IN-SITU ENVIRONMENTAL XRF

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ABSTRACT

Reductions in the size of detectors and X-ray tubes have made it possible to bring an X-ray fluorescence (XRF) spectrometer into direct contact with underground soils at depths down to 50 meters to measure heavy metal contaminants. A unique XRF spectrometer has been constructed and tested for this purpose which is deployed via a cone penetrometer. It allows XRF spectra to be collected from a sensor which fits within the penetrometer pipe and produces high-quality spectra in 100 seconds. The unit uses a miniature X-ray tube developed expressly for this device and a commercial PIN diode detector.

The device has been used to map the lead contamination at DOD munitions plants to evaluate its capabilities. The operation revealed the extent of lead contamination beneath the surface to depths of 250 cm (8 feet) without any drilling or removal of samples. Detection limits, reproducibility, and quantitative performance of the sensor are presented. The field tests provided sufficient data to evaluate the performance of the sensor under operating conditions, establish its ruggedness, and identify problem areas for future improvement. Results are in agreement with conventional sampling methods.

INTRODUCTION

In-situ analysis of soils implies that the measurement device is inserted into the soil and the measurement made in place below the soil surface. This can be achieved using cone penetrometry techniques1, which were developed in the late 1800s to explore the foundations of railroad beds. A hardened steel rod with a sharp point is hydraulically pushed into the soil, and the displacement resistance and friction allow classification of the soil type. The Department of Defense is developing sensors to fit within the penetrometer pipe which will perform in-situ analysis of soil contaminants. The Tri-Service Site Characterization and Analysis Penetrometer System (SCAPS) has developed a number of sensors for contaminants from volatile organic compounds to heavy metals2. The sensor described in this paper is one of three heavy metals sensors being developed by SCAPS. The other two heavy metal sensors utilize Laser Induced Breakdown Spectroscopy (LIBS)3. The design, performance, and field results of the SCAPS XRF Metals Sensor will be covered in this article.

SENSOR DESIGN

The SCAPS XRF Metals Sensor is designed to employ X-ray fluorescence4 to detect all heavy metals (above calcium) while deployed at the full penetrometer depth (which can reach as much as 50 meters). The detection limits are about 100 ppm and the calibration and reproducibility are sufficient for quantitative work at the field screening level. The results are available in real time.
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while the measurements are being made, so that results in one location can guide further exploration. The sensor is intended for use in characterizing contaminated environmental sites but is also useful for testing the effectiveness of remediation efforts and for any underground or underwater metals investigations. XRF operates well under water with little additional matrix corrections and is well suited to investigating sediments in harbors and estuaries. 

_In-situ_ measurement implies that no samples are extracted, eliminating waste generation and well drilling. The size of the sensor makes it relatively easy to transport and to push and the data is comparable to or better than the data typical of hand-held field instruments. No radioactive source is used, the unit is rugged and designed to be modular for field serviceability, and the data interpretation is straightforward.

To achieve these goals, the sensor consists of an X-ray head which fits inside the penetrometer pipe and is coupled via an umbilical to analysis electronics and computer at the surface. The X-ray head contains an X-ray source, collimators and filters, and an energy dispersive X-ray detector. The X-rays access the soil through a rugged but transparent window in the side of the pipe. The umbilical carries the necessary voltages and signals to power supplies and pulse shaping electronics in the penetrometer truck. The X-ray pulses from the detector go to a conventional multichannel analyzer and a laptop computer. An interlock sleeve assures that the sensor is enclosed or underground before the X-ray source is energized. Note that the interlock sleeve also has a sample introduction port for field measurement of calibration, check, and blank samples. A sketch of the sensor system as it appears in the truck is shown in Figure 1.

Figure 1. SCAPS XRF Metals Sensor showing all components as they are arranged in the SCAPS penetrometer truck.
An X-ray tube was chosen as the source to avoid the safety and licensing problems associated with radioactive sources and to provide faster data collection. The tube was developed especially for this sensor by two different vendors. The tubes are less than 1.6 cm (5/8 inch) in diameter and operate at 30 kV and 10 to 100 microamperes. Both molybdenum and tantalum anodes are used, with suitable filtration to remove the continuum radiation at energies where emission lines of interest are located. A 0.051 mm Mo filter is used with the Mo tube and 0.2 mm of Al is used with the Ta tube.

