

# Emerging Portable X-ray Fluorescence Technology for Measuring Multiple Airborne Metals: An Evaluation of A Battery Powered X-Ray Tube Instrument

Nicholas J. Lawryk, MPH, Ph.D.  
CDC / NIOSH, Morgantown, WV



In this study, I look at the application of the newly introduced portable battery powered x-ray tube XRF technology for airborne multi-element analysis.

## Disclaimer

Mention or illustration of specific products in this presentation do not express or imply endorsement by the Centers for Disease Control and Prevention.

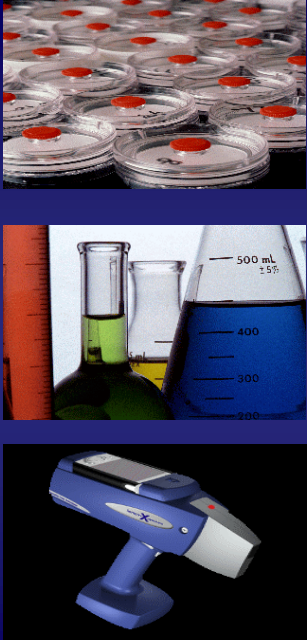


# Metalworking Facts and Figures

- ❖ More than 6 million full-time workers in construction, mining, and welding in U.S.
- ❖ Exposures vary depending on process
- ❖ NIOSH Recommended Exposure Limit for welding fumes has been discontinued





Nationwide, millions are involved in metalworking , including mining, welding, construction, fabrication, maintenance and repair operations. The OEL for welding based on fume mass per unit volume of air has been discontinued...elemental exposures are now the biggest concern. But first, how are samples collected and analyzed???



## Methods for Analyzing Airborne Metals

- ❖ Collect Samples on Filters
- ❖ Wet Chemistry (ICP, NIOSH 7300)
  - ✓ *Destroys sample*
  - ✓ *Non-portable*
  - ✓ *Lengthy wait for results*
- ❖ Portable XRF
  - ✓ *Non-destructive*
  - ✓ *Field-portable technology*
  - ✓ *Same day analysis*



Samples are first collected on filters in cassettes and then analyzed in the lab by wet chemistry procedures such as NIOSH method 7300 are used, which involves digesting filter and analyzing it by ICP. It takes time to get results this way, sometimes months. Portable XRF offers direct analysis on filters, is non-destructive (allowing follow-up confirmatory analysis), and quick (10-15 minutes per sample). So, I'm hypothesizing that....

## Hypothesis

*The field-portable X-ray fluorescence spectrometer (XRF) with X-ray tube technology can measure airborne metals with limits of detection (LOD), limits of quantitation (LOQ), and accuracy that are as good as instruments using conventional sealed radioactive sources.*



Field portable XRF using a battery powered X-ray tube can give timely readings of metal exposures (same day speed) comparable to instruments traditionally seen which use radioactive sealed sources to generate the x-rays. And that performance criteria such as LOD, LOQ, and accuracy are at least comparable to these older technologies. TO DO THIS, I WILL LOOK AT ASPECTS SUCH AS...

## Specific Aims

### Evaluate Instrument performance

- ✓ *Limits of detection and quantitation*
- ✓ *Calibration with certified standards*
- ✓ *Determine bias, precision, accuracy*
- ✓ *Compare results against sealed source instruments*



How well it can read certified standard materials, look at LODs (NIOSH SOP 18...3 standard deviations over mean blank signal) and LOQs (10 sigma), as well as bias, precision, and accuracy as determined by NIOSH protocol, and a comparison of these results against instruments that use radioactive sealed sources.

## Elements to be Examined



- ❖ Nickel (Ni)
- ❖ Chromium (Cr)
- ❖ Manganese (Mn)
- ❖ Cadmium (Cd)
- ❖ Copper (Cu)
- ❖ Lead (Pb)
- ❖ Iron (Fe)
- ❖ Arsenic (As)



The metals I'm looking at are the ones commonly encountered in the workplace air for metalworkers

THESE METALS...

