Field Screening for Metals by
Energy Dispersive X-Ray Fluorescence (EDXRF) in Contaminated Soil

Conducted by:
Onsite Environmental Laboratories, Inc., Fremont, CA

In cooperation with:
Bay Area Defense Conversion Action Team Environmental Technology Partnership

Introduction

Energy Dispersive X-Ray Fluorescence (EDXRF) analysis is an innovative site characterization technology that provides rapid, cost-effective analysis of metal contaminants on site. The technology provides real-time analysis of a large number of soil samples for a wide range of metal contaminants. The ability to rapidly screen numerous samples increases the efficiency of analytical programs. This analytical efficiency may be applied to increase the quality of site characterization or allow more accurate control of treatment processes. Table 1 lists elements that can be analyzed using EDXRF.

Onsite Environmental Laboratories, Inc. participated in a field demonstration of EDXRF technology sponsored by the Bay Area Defense Conversion Action Team (BADCAT) under the Environmental Technology Partnership (ETP) Project. BADCAT ETP is a public-private partnership of the Bay Area Economic Forum, Bay Area Regional Technology Alliance, California Environmental Protection Agency, U. S. Environmental Protection Agency, U. S. Navy, Chevron Research and Technology Company, San Francisco State University Center for Public Environmental Oversight, and other technical experts working to expedite the cleanup and conversion of Bay Area closing bases through the application of new environmental technologies.

The demonstration was conducted using contaminated soils from the Hunter’s Point Shipyard, located in

<table>
<thead>
<tr>
<th>Element</th>
<th>EDXRF Data Reporting Limit (mg/kg)</th>
<th>U.S. EPA Residential PRGs (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony</td>
<td>10</td>
<td>31</td>
</tr>
<tr>
<td>Arsenic</td>
<td>10</td>
<td>22</td>
</tr>
<tr>
<td>Barium</td>
<td>10</td>
<td>5,300</td>
</tr>
<tr>
<td>Cadmium</td>
<td>10</td>
<td>38</td>
</tr>
<tr>
<td>Chromium</td>
<td>20 (c)</td>
<td>210</td>
</tr>
<tr>
<td>Copper</td>
<td>10 (c)</td>
<td>2,800</td>
</tr>
<tr>
<td>Lead</td>
<td>10 (c)</td>
<td>400</td>
</tr>
<tr>
<td>Manganese</td>
<td>10</td>
<td>3,200</td>
</tr>
<tr>
<td>Mercury</td>
<td>10</td>
<td>23</td>
</tr>
<tr>
<td>Nickel</td>
<td>10</td>
<td>1,500</td>
</tr>
<tr>
<td>Selenium</td>
<td>10</td>
<td>380</td>
</tr>
<tr>
<td>Silver</td>
<td>10</td>
<td>380</td>
</tr>
<tr>
<td>Thallium</td>
<td>10</td>
<td>6.1</td>
</tr>
<tr>
<td>Zinc</td>
<td>10 (c)</td>
<td>23,000</td>
</tr>
</tbody>
</table>

(a) Spectrace Instruments Model 6000.
(b) PRGs = preliminary remediation goals.
(c) Screening of these metals was demonstrated during this project.
San Francisco, California. The site selected for the demonstration was a portion of a scrap yard that had handled a wide range of metal-containing wastes, including electrical equipment and lead-acid storage batteries. The soil types at the site included silts and sands. The demonstration of EDXRF analysis involved analysis of treated and untreated soils produced in conjunction with a demonstration of the ChemTech Soil Treatment System. The soil treatment demonstration is described in a separate TechData Sheet, “Removal of Metals and Hydrocarbons from Contaminated Soils at Hunter’s Point Shipyard: A Demonstration of the ChemTech Soil Treatment System.”

Purpose

The project was conducted to demonstrate the mobilization and operation of EDXRF technology for analysis of environmental samples in the field. The demonstration was structured to test the ability to rapidly and efficiently mobilize EDXRF equipment to a site, provide near real-time analytical capability, and give quantitative determination of metals concentrations in solid matrices. The metals of interest in this study were antimony, chromium, copper, lead, and zinc. The environmental matrices were treated and untreated soil and sludge. Results were compared with conventional analytical method SW-846, developed and published by the U.S. EPA.

