Using Handheld XRF Technology to Determine Surface Mercury Concentration – the Yeh/Kibogy method

Jannette Kibogy
API Industrial Hygiene TF Workshop
Hyatt Hotel, Denver CO
May 25th 2010

Outline

- Mercury –Properties
- Impacts of Mercury
- Opportunity Statement
- Background on XRF
- XRF Testing and methodology
- Summary
- Questions

Unique Properties

- Only common metal liquid at room temperature
- Boiling Point: 356.73°C (674.1°F)
- Very high surface tension
- Heavy – 2 Tblsp ~ 1 lb (0.45 Kg)
- Alloys easily with other metals
- High vapor pressure – doubles every 10°C
- Vapor is colorless, tasteless, odorless
- Will "Hide" in the pores of concrete and metal

Mercury (Hg) in crude

- Naturally occurring element present in virtually all oil and gas worldwide
- Concentrations in reservoirs vary from low part per billion (ppb) to hundreds of ppb depending on geology
- Hg Species in crude appears to be largely elemental and/or inorganic compounds such as mercuric sulfide
- Hg Species from crude may accumulate in process equipment over time

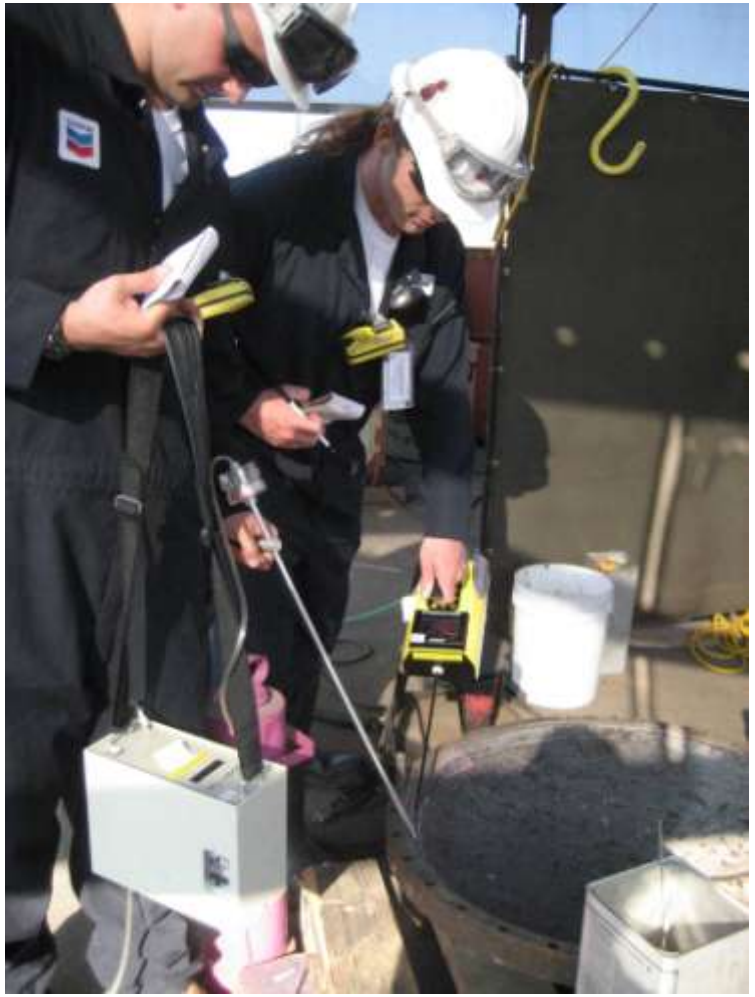
Impact of Mercury in Oil Production and Processing

Mercury accumulations may require special procedures in the following areas:

- Environment
  - Potential Waste issues
- Health: Manage Exposures from
  - Volatile - Inhalation
  - Absorptive - Surface contamination
  - Particulate - In hot work processes
- Safety
  - Prevention of corrosion in process equipment caused by potential metal amalgamation or possible liquid metal embrittlement (LME)

Opportunity Statement

- Develop a method for proper detection of mercury surface concentrations which will assist in future planning and management of Hg containing materials
- The XRF field technique provides a significant improvement over our current best practices and is cost effective