## Some Health Effects from Airborne Metal Exposures

	Ni	Cr	Mn	As	Cu	Pb	Fe
Metal Fume Fever					☾		
Liver Damage				☾	☾		
Cancer	☾	☾					
Asthma	☾						
Sinus Problems		☾					
Parkinson's Disease			☾				
CNS Disorders				☾		☾	
Pneumoconiosis							☾
Kidney Damage				☾		☾	



...have an array of ill-effects depending on exposure frequency and duration. Ranging from metal fume fever with short-term copper oxide inhalation to parkinsonism with long-term manganese exposure, to pneumoconiosis associated with iron exposures. SO, WHY IS PORTABLE XRF TURNING HEADS FOR MULTI-ELEMENT ANALYSIS OF AIR SAMPLES???

## XRF: An Historic Overview

- ❖ Lab-based XRF analysis of welding fumes (NIOSH Standard Analytical Method 7200 [abandoned])
- ❖ Field-portable XRF units for lead measurement at Superfund sites
- ❖ New field-portable XRF analysis for airborne lead (NIOSH Standard Analytical Method 7702)
- ❖ Emerging technologies now appearing



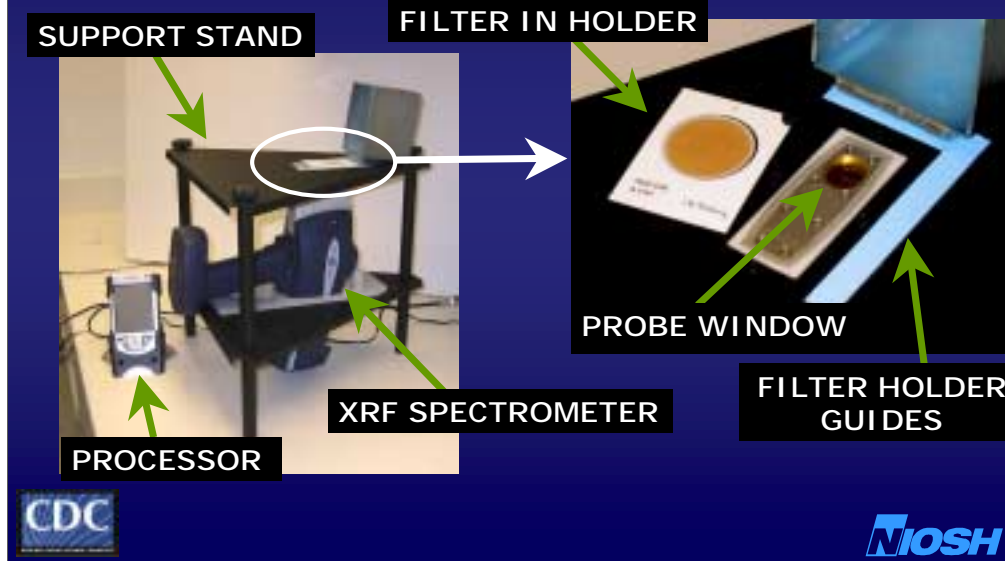
NIOSH method 7200 – Lab based XRF was abandoned in the 1990s as method 7300 (ICP-ES) became the method of choice for multiple metal analysis of air sample filters. HOWEVER, field portable units which were useful for lead analysis at Superfund sites for surface lead contamination analysis were also found to be useful for measuring metals collected from the air on sample filters. In 1999, this led to the release of NIOSH method 7702 for lead on air sample filters. Field portable XRF is not as sensitive as bench top XRF, but it is a proven screening tool.

## Portable X-Ray Tube XRF



Oxford, Metorex and Edax all manufacture instruments that use battery powered X-ray tubes, although to the best of my knowledge, only NITON and Innov-x have developed their instruments for thin-sample applications such as the analysis of 37mm air filters.

