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Office of Research and Development
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EPA

Innovative Technology Verification Report

Field Measurement Technology for Mercury in Soil and Sediment

Metorex's X-MET ® 2000 X-Ray Fluorescence Technology

SITE

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Office of Research and Development
Washington, DC 20460

MEASUREMENT AND MONITORING TECHNOLOGY PROGRAM VERIFICATION STATEMENT

TECHNOLOGY TYPE: **Field Measurement Device**

APPLICATION: **Measurement for Mercury**

TECHNOLOGY NAME: **Metorex's X-MET® 2000 (X-MET 2000)**

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VERIFICATION PROGRAM DESCRIPTION

The U.S. Environmental Protection Agency (EPA) created the Superfund Innovative Technology Evaluation (SITE) and Measurement and Monitoring Technology (MMT) Programs to facilitate deployment of innovative technologies through performance verification and information dissemination. The goal of these programs is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. These programs assist and inform those involved in design, distribution, permitting, and purchase of environm ental technologies. This document summarizes results of a demonstration of the X-ray fluorescence technology X-MET 2000 developed by Metorex Inc.

PROGRAM OPERATION

Under the SITE and MMT Programs, with the full participation of the technology developers, the EPA evaluates and documents the performance of innovative technologies by developing demonstration plans, conducting field tests, collecting and analyzing demonstration data, and preparing reports. The technologies are evaluated under rigorous quality assurance (QA) protocols to produce well-documented data of known quality. The EPA National Exposure Research Laboratory, which demonstrates field sampling, monitoring, and measurement technologies, selected Science Applications International Corporation as the verification organization to assist in field testing five field measurement devices for mercury in soil and sediment. This demonstration was funded by the SITE Program.

DEMONSTRATION DESCRIPTION

In May 2003, the EPA conducted a field demonstration of the X-MET 2000 and four other field measurement devices for mercury in soil and sediment. This verification statement focuses on the X-MET 2000; a similar statement has been prepared for each of the other four devices. The performance of the X-MET 2000 was compared to that of an off-site laboratory using the reference method, "Test Methods for Evaluating Solid Waste" (SW-846) Method 7471B (modified). To verify a wide range of performance attributes, the demonstration had both primary and secondary objectives. The primary objectives were:

(1) Determining the instrument sensitivity with respect to the Method Detection Limit (MDL) and Practical Quantitation Limit (PQL);
(2) Determining the analytical accuracy associated with the field measurement technologies;
(3) Evaluating the precision of the field measurement technologies;
(4) Measuring the amount of time required for mobilization and setup, initial calibration, daily calibration, sample analysis, and demobilization; and
(5) Estimating the costs associated with mercury measurements for the following four categories: capital, labor, supplies, and investigation-derived waste (IDW).

Secondary objectives for the demonstration included:

(1) Documenting the ease of use, as well as the skills and training required to properly operate the device;

(2) Documenting potential health and safety concerns associated with operating the device;
(3) Documenting the portability of the device;
(4) Evaluating the device durability based on its materials of construction and engineering design; and
(5) Documenting the availability of the device and associated spare parts.

The X-MET 2000 analyzed 58 field soil samples, 27 field sediment samples, 42 spiked field samples, and 70 performance evaluation (PE) standard reference material (SRM) samples in the demonstration. The field samples were collected in four areas contaminated with mercury, the spiked samples were from these same locations, and the PE samples were obtained from a commercial provider.

Collectively, the field and PE samples provided the different matrix types and the different concentrations of mercury needed to perform a comprehensive evaluation of the X-MET 2000. A complete description of the demonstration and a summary of the results are available in the Innovative Technology Verification Report: "Field Measurement Technology for Mercury in Soil and Sediment—Metorex's X-MET® 2000 X-Ray Fluorescence Technology" (EPA/600/R-03/149).

TECHNOLOGY DESCRIPTION

The Metorex X-MET 2000 analyzer is based on X-ray fluorescence technology. The sample to be measured is irradiated with a radioactive isotope. The isotopes most commonly used in soil analysis are Cd-109 and Am-241. Four different isotope source types are available for use with the X-MET 2000 probes: Fe-55,Cm-244, Cd-109, and Am-241. During the demonstration Cd-109 was used to analyze all 197 soil samples.

An X-ray source can excite characteristic x-rays from an element if the source energy is greater than the absorption edge energy for that elem ent. W hen an atom absorbs the source X-rays from the isotope source, the incident radiation dislodges electrons from the innermost shells of the atom thereby creating vacancies. The electron vacancies are filled by electrons cascading in from outer electron shells. Electrons in outer shells have higher energy states than inner shell electrons, and the outer shell electrons give off energy as they cascade down into the inner shell vacancies. T his rearrangement of electrons results in emission of excess energy as X-rays, characteristic of the given atom. The emission of x-rays, in this manner, is termed x-ray fluorescence.

The instrument's detector converts the energies of X-ray quanta to electrical pulses. The pulses are then measured and counted. The intensity (counts in a certain time) from the measured element is proportional to the concentration of the element in the sample. The measurement technique is fast and nondestructive, and multiple elements can be measured simultaneously. The chemical or physical form of the atom does not affect the X-ray energy, because the electrons producing X-rays are not valence (outer) shell electrons. Both identification and quantitation can be accomplished from a single measurement. The high-resolution silicon-PIN detector is stable and accurate, and continuous self-testing and automatic source decay correction ensures the reliability and accuracy of the measurement.

During the demonstration, intrusive measurements were made by placing the probe nose on the sample and pressing the start button on the probe. This opened the source and the sample was exposed to the source. The trigger was then pressed and the sample was measured for a preset time. One analysis takes from 30 seconds to 10 minutes, depending on the desired accuracy. During the demonstration, soil samples from Carson River, Oak Ridge Y-12, and Puget Sound were measured for 240 seconds each, while the Manufacturing Site samples were analyzed for 180 seconds each. Upon completion of the measurement, an assay was displayed. Data collection and analysis were completely automated. Connection to a remote computer, if desired, could allow transfer of the collected data for further evaluation and report generation.

ACTION LIMITS

Action limits and concentrations of interest vary and are project specific. There are, however, action limits which can be considered as potential reference points. The EPA Region IX Preliminary Remedial Goals (PRGs) for mercury are 23 mg/k g in residential soil and 310 mg/k g in industrial soil.

VERIFICATION OF PERFORMANCE

To ensure data usability, data quality indicators for accuracy, precision, representativeness