Background on XRF

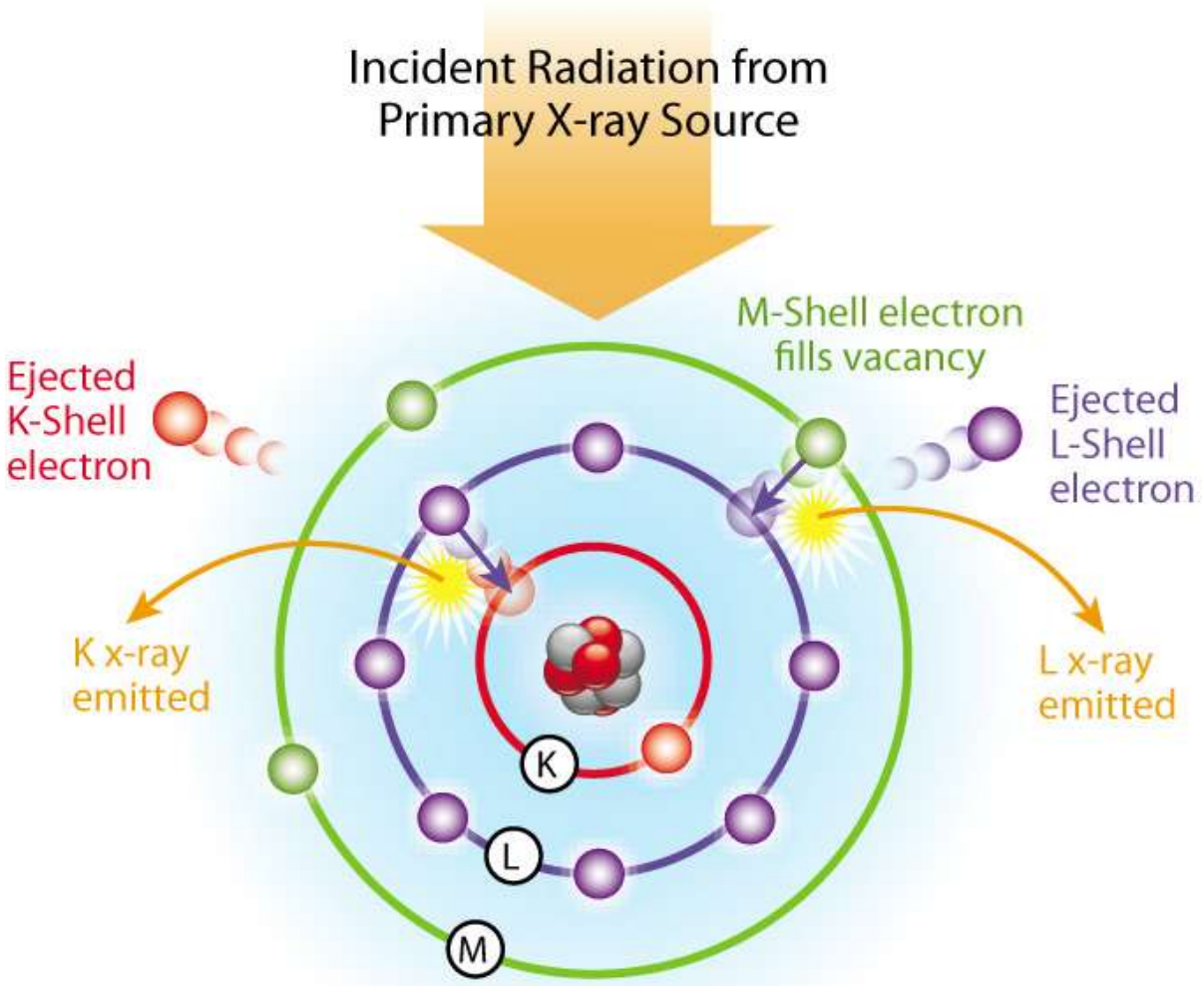


Photo courtesy of Thermo FisherScientific.