Advantages and Limitations

Screening for metal contaminants in soil using EDXRF analysis has the following distinct advantages:

- **Provides on-site analysis.** EDXRF analysis equipment is portable and can be mobilized and ready for use on site in minutes.

- **Provides rapid turnaround.** Preparation and analysis of a single sample can be completed in about 15 minutes. Site characterization plans or process operations can be quickly adapted to actual site conditions or processing results using EDXRF results. The availability of near real-time results allows time-critical decision making to maximize the effective use of resources.

- **Allows efficient screening of many samples.** With EDXRF equipment, more samples can be analyzed on a fixed budget than can be analyzed with conventional analytical methods. Increasing the number of data points reduces uncertainty about the nature and extent of contamination or process operating characteristics.

- **Can simultaneously analyze multiple elements.** Emission spectra of x-ray fluorescence transitions provide element selectivity. Simple emission line patterns permit elemental identification and quantitation. As many as 15 to 20 elements can be analyzed at one time.

- **Does not use hazardous reagents.** Unlike conventional wet chemical analysis methods, EDXRF does not require the use of strong acids to extract metals from the soil. Avoiding the use of acids reduces worker exposure to hazards, decreases waste generation, and increases processing speed.

- **Accepted as a screening technique by regulatory agencies.** EDXRF results have been accepted by regulators when the method is supported by confirmation samples analyzed by EPA SW-846 methods.

The EDXRF analysis technique has the following limitations:

![Figure 1. Conceptual Model of X-Ray Fluorescence Analysis](image)
High lead concentrations affect the detection limit for arsenic. Typically, arsenic can be detected at 10% of the lead concentration in a soil sample.

EDXRF analysis results are not accepted for compliance decisions. The EDXRF results can be an important part of analytical programs, but the EDXRF results must be validated and supported by comparison with conventional analytical methods.

Matrix constituents may affect instrument response. EDXRF generally provides adequate accuracy for screening samples. Calibration with a representative matrix may sometimes be useful, depending on site conditions.

EDXRF technology provides a total metals result. EDXRF measures all forms of the element, causing it to give higher results than SW-846 methods, which report only acid-extractable forms.

Technical Description

EDXRF analysis is a method to determine the concentrations of metals by ionizing the metallic atoms using a beam of high-energy x-rays and measuring the emitted x-radiation when the atom returns to the ground state. The energy spectrum of the emitted x-rays allows determination of the type of metal, and the intensity of the spectrum is used to determine the concentration of the metal.

The conceptual model of the EDXRF analysis process is illustrated in Figure 1 using the Bohr atomic model. The dried, ground sample is exposed to an intense beam of x-rays, generated by a high-voltage x-ray tube. The high-energy x-rays eject an electron from an inner orbit around an atom. Electrons in outer orbits begin to cascade inward to fill the vacated orbit and in the process emit x-ray fluorescence. The energies of the x-ray fluorescent spectrum generated by the electrons moving into the inner orbit are specific to individual elements. Background noise from scattered x-rays is reduced by filtering the excitation x-rays in the energy region of the analytes of interest. The fluorescence x-rays are detected by a lithium activated silica (SiLi) detector. Computer analysis of the x-ray spectrum allows identification and quantification of the metals concentration in the sample. The EDXRF instrument is calibrated using elemental copper samples and certified National Institute of Standards and Technology (NIST) soil standards.

EDXRF analysis is performed using the following steps:

- Sample preparation by drying, sieving, and grinding.
- Sample analysis by placing the prepared sample in the EDXRF spectrometer for a preset time.
- Data reduction by signal processing, filtering, and quantification using Spectrace Instruments hardware and software.

The Spectrace Instruments Model 6000 transportable EDXRF analysis unit consists of three modules: (1) a spectrometer, (2) control/pulse processing electronics, and (3) a computerized data analysis system. The setup and application of a field portable EDXRF unit is illustrated in Figure 2. The unit can quantitate concentrations of elements with atomic number 11 or higher at concentrations from a few mg/kg up to 100%. No radioactive sources are required for operation. The exciting x-ray beam is produced by a low-power rhodium anode x-ray tube with a 0.35-mA maximum current output and 4- to 50-Kev voltage output. The x-ray tube is connected to hardware and software interlocks to ensure (for maximum safety) that the analyzer shuts down if the side panels are opened.