# Filter Analysis Configuration



The instrument is battery powered, portable, can store and download data to a PC through a PDA which it uses for on-board data collection. Probe and CPU can be attached or detached as shown here, and has the capability of analyzing a wide range of elements similar to a tri-source sealed source instrument. Safety of X-ray tube is important in transit. Replacement costs will go down as technology becomes more prevalent (~ \$4k for this instrument). Life of latest version of tube is uncertain (first one was replaced for free within warranty). This picture shows how the instrument is set up for filter analysis. The probe is facing up and the filter removed from its cassette and placed in a Mylar lined filter holder positioned so the center of the filter (using the guides) is over the probe window. Then the radiation cover is closed and the filter is analyzed. LET'S TAKE A LOOK AT THE DATA...

## Timeline: From Introduction to Functional Model

### *Or... Labor of Love – XRF Style*

- 2001 Oct ● New instrument introduced to market
- 2002 Sep ● Instrument delivered
- Initial characterization studies
- Oct ● Instability in calibration, S/N ratio
- Satisfactory operation resumes
- Nov ● Instrument repeatedly shuts off
- 2003 Feb ● Instrument returns from factory
- Mar ● Some minor download problems
- Apr ● Satisfactory operation
- May ● X-ray tube replacement needed



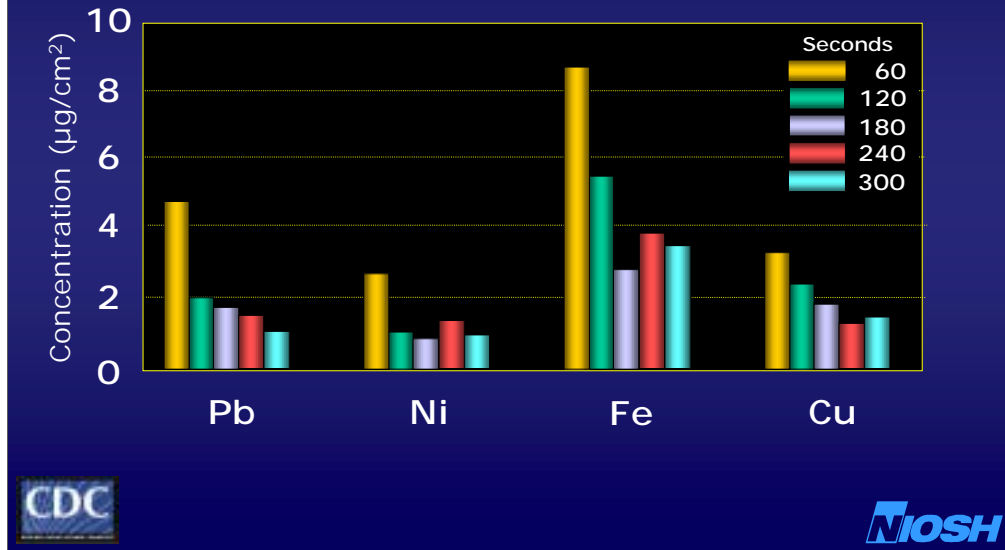
October 2001, first caught wind of this instrument.

February 2002, order placed...

Like the first model year for a car, there are usually some problems that need to be worked out.

