Four Key Advantages of XRF for Many Applications

SIMPLICITY

• Relatively simple theory, instrument, and spectra (versus IR, MS, NMR)

MINIMAL SAMPLE PREP

• For many screening applications, samples can often be analyzed “as is” with minimal sample processing
• For accurate quantitative analysis, samples must be ground up and homogenized (faster and easier than acid digestion required for conventional atomic spectrometry methods)

TYPICAL ANALYSIS TIMES ON THE ORDER OF 1 MINUTE

• For determining % levels of an element (which typically gives high count rates), measurement times can be as short as a few seconds
• For ppm-level detection limits, measurement times on the order of 1-10 minutes are needed

PORTABILITY

• Instrument can be brought to the samples
- Use XRF for "sample triage" (sort into "detects" and "non-detects")
- Avoid wasting time trying to quantify non-detectable levels of a toxic element with more time consuming methods such as ICP-MS
- Avoid problems trying to quantify % levels of a toxic element with a very sensitive technique such as ICP-MS (contaminating digestion vessels, glassware, instrument, etc. in low-level process stream)
- Perform accurate quantitative analysis (via XRF or ICP-MS) where warranted Typical analysis protocol More intelligent analysis protocol
Toxic Elements in Tableware

Pb and other elements are still causing problems

- Ceramic plates may contain toxic elements that can leach into food
- XRF can be used to quickly identify elements and their concentrations in tableware, glazes, and base ceramic material, and food

Pb in Imported Tableware and Food Products

“The prevalence of elevated blood lead levels was significantly higher in 1 of the 3 clinics (6% among screened children and 13% among prenatal patients)”

“Consumption of foods imported from Oaxaca was identified as a risk factor for elevated blood lead levels in Monterey County, California.”


“…the source was found to be related to contamination of foods in Mexico that was inadvertently transported to California through a… practice, called ‘envíos’ (Spanish for send or transport) … the frequent transport of prepared foods from Mexico to California. Envíos in fact are ‘mom and pop’ express air transport businesses in which foods are sent from home in Oaxaca to home in California, often on a daily basis. Unfortunately, it was discovered that some of the foods contained lead. The as yet unidentified sources of the lead are currently undergoing investigation.”


“An interdisciplinary investigation…was undertaken to determine the contamination source and pathway of an on-going outbreak of lead poisoning among migrants originating from Zimatlán, Oaxaca, Mexico and living in Seaside, California, and among their US-born children…”

The focus in the present work concentrates on the Oaxacan area of origin of the problem in Mexico, and two potential sources of contamination were investigated: wind-borne dusts from existing mine residues as potential contaminants of
soil, plant, and fauna; and food preparation practices using lead-glazed ceramic cookware…

The results indicated significant presence of lead in minewastes, in specific foodstuffs, and in glazed cookware, but no extensive soil contamination was identified. In-situ experiments demonstrated that lead incorporation in food is made very efficient through grinding of spices in glazed cookware, with the combination of a harsh mechanical action and the frequent presence of acidic lime juice, but without heating, resulting in high but variable levels of contamination.”


### Pb in Tableware

**Samples from Monterey County, CA**

Analysis via handheld XRF calibrated with Pb standards

<table>
<thead>
<tr>
<th>Item Description</th>
<th>Pb Level (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pitcher, green-grey glaze, Central Market Zimatlan, Mexico</td>
<td>10%</td>
</tr>
<tr>
<td>bean pot, grey glaze, Central Market Zimatlan, Mexico</td>
<td>11%</td>
</tr>
<tr>
<td>small bowl (chimoleera), green glaze, Central Market Zimatlan, Mexico</td>
<td>7%</td>
</tr>
<tr>
<td>incense burner, green glaze, 3-legged, El Milagro</td>
<td>8%</td>
</tr>
<tr>
<td>clay pot, red glaze, 12” diam, smooth inside, El Milagro</td>
<td>11%</td>
</tr>
<tr>
<td>clay pot, green glaze, 10” diam, for grating, El Milagro</td>
<td>10%</td>
</tr>
<tr>
<td>small bowl (chimoleera), envios julietta</td>
<td>7%</td>
</tr>
<tr>
<td>bowl, green glaze, lace on inside edge</td>
<td>48%</td>
</tr>
<tr>
<td>bird dish, green glaze</td>
<td>37%</td>
</tr>
<tr>
<td>dish, unglazed</td>
<td>40%</td>
</tr>
<tr>
<td>large brown bowl, unglazed (from Celeste)</td>
<td>26%</td>
</tr>
<tr>
<td>large pitcher (from Celeste)</td>
<td>33%</td>
</tr>
<tr>
<td>small decorative bowl, red glaze</td>
<td>1%</td>
</tr>
<tr>
<td>pottery, black glaze</td>
<td>66 ppm</td>
</tr>
</tbody>
</table>