EDXRF sensitivity is a function of the sample matrix. Because moisture levels greater than 20% may negatively impact results, samples are dried to below 10% moisture. In addition, samples are manually or mechanically ground to a powder form, generating smaller, uniform grain sizes. Factors which affect the lower limits of detection for an analyte include atomic number, absorbing characteristics of the matrix, excitation efficiency, detector resolution, spectral interferences, and analysis time. As indicated in

**Figure 2. Setup and Application of a Field Portable EDXRF Analysis Unit**
Table 1, EDXRF is able to analyze for a wide range of metals of environmental interest with acceptable sensitivity for remedial action screening.

Demonstration Results

Eighty soil and sludge samples were analyzed during the demonstration at Hunter’s Point. The program demonstrated the ability to quickly mobilize an EDXRF laboratory to a field site, provide near real-time results in a field setting, and give acceptable analytical correlation to confirmation data and precision for support of time-critical decisions on site.

EDXRF analysis was compared with confirmation analysis performed using U.S. EPA SW-846 solid and hazardous waste analytical procedures. Twenty-three of the eighty samples analyzed by EDXRF were sent off site for confirmational analysis. Analysis of the statistical correlation between the EDXRF and confirmation analysis data sets gave correlation factors of 0.772, 0.964, 0.938, 0.991, and 0.995 for antimony, chromium, copper, lead, and zinc, respectively. These correlation factors exceeded the planned data quality objective (DQO) of 0.9 with a 95% confidence interval for all metals except antimony. The poorer correlation for antimony was attributed to the low concentration of antimony in the Standard Reference Material available from NIST.

Direct comparison of results for individual samples showed the percent difference generally met the project DQO of < 25% for copper, lead, and zinc. The DQO was not met for antimony and chromium, with the average of the percent difference values calculated at -99% for antimony and -159% for chromium. The negative percent difference values indicate that EDXRF gave higher results than the confirmation analysis, a difference attributed to limitations imposed by the digestion method used for the confirmation analysis. Digestion in an acidic solvent is required to transfer metals from the soil matrix to an aqueous solution to allow measurement of the metal concentration. Prior results indicate that antimony and chromium are difficult to fully dissolve from soil samples. The confirmation method may not have removed all of the metal from the soil, whereas the EDXRF method directly analyzes the metal content of the sample.

The precision of the EDXRF method was measured by replicate analysis of duplicate samples. Ten duplicate analyses were performed during the Hunter's Point demonstration. The precision DQO of < 25% variation between duplicates was met for all tests, with the exception of antimony in one sample because the concentration was too close to the reporting limit.

The DQO for completeness, a measure of the valid data obtained, was set at 90% for soil samples. The DQO was met for lead and zinc. Discarding data points with analyte concentrations less than 5 times the reporting limit allowed the data for antimony, chromium, and copper to meet the completeness goal of 90%.

Cost

The cost of using EDXRF for on-site analyses of metals is a function of the number of samples and the number of elements in each sample. Historically, costs for the bench-top EDXRF unit range from $30 to $50 per sample, or an average of $40. Table 2 compares on-site EDXRF to off-site analysis at a fixed laboratory.

Table 2. On-Site EDXRF versus Fixed Laboratory: Average Cost per Element

<table>
<thead>
<tr>
<th>Number of Elements per Sample</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bench-Top</td>
<td>40.00</td>
<td>20.00</td>
<td>13.33</td>
<td>10.00</td>
<td>8.00</td>
</tr>
<tr>
<td>Timeframe</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Off-Site Fixed Laboratory</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 Days</td>
<td>25.00</td>
<td>17.50</td>
<td>15.00</td>
<td>13.75</td>
<td>13.00</td>
</tr>
<tr>
<td>24 Hours</td>
<td>50.00</td>
<td>35.00</td>
<td>30.00</td>
<td>27.50</td>
<td>26.00</td>
</tr>
</tbody>
</table>

For more information on EDXRF analysis or BADCAT ETP, contact:

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BADCAT ETP Cost and Performance Review Board
Naval Facilities Engineering Service Center
U.S. Environmental Protection Agency
California Environmental Protection Agency
Chevron Research and Technology Company
Lawrence Berkeley National Laboratory
SW Div, NAVFAC Engineering Command

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