Background on XRF

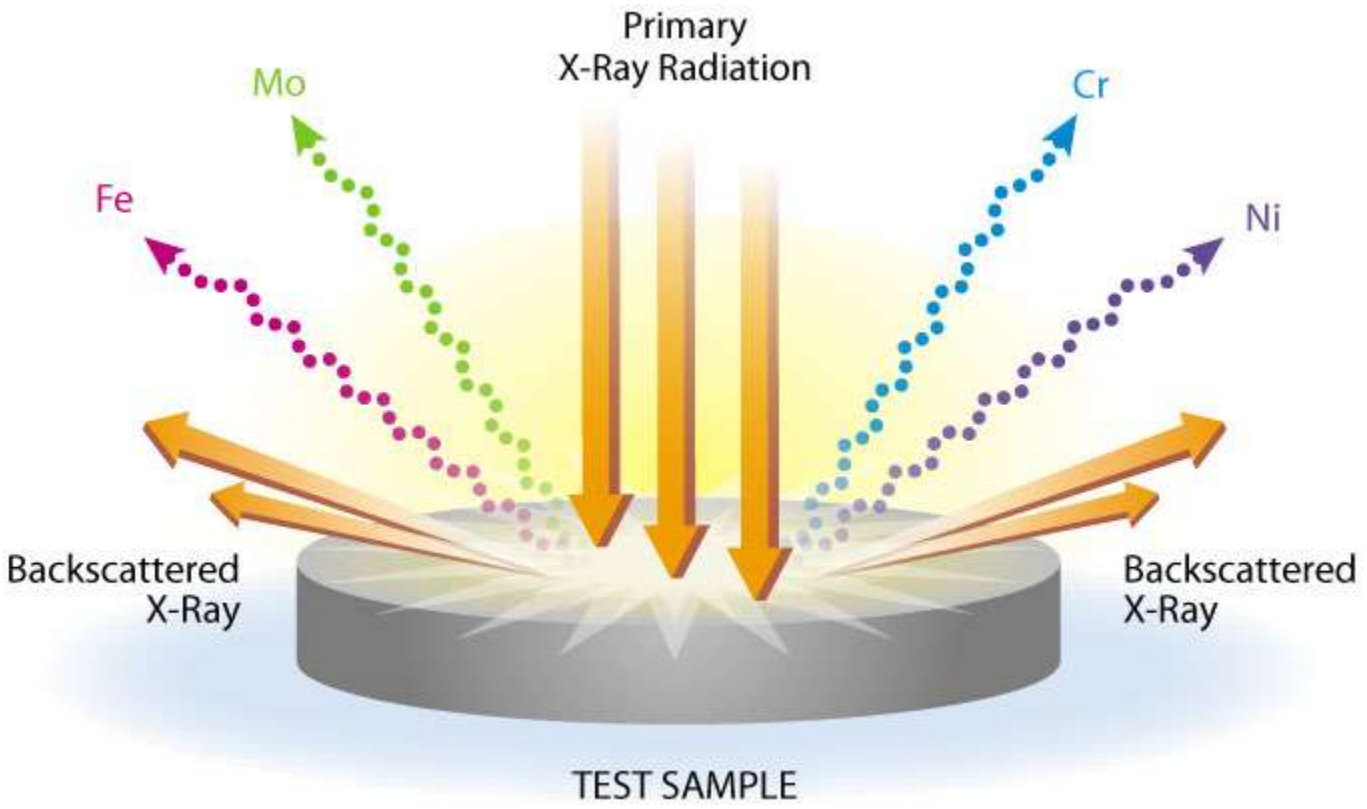


Photo courtesy of Thermo FisherScientific.

Handheld XRF

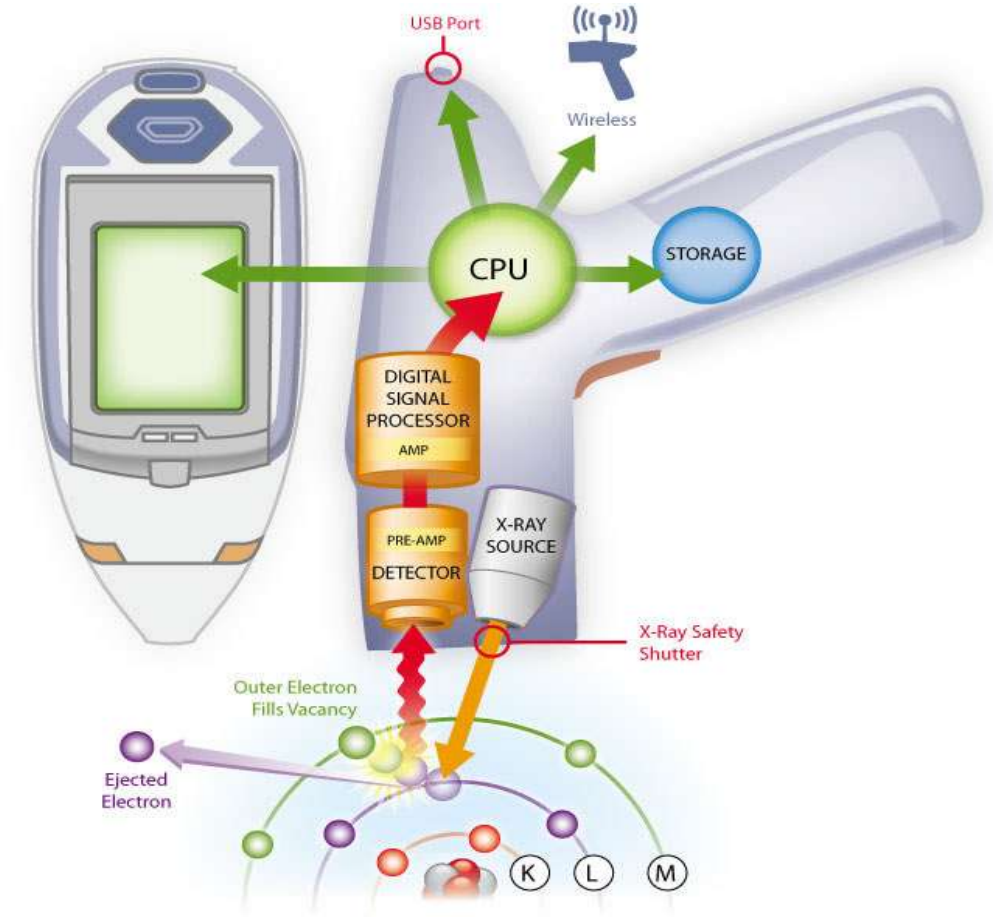


Photo courtesy of Thermo FisherScientific.

Initial XRF testing

- Promising but missing field and lab verification data
- XRF units could easily detect the presence of high concentrations of mercury on the surface of metal >% levels
- What is needed for this method to be practical
  - A way to determine the limit of detection (LOD)
  - A way to interpret the unit readings (ppm or $\mu g/cm^2$)

Refinery Pipe Segment Analysis

- Obtained pipe from refinery
- Detected high mercury vapor readings during torch cutting (max – 3.2 mg/m^3)
  - Average readings in the area >0.015 mg/m^3
  - All workers wearing appropriate PPE
- The cut line had no visible mercury or vapor readings when cool, suspected mercury sulfide deposits
- Received sample sections cold cut into sample panels for XRF testing