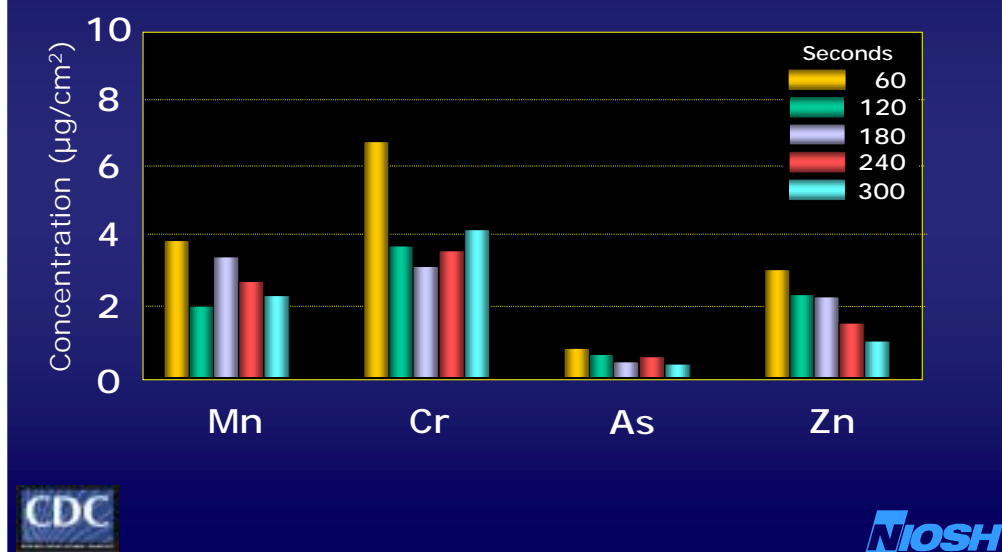
A few more glitches happened in the past six months, most recently, the need for a new x-ray tube. It appears that the retrofit of a medical x-ray grade tube used in chemotherapy was not durable enough, so improvements in the tube design were made and we'll see how this new and improved tube does when it comes back this week in our laboratory and we put it through the tests.

## Limits of Quantitation by Analysis Time



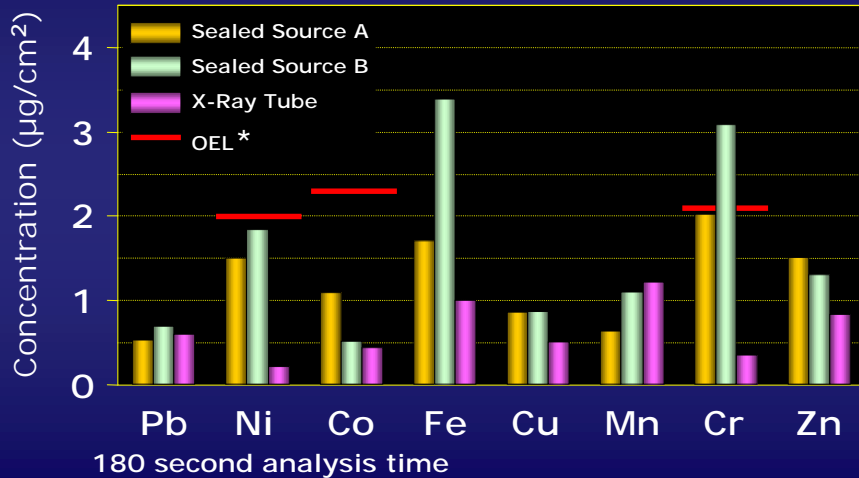
For this preliminary study I used the LOQ definition in NIOSH SOP 18, which is 10 times the mean blank signal level (in this case, 10 clean blank cellulose ester filters were analyzed at each time). Analysis times from 60 to 300 seconds generally results in lower LOQ values. Note that for most elements, levels from 120 seconds and longer were not much different, with longer times not giving much more improvement in the LOQ.

## Limits of Quantitation by Analysis Time (Cont'd)



Again, for these elements, with the exception for Cr and Mn, the general trend is for lower limits of quantitation with increasing analysis time. Generally, it appears most advisable to use analysis times of 120 seconds or greater. By and large, 180 seconds gives the lowest limits of detection and quantitation for most of the elements of interest. Beyond this time, there are diminishing returns with longer times, so 180 seconds was selected as the analysis time of choice to study accuracy.