H. Gregory, P.T. Palmer, manuscript in prep

### Pb in Food and New Tableware

**Samples from Monterey County, CA**

Analysis via handheld XRF calibrated with Pb standards

<table>
<thead>
<tr>
<th>Item Description</th>
<th>Pb Level (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>chapulines, ag (Emilio's sisters)</td>
<td>406 ppm</td>
</tr>
<tr>
<td>chapulines, ag (extended Aquino family members)</td>
<td>387 ppm</td>
</tr>
<tr>
<td>chapulines, harvested in Ang, Central Market Zimatlan, Mexico</td>
<td>131 ppm</td>
</tr>
</tbody>
</table>
Museum Artifacts Preserved With As and Hg

Ideal for nondestructive testing via handheld XRF
Results From Basket Collection

Handheld XRF calibrated with Hg and As standards

Detectable Hg contamination on 17% of the baskets
Results From Bird Collection

Handheld XRF calibrated with Hg and As standards

Significant As contamination on most of the birds

Determination of Cr in Stainless Steel

Handheld XRF analysis of Kervorkian-designed biopsy forceps
Atomic absorption method gave 12.7% Cr (difficult prep and digestion, >1-day effort)

XRF analysis gave 12.8% Cr and correctly identified alloy (no sample prep, FP mode, empirical calibration with Cr standards, <1 min reading)

Results used to confirm labeling requirements for Cr content in surgical products used in medical applications


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**XRF vs Atomic Absorption for Cr in Stainless Steel**

- t test indicates no significant differences at the 95% confidence level between handheld XRF and conventional Atomic Absorption Spectrophotometry method
- Such data demonstrate that XRF can give accurate quantitative results
Chinese Herbal Medicine - Niuhuang Jiedu Pian

- Product manufactured in China (Cow yellow detoxification tablet), Intended to treat mouth ulcers, relieve toothaches, reduce fever, and "release toxins", product import document indicated that As in the form of realgar (As$_4$S$_4$)
- ICP-MS showed 6.85% As (note low value here versus XRF may be due to inability of acid digestion procedures to dissolve realgar)
- Handheld XRF showed 11.7% As in product (Compton Normalization mode, empirical calibration with As standards, diluted sample into range of standards)
- Recommended max dose of 9 tablets per day is equivalent to consumption of 0.173 g of As (minimum lethal dose ~0.130 g*)


Toxic Elements in Supplements

- Dietary supplement sales in the U.S. surpassed $21 billion in 2006 and 60% of people use them on a daily basis
- The Dietary Supplement Health and Education Act (DSHEA) does not require manufacturers to perform any efficacy or safety studies on dietary supplements
- FDA’s Current Good Manufacturing Practice (cGMP) requirements for Dietary Supplements provides no recommended limits for specific contaminants
- Numerous studies have reported the presence of toxic elements in a large numbers of domestic and imported supplement products
- Concerns for consumer safety have led to a Canadian ban on imports of Ayurvedic medicines in 2005 and a call for more testing and better regulation of these products
- Clearly XRF is an ideal tool for this application
Ayurvedic Medicines – Pushpadhanwa

• Ayurvedic medicine *Pushpadhanwa* (ironically, a fertility drug), label information indicates that it contains the following:

  Rasasindoor = Pure mercury and sulfur
  
  Nag Bhasma = Lead oxide (ash)
  
  Loha Bhasma = Grom oxide
  
  Abhrak Bhasma = Mica oxide

• Santa Clara County Health Dept issued a press release (Aug 2003) regarding this product which caused two serious illnesses and a spontaneous abortion

• Atomic absorption analysis by private lab showed 7% Pb in this product

• Handheld XRF analysis showed 8% Pb and 7% Hg (Compton Normalization mode, empirical calibration with authentic standards, diluted sample into range of standards)


Imported and Domestic Supplements


• A subset of these samples (28) were the focus of a study to compare and evaluate several different XRF analysis methods

• This represents a very challenging application for XRF due to
  ◦ Low levels of toxic elements in these samples (highest was 50 ppm)
  ◦ Tremendous variability of sample matrices and preparation of appropriate standards for an empirical calibration (cellulose was used to approximate the predominantly organic content of the samples)
  ◦ As and Pb spectral overlaps and co-occurrence of both in some samples

• Our goal was to evaluate XRF in two different modes of operation
  ◦ Screening products “as is” using an empirically calibrated handheld XRF (results not included in this
Accurate quantitative analysis of homogenized products using an empirically calibrated lab-based XRF (completely automated data acquisition, calibration, quantitative analysis, and report generation)

XRF vs ICP-MS for Toxic Elements in Supplements

- t test indicates no significant differences at the 95% confidence level between lab-grade XRF and conventional ICP-MS method
- Such data demonstrate that XRF can give accurate quantitative results (impressive considering most samples contain these elements at concentration that are very close to the detection limit)