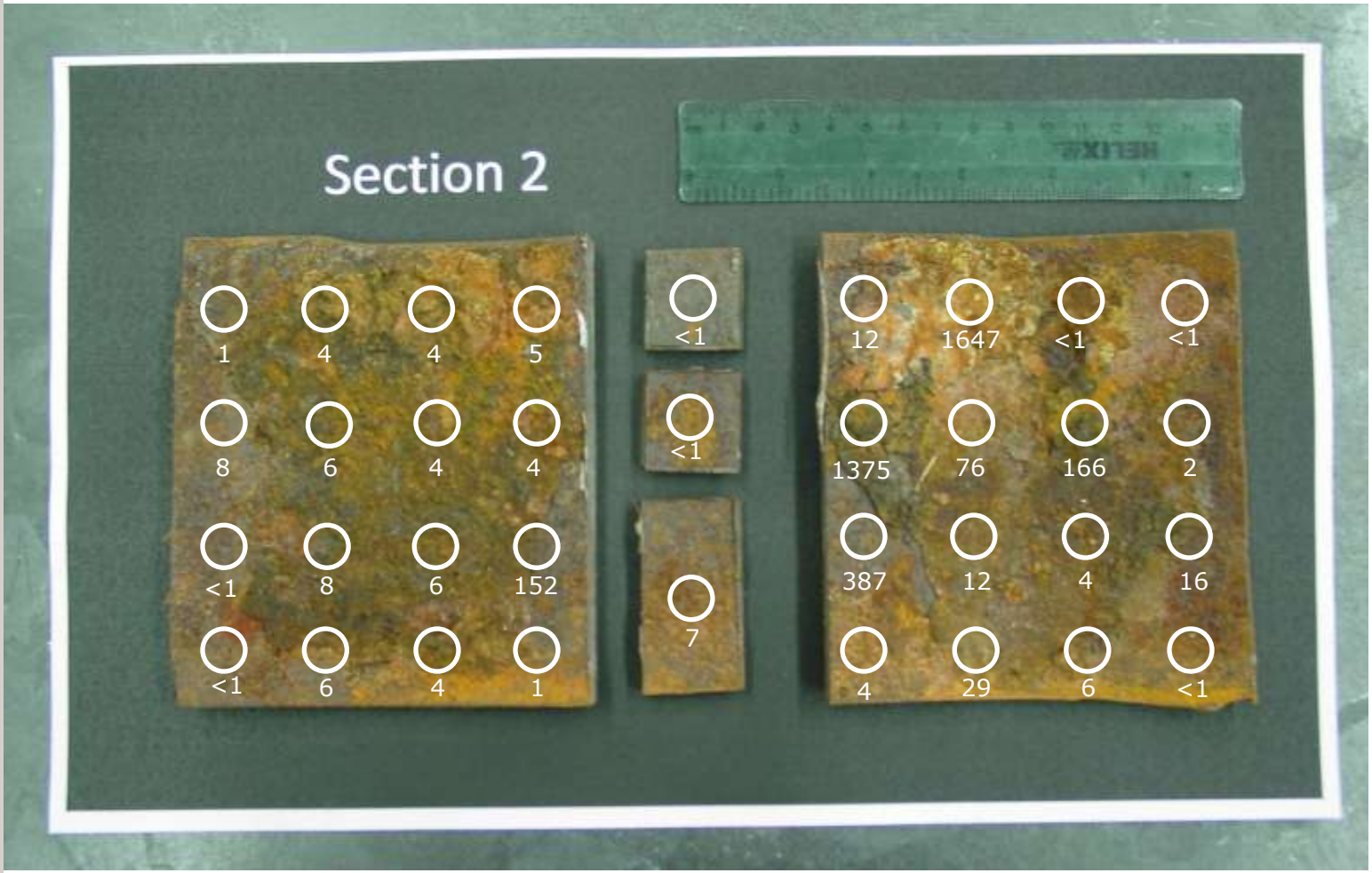
Pipe Segment Analysis

- The prepared sample panels were tested with a vendor's demonstration XRF unit
- The results confirmed that XRF units could detect low levels of mercury surface contamination and lead us to further develop the idea of generating standard coupons for field measurement calibration
- We decided to compare two different brands of XRF machines

Pipe Segment: Hg Concentrations by Handheld XRF in µg/cm²

- A sample grid was used to both protect the sample and guide repeatable measurements
- The field samples showed great variation in the mercury concentration deposited on the surface
- We did not know the original orientation of the pipe

Hg concentration for Section 2 varied widely and illustrates one limitation of XRF testing