## Limits of Detection by Instrument



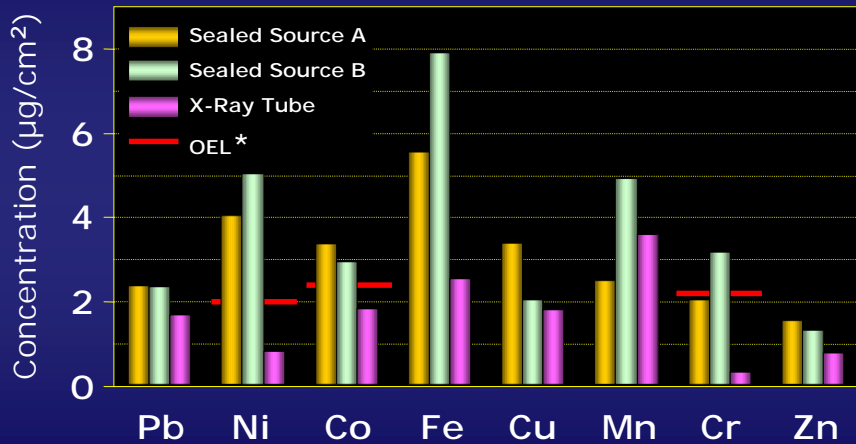
\*OEL *only* listed when in range of graph



Holding the analysis times constant at 180 seconds across two portable sealed source instruments and the X-ray tube instrument, I found that the LIMITS OF DETECTION were well below the OEL for all elements on the X-ray tube instrument, with the improvement being substantial for Ni, Fe, Cu, Cr, and Zn.

The OEL is defined here as the lowest of the ACGIH TLV, NIOSH REL, and OSHA PEL for the fume or airborne dust. Assuming 2 L per minute sampling time for an 8 hour shift at that concentration on a 37 mm filter (effective sample diameter of 33 mm). Reported OEL is in micrograms per cubic centimeter. Metals where no red OEL line signifies concentrations that are “off the scale” or beyond the scope of the graph (greater than 4.5 micrograms per square cm).

## Limits of Quantitation by Instrument



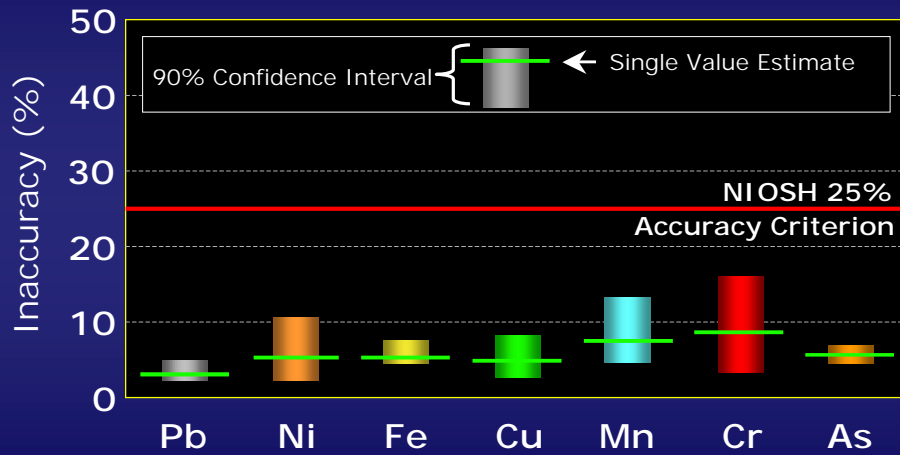
180 second analysis time

\*OEL *only* listed when in range of graph



Looking at LIMITS OF QUANTITATION (NOTE CHANGE IN SCALE ON CONCENTRATION OR Y-AXIS IN THIS GRAPH), the X-ray tube instrument shows an improvement over the sealed source instruments for all except Mn. Most notable is that with the X-ray tube, all limits of quantitation are below the OEL for these elements. This was not the case for sealed source portables before.