The detector is a Si-PIN diode which is commercially available. The preamplifier is located adjacent to the detector in the pipe and was physically modified slightly from its original package to fit. The detector resolution is less than 250 eV from the manufacturer and operates at about 265 eV to 290 eV in the sensor with a 40 meter umbilical. The detector element is cooled by a Peltier cooling stage and collects a usable spectrum from about 2 to 20 kV.

The components of the X-ray head are arranged linearly along the pipe diameter, which provides the principal constraint to the sizes of the components. The pipe inner diameter is 3.3 cm. The components are mounted on a rail for alignment and ease of insertion into the pipe. The X-ray tube and the detector fit into a collimator block which assures the critical alignments. Holes in the collimator block provide beam collimation for the incident and secondary beams.

The location of the sensor components and the overall operation of the sensor systems are shown in Figure 2.
This design provides a sensor which is rugged, fits within a penetrometer pipe which can be pushed by conventional rigs, and achieves detection limits of 100 ppm for lead in the field. The principal factor determining the detection limits is the scattering of the continuum radiation from the X-ray tube. The flux from the tube is sufficient to saturate the detector, so overall counting statistics are adequate. A filter in the incident beam is used to reduce the continuum radiation scattered by the window in the energy region where the emission lines from the metals of interest lie. This optical arrangement permits detection limits of about 100 ppm to be achieved in 100 seconds. Better detection limits could always be achieved with longer counting times.

The sensor was calibrated for lead using two different calibration samples. The first were Standard Reference Materials from the National Institute of Standards and Technology. SRM 2709, 2711, and 2710 are soil matrices with 19, 1162, and 5532 ppm of lead respectively. In addition, intermediate value samples were constructed by adding lead sulfide to silicon dioxide in known quantities and verifying the composition by laboratory analysis. The resulting calibration curve is shown in Figure 3. Note that the matrix effects for silicon dioxide (sand) and the San Joaquin and Montana soils used in the SRMs are similar enough to be ignored in the calibration. A linear calibration curve was used to provide good quantitation at low levels, where the combined errors were about 20% worst case. Some levels measured in the field reached as high as a few percent. Extrapolation of the linear calibration curve to this range will produce larger errors, up to 50% relative at concentrations above 100,000 ppm.

![Figure 3. Calibration curve of the SCAPS XRF Sensor for lead. The circles are the actual values of the samples used for calibration, the line is the calibration curve, and the squares are the measured values of the calibration samples calculated with the calibration curve.](image-url)
FIELD DEPLOYMENT

The SCAPS platform consists of a hydraulically operated cone penetrometer test unit mounted in a custom-engineered 20-ton truck with on-board computers that provide real-time acquisition and processing of sensor data. The truck is capable of pushing instrumented cones for geotechnical data such as subsurface soil stratigraphy and groundwater depth. The SCAPS truck has available samplers for use in collecting retrieval samples from specific depths of subsurface contaminants.

For the collection of *in-situ* XRF spectra, the XRF Metals Sensor is set up in the truck and the umbilical threaded through the penetrometer pipe. The sensor is pushed to the desired depth and stopped during data collection. For the measurements reported here, data collection times were 100 seconds. The X-ray tube was operated at 30kV, with 20 microamps on the Ta tube and 100 microamps on the Mo tube. Separate calibration curves were used for the two tubes, but instrument sensitivities were similar at these settings and were typically about 1 count integral under the lead L alpha peak per ppm lead in the soil for 100 second live time (6% dead time). The peaks were integrated over a fixed region around the lead peaks after removal of a linear background. Further details of the field operation of the sensor have been reported elsewhere.

After a spectrum was obtained at a given depth, the penetrometer pushed the sensor to the next depth and another 100 second spectrum was obtained. The typical distance between successive spectra was 5 cm. Figure 4 is a spectrum obtained at a depth of 140 cm (4.6 feet) under typical operating conditions.

![Figure 4](JA006AT2.PLT)

Figure 4. Spectrum from push 6 with the sensor window at 140 cm below ground surface. The lead L alpha and L beta peaks are prominent at 10.5 and 12.6 keV respectively. The lead concentration is about 14,000 ppm. The peaks at 6.4 and 8 keV are from iron and copper and the large peak at 16.8 keV is Compton scatter from the molybdenum X-ray tube.