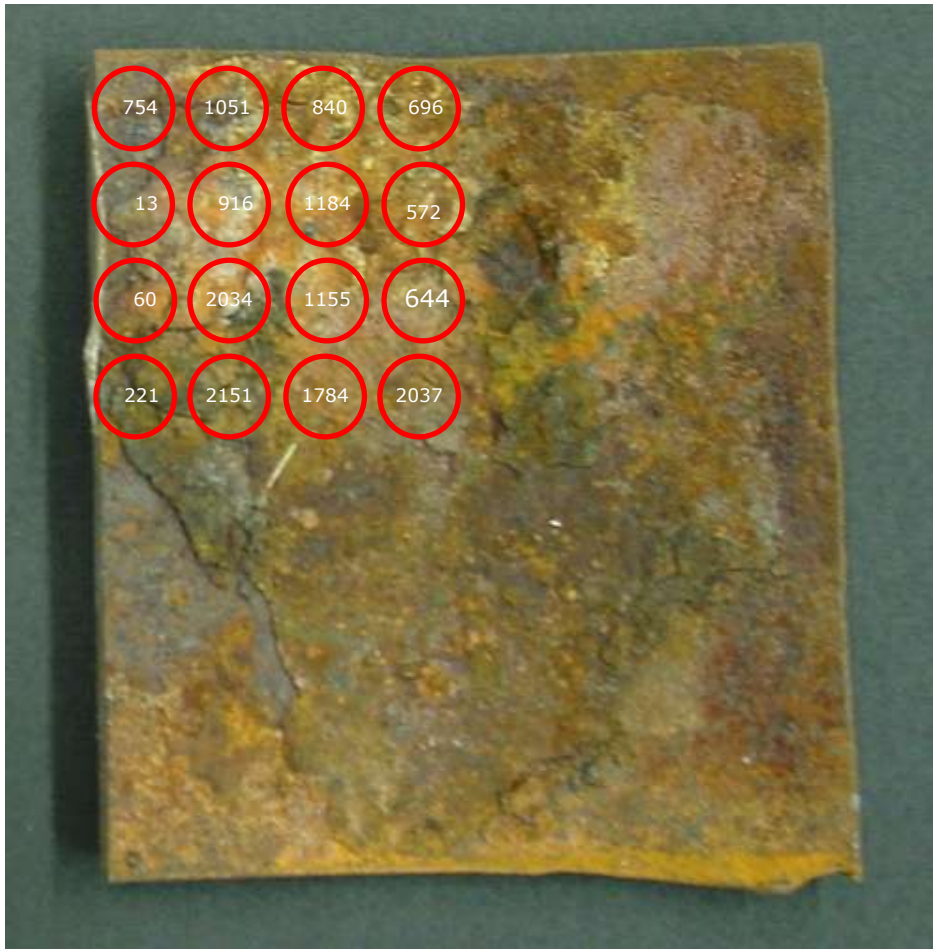


- XRF will only see what the detection window covers

Additional analyses for Section 2, with a finer grid over the area where high concentrations were observed

Hg concentrations, in µg/cm^2

Se concentrations, in µg/cm^2

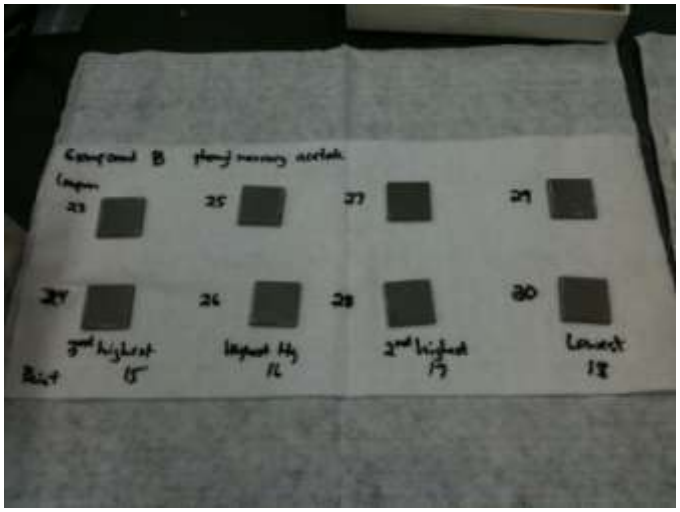


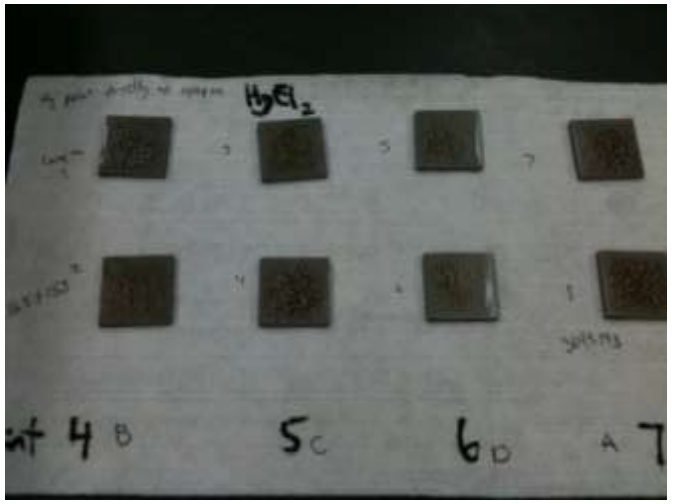
Generation of Coupon Standards for XRF testing

- XRF is limited to measuring superficial mercury
- Supported by studies of O/H pipe, subsurface pipeline and tank samples
- In these cases, the contact occurred under conditions where Hg oxide was stable
- To date we have not seen evidence that the mercury penetrates beyond the depth of XRF sensitivity
- Based on the good performance on the pipe samples a range of metal coupons were created with different surface contamination levels
- The purpose was to create standards that could be used to field calibrate a portable XRF unit and determine the Limit of Detection (LOD) on a metal substrate

Coupons were treated with Mercury containing paints

- Mimics surface contamination observed for tested specimens, in a stable, adherent matrix, clear paint was used – no pigment interference
- Range of surface concentrations 0 to 7 µg/cm^2
- Some paints formulated with inorganic Hg ($HgCl_2$), other with organic (diphenylmercury), and no difference in the XRF sensitivity was observed