## 90% Confidence Interval Estimates of Method Accuracy

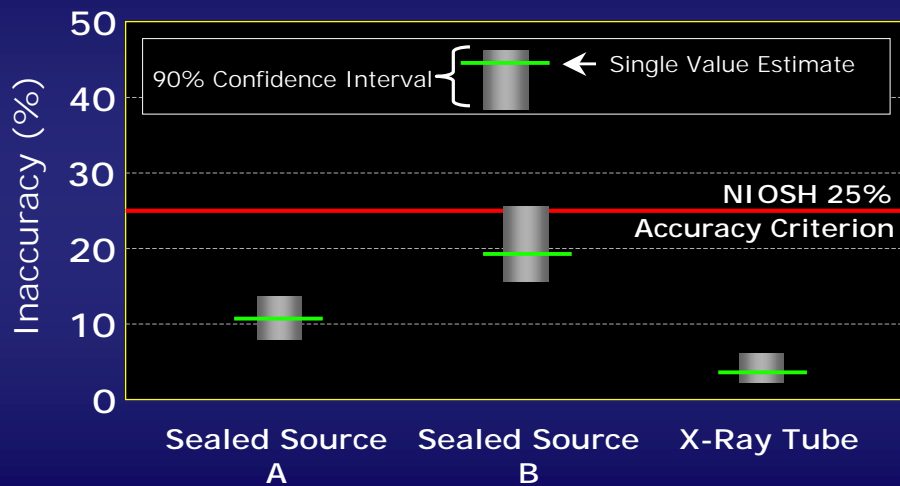


180 second analysis time



HOW ABOUT ACCURACY? Single element standards with Mylar bases in at least 3 concentration ranges were each measured 5 times for 180 source seconds on the X-ray tube instrument. Bias and precision were calculated according to NIOSH procedures. Accuracy was calculated by the Bonferroni Procedure. For the majority of elements, the 90% confidence interval falls within the NIOSH 25% inaccuracy criterion. This test is highly idealized, but the results are remarkable. Unlike the sealed source models we have tested in the past, the accuracy for all elements of interest had single point values below 10% and the 90% CI did not exceed 16% for any element.

## Accuracy by Instrument: Lead (Pb)

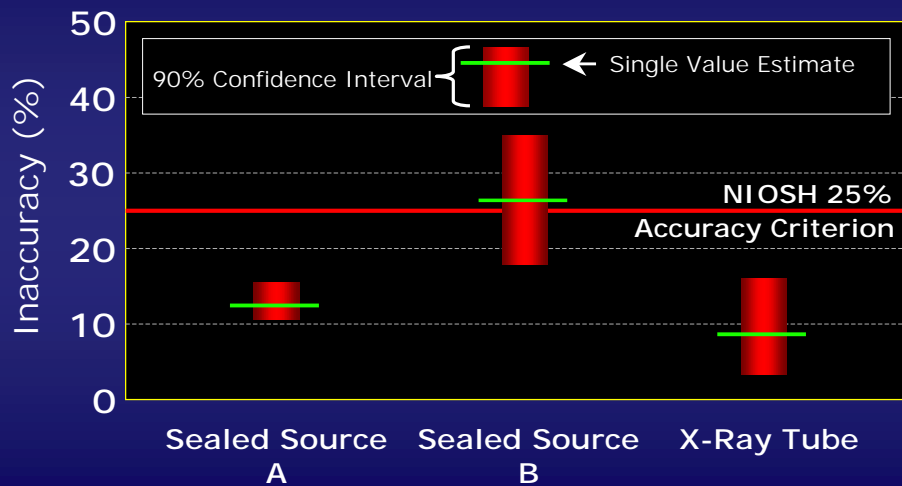


180 second analysis time



This accuracy improvement is apparent when compared against the two sealed source instruments for lead.