FIELD RESULTS

The first field demonstration was conducted at the Joliet Army Ammunition Plant near Joliet, Illinois. Measurements were made in the lead azide area, which contained a lagoon for wastewater from the manufacture of lead azide munitions primer. The area had since been smoothed and only
A grassy field was visible to the unaided eye. A series of 10 pushes was made in different locations, chosen during the course of the investigation. The goal was to obtain a range of data with the sensor and no attempt was made at a complete investigation of the area. The measured concentrations of lead in the soil ranged from below the detection limit to several percent by weight. A pseudo-three-dimensional plot of the push locations and concentration ranges observed is given in Figure 5. Note that in some cases the concentration changes by several orders of magnitude in a distance of 5 cm.

![Figure 5](image-url)  
Figure 5. Subsurface lead concentrations in the lead azide area of Joliet Army Ammunition Plant. Each rod represents the location of a penetrometer push, with the darkness of the rod indicating the lead concentration range. The gray areas show the measured lead concentration, with the lightest gray representing below 2000 ppm and the darkest above 10,000 ppm. The black areas are below the detection limit. The vertical axis range corresponds to 30 cm of depth below the ground surface.

A second demonstration was conducted at an area used as a burn pit for ammunition located at the Lake City Army Ammunition Plant near Kansas City, Missouri. Only 6 locations were sampled with the penetrometer but verification samples were also collected at the same locations with a hand auger. The auger samples were split with one set going to a laboratory for analysis and the other retained for measurement with the XRF Sensor in the laboratory. The concentration ranges found were similar to those at Joliet. Since the locations were all in a line, the Lake City data are shown as a series of concentration versus depth plots in Figure 6. Note that the concentrations again vary widely with depth. Data were collected at depth intervals of 15 cm to match the depths sampled with the hand auger.
The data in Figure 6 required about one and one-half working days, or about 12 hours, with a crew of four. Data was available immediately and each operation could be guided by the results from the previous measurements. This operation can be optimized considerably for routine field work, probably dropping to a crew of two. With a 0.5 cm per second push rate and continuous data collection, over 100 meters of linear production per day could be achieved. For the samples collected by hand auger, a similar collection time was required (one and one-half days for six locations). A crew of six was employed and the result was a box of samples to be shipped to the laboratory for analysis, with the data available weeks to months later. This sampling process is limited to shallow depths, leaves little room for optimization, and requires the waste material to be properly disposed and large holes to be filled.

Figure 7 presents a comparison of the concentration versus depth for hole W2 measured during a direct push and by sample removal with a hand auger. Both measurements were made by the XRF sensor, the first in the field and the second in the laboratory a few weeks later. The plot indicates a very good correlation between the in-situ measurements and the conventional approach.
Figure 7. Comparison of in-situ measurements with conventional samples removed by a hand auger. The line is the data obtained while pushing and the circles represent the extracted samples. Both measurements were made with the XRF Metals Sensor and plot lead concentration in ppm versus depth. The auger samples were homogenized over a depth range of approximately 15 cm.

CONCLUSION

XRF via cone penetrometry has proven to be a viable method for obtaining in-situ measurements of heavy metal concentrations in underground soil. The results agree well with conventional sampling methods and are available in real time. Miniature X-ray tubes are rugged enough for deployment via direct push techniques, replacing the requirement for radioisotope X-ray sources. The Naval Research Laboratory currently has two probes operational and has secured two vendors of miniature X-ray tubes. Detection limits are 100 ppm for lead in soil and were obtained by reducing the continuum radiation scattered by the window in the region of the lead peaks. The next phase is proceeding under the Environmental Security Technology Certification Program (ESTCP). It consists of validation of the sensor performance by the California EPA Certification Program and field demonstrations for regulators and potential commercial partners.

The major planned technical improvement is to implement continuous data collection while the sensor is being pushed. This has been tested but software modifications and communication with the SCAPS computer to allow depth readout are necessary before it is viable. No limitations of the
sensor performance during push were observed. Detection limits will be further improved as much as possible and performance will be improved at lower energies by optimizing the window design.

The ultimate goal of this program is acceptance by environmental regulators and commercialization of the technology to make it available to a broad array of users.

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