Comparison of Instruments

Brand A Handheld XRF

- Modified the Refinery's Materials Group's instrument

Brand B Handheld XRF

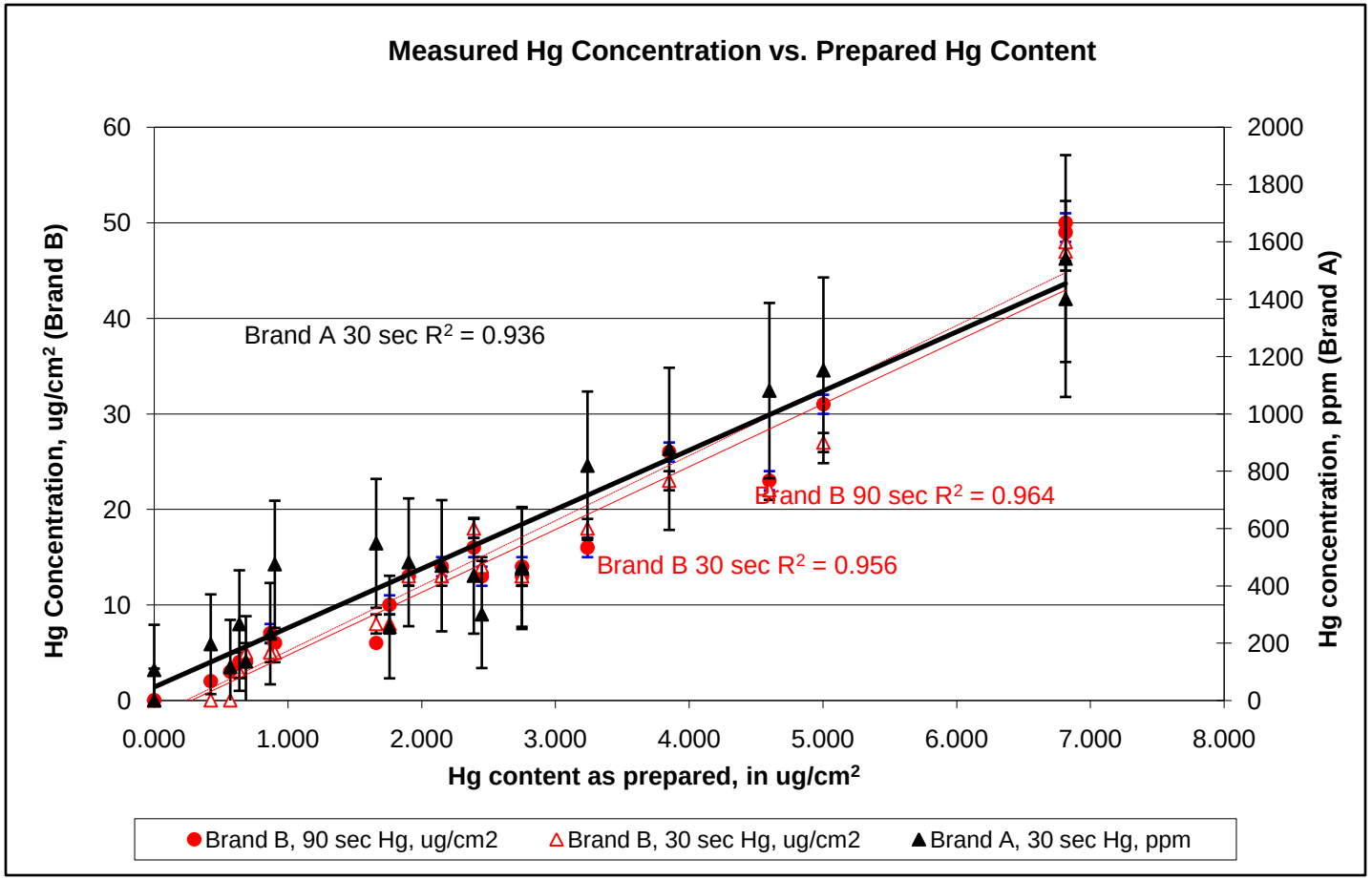
- Used a demonstration instrument from a local distributor

Both instruments performed well, with R^2 for correlations between measured concentration and prepared concentrations ranging from 0.936 to 0.964

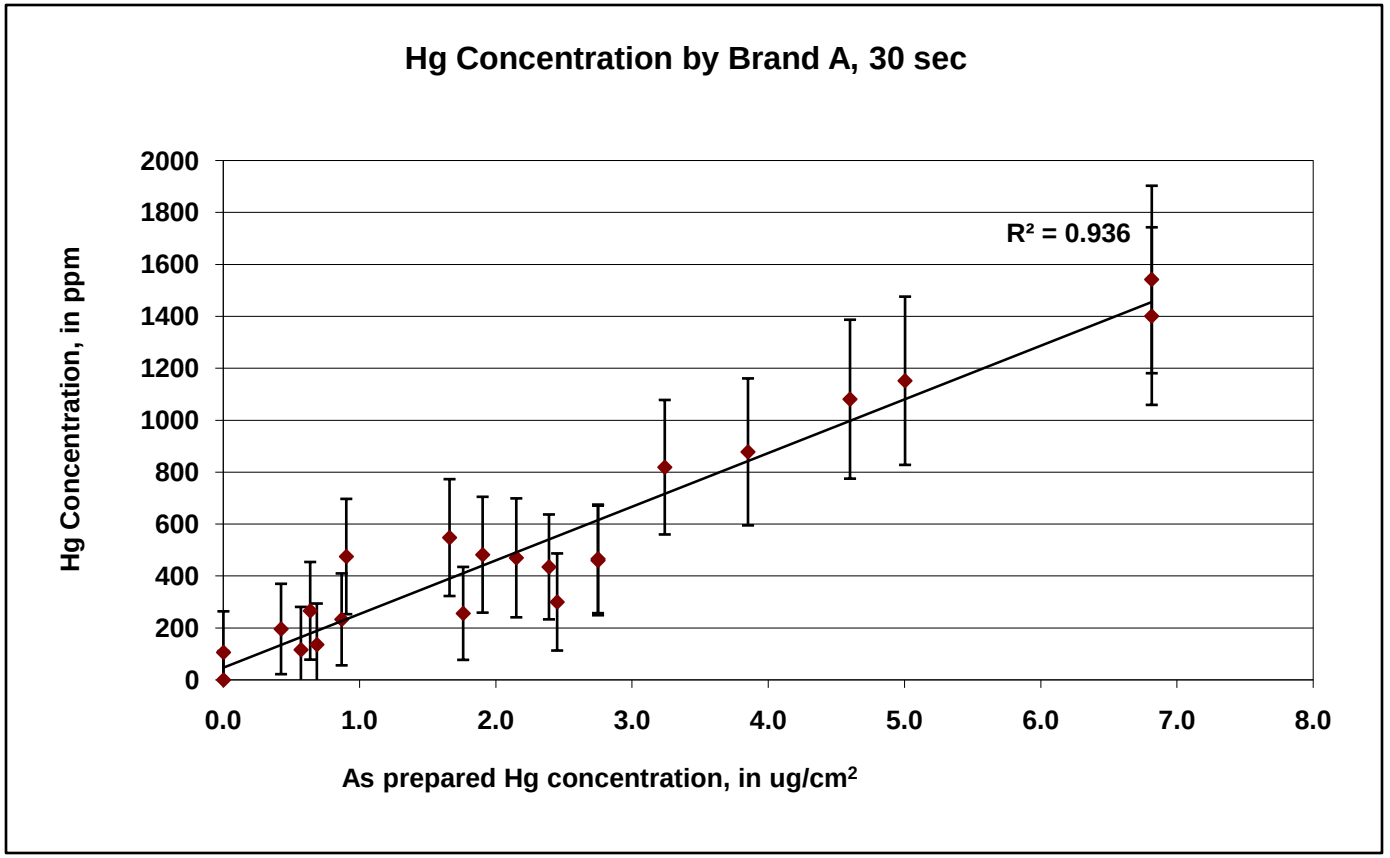
Coupons measured using both instruments at various time settings

