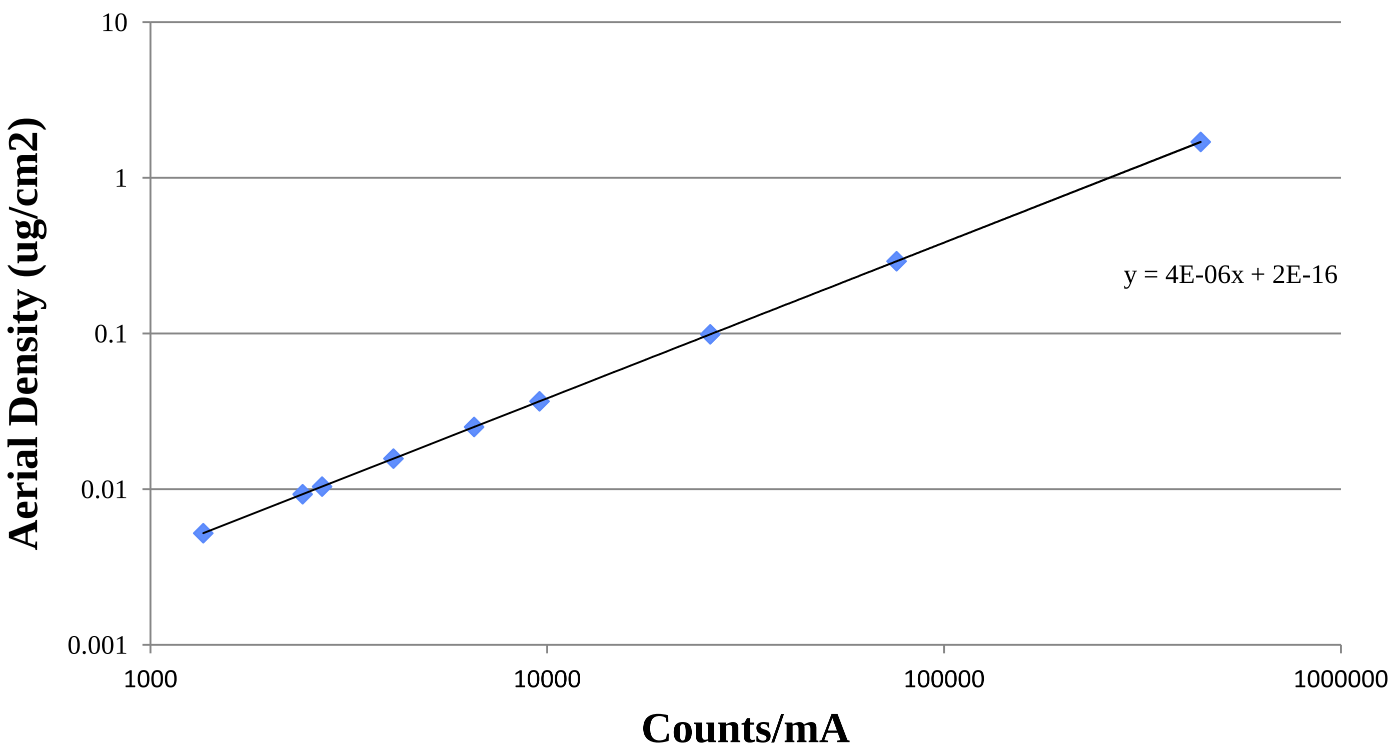
TXRF Sample Details

- Samples were prepared on 30mm diameter quartz disks
- Deposit 10ug/cm^2 of 99.999% pure Ag
- Expose these to different level of Hg vapor for various times (10 seconds to 1 hour) at room temperature.
- PicoFox TXRF measurement time was 1,500 sec
- Other conditions: Mo anode, 9 um Mo filter, 50KV, 600 uA,
- Obtained concentrations from 5ng/cm^2 to 3ug/cm^2

Hg-Ag Spectra from S2 Picofox



TXRF Data



Aerial Density (ug/cm2)
10
1
0.1
0.01
0.001
y = 4E-06x + 2E-16
1000
10000
100000
1000000
Counts/mA

Conclusions

- Demonstrated a technique to fabricate ng/cm^2 mercury standards
- Technique can be used for capturing total gaseous mercury from the flue gases at EGUs
- TXRF was used to measure Hg in the $5ng/cm^2$ ($50pg/mm^2$)
- Next step is implementation at a Power Plant.

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MERCURY EMISSIONS MONITORING BY TXRF

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In December 2011, the Environmental Protection Agency (EPA) announced the Mercury and Air Toxics Standards (MATS) for power plants. This rule requires existing and new coal-fired power plants to meet stringent mercury reduction levels. Specifically, the rule applies to new and existing electric generating units (EGUs) that burn coal or oil to generate greater than 25 megawatts (MW) of electricity for sale and distribution through the national electric grid to the public. These new standards limit mercury emissions on the order of tenths to ten-thousandths of a pound/gigawatt-hour of gross electrical output (lb/GWh) depending upon the coal type, whether the plant is existing or new, and the power plant technology. Robust, novel sensor technologies are needed that can accurately, precisely, and continuously monitor and measure mercury emissions levels to determine compliance with these standards and monitoring requirements for coal- and oil-fired EGUs.

NanoXRF @ UHV Technologies, Inc. is developing a TXRF technology to collect trace mercury amounts emitted from EGUs and measure mercury concentrations in ng/cm2 in a continuous manner. In this paper, we will present our efforts on the development of sub-microgram/cm2 mercury standards, substrate development for TXRF samples and recent results on TXRF measurements.

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