## Accuracy by Instrument: Nickel (Ni)

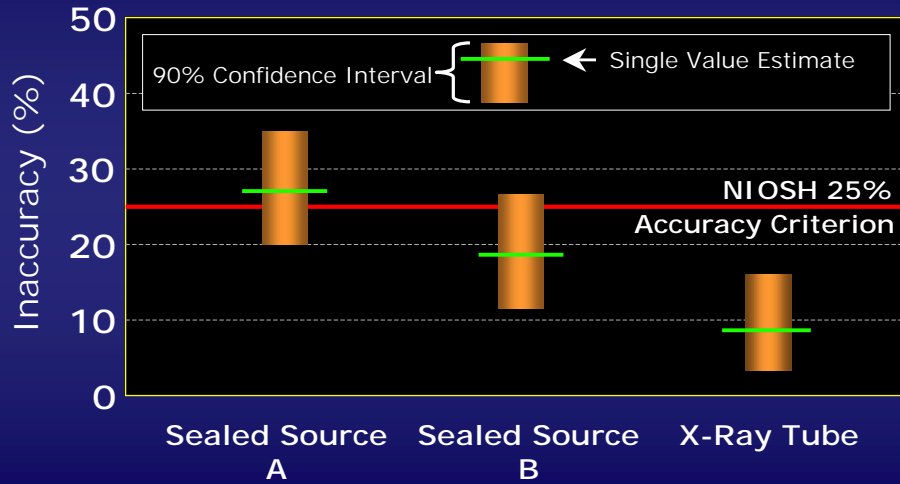


180 second analysis time



The accuracy improvement for the X-ray tube instrument is also noted for nickel, but to a lesser extent.

## Accuracy by Instrument: Chromium (Cr)



180 second analysis time



With chromium, The X-ray tube instrument also performed much better than its portable sealed source counterparts.

## Summary

- ❖ Improvements over earlier generation sealed source instruments
  - Limits of detection and quantitation
  - Bias, precision, accuracy
- ❖ 'New model' problems in first year of use, but performance good overall
- ❖ Transport
  - Generally easier than sealed sources in US
  - Can't use in Canada
- ❖ X-ray tube instruments may be easier and potentially more cost efficient to maintain in out-years



## Future Research Directions: Specific Aims In Progress

- ❖ Evaluate additional emerging technologies
  - Americium 241 single sealed source
  - Other X-ray tube instruments (inter-model evaluation study)
- ❖ Measure workplace samples on XRF in laboratory
  - Confirmatory analysis with established method (ICP - NMAM 7300)
- ❖ Measure workplace samples on-location
- ❖ NIOSH method development for some elements



Analysis of real workplace and experimentally generated fume samples with comparison to confirmatory analysis should validate the XRF as a portable method for screening a variety of airborne metals in the workplace. The advent of the portable XRFs with battery powered X-ray tubes provides a safer option and may resolve some of the instability issues inherent with traditional sealed source instruments, and these will be investigated this summer. Ultimately, technology and design improvements can be suggested to the manufacturer and elements that are successfully measured can form the basis for expanding the elemental base of the already established method using portable XRF for airborne lead.

## Conclusion

Preliminary results show that XRF spectrometry using a battery powered X-ray tube performs at least as well as sealed source units for analyzing metals which may be present in the air at metalworking operations.



So the battery-powered x-ray tube XRF is indeed alive and well as a technology for airborne multi-element analysis and, once it is proved to be rugged in field testing, could be a viable and arguable safer alternative to radioactive sealed source instruments for field screening for airborne metals collected on filters. Possible NIOSH standard methods may be developed later this year pending ongoing field studies.

## Acknowledgements

- ❖ Bruce Pacolay & Martin Harper (*CDC / NIOSH / HELD*)
- ❖ Kevin Ashley & Amy Feng (*CDC / NIOSH / DART*)
- ❖ Brian Bower, Rose Kotch, Don Sackett (*Innov-X Systems*)
- ❖ THERMO Noran Corporation
- ❖ Joanne Heagney (*MicroMatter*)
- ❖ Jon Shein & Hal Grodzins (*NITON Corporation*)
- ❖ J. Clinton Morley (*General Electric*)



There's a gaggle of people too numerous to mention by name who have contributed to this project. The major players are listed here. Thank you for your time and attention. I now open the floor to any questions you may have.