- Each coupon was sampled by both instruments
- Data uncertainties between the two instruments are substantial
- Both units demonstrate a workable LOD with the Brand B demonstrating a lower limit

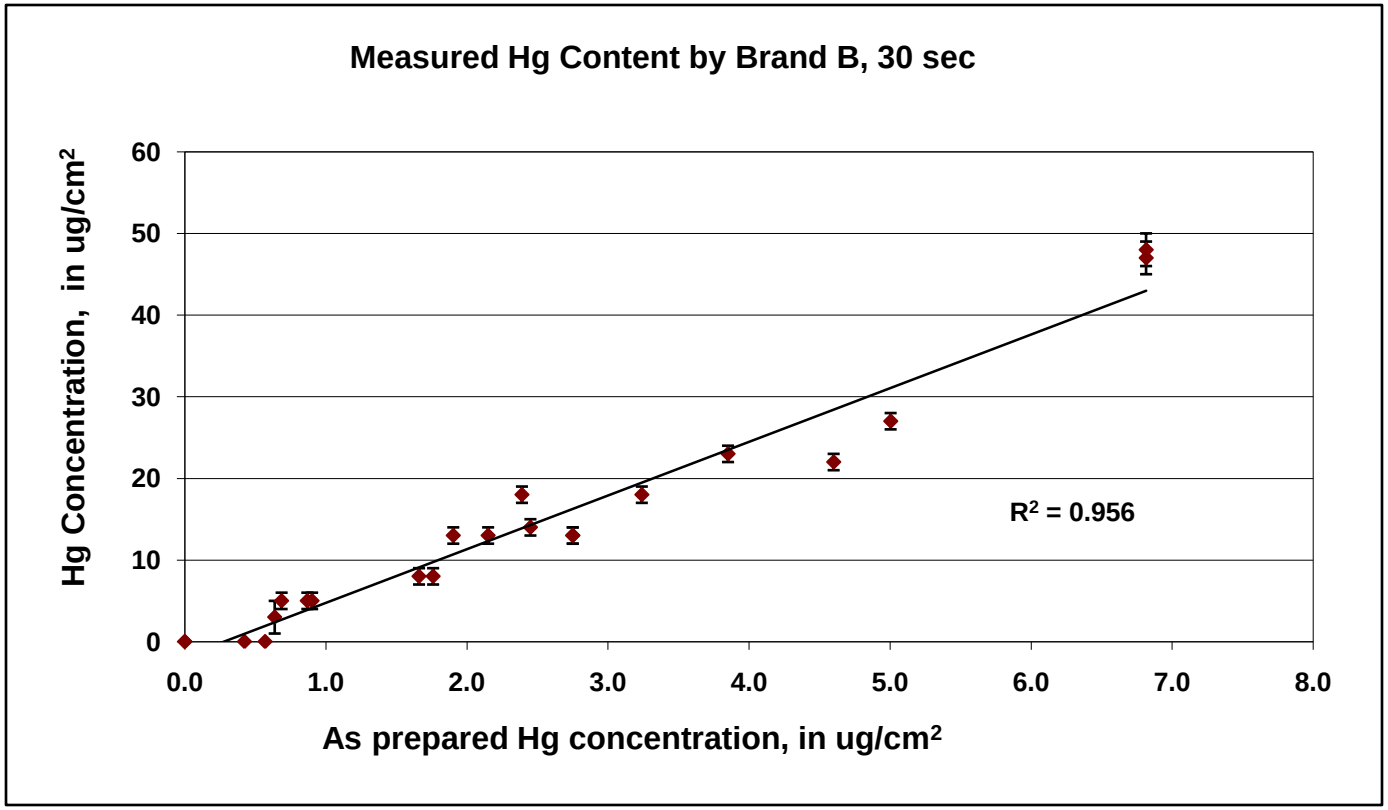
Cross-plot of measured Hg concentration vs. Hg content



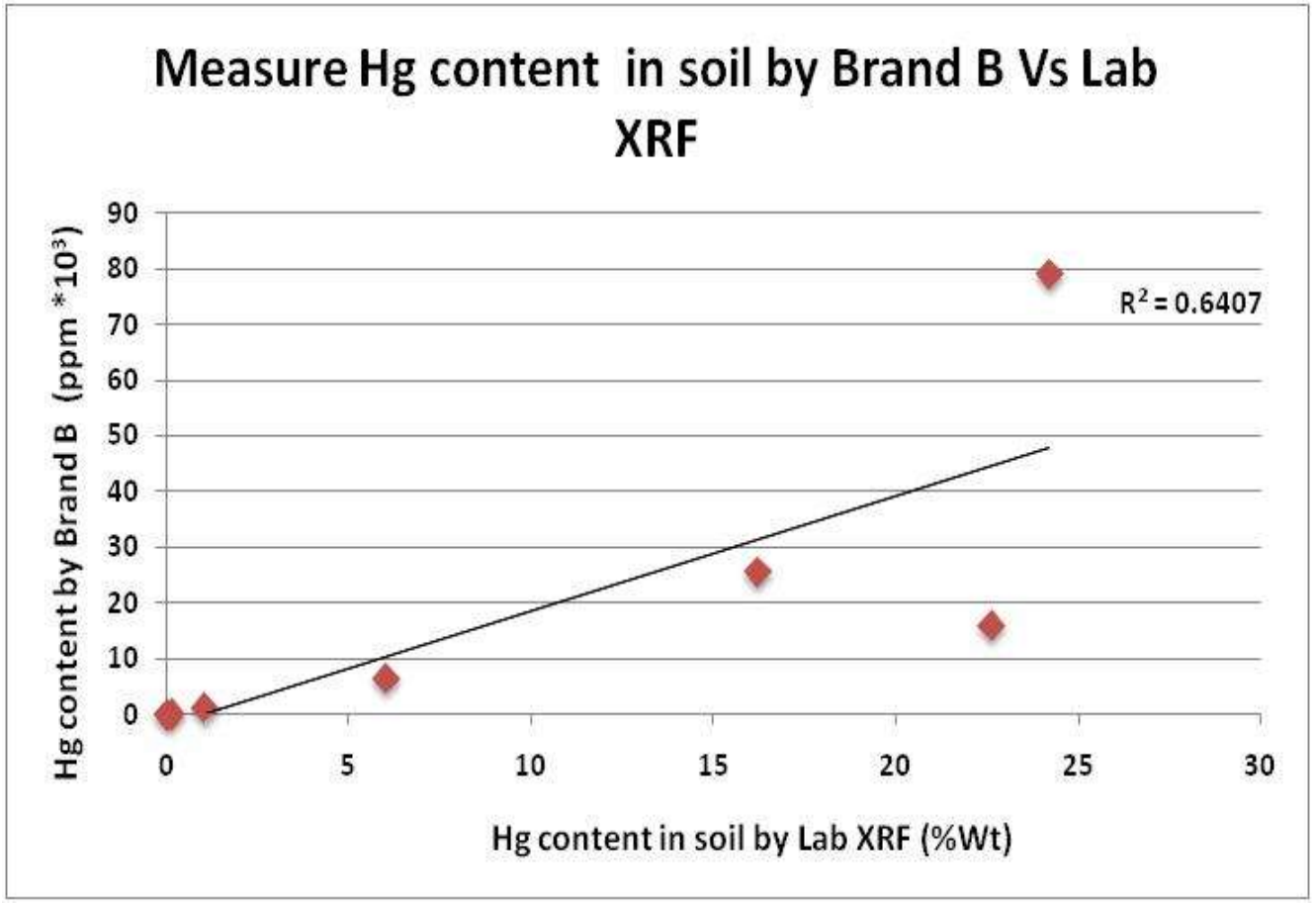
Measurement uncertainties were much larger for Brand A instrument



We favored the Brand B XRF for additional ease of use features, as well as its tighter uncertainties



Cross-plot of measured Hg concentration in soil by Brand B XRF vs. Hg content by Lab XRF



Developing a Draft "How Clean is Clean" Limit

- US EPA has issued guidance regarding the smelting of scrap cars that potentially have mercury containing electronic switches
  - The guidance uses a level of 0.5 grams mercury per 1.4 metric tons of steel – the approximate weight of a crushed car for recycling
  - Can we extrapolate/ translate this guidance into a mercury surface contamination limit in metal?
  - Will the limit be within the detection range of portable XRF units?
- Will the limit be low enough to also address Occupational Health concerns?

Draft Scrap Clearance levels based on surface contamination by various metal thickness level

Summary

- XRF field technique offers a quick, real time and cost effective way of screening mercury surface contamination
- XRF technology adopted in other industries. Electronics industry use XRF to test electric/electronic products for compliance with EU Restriction of Hazardous Substance (RoHS) directive –July 2006
- Growing use of XRF technology for first step screening of exposure/contamination and in some cases for confirmatory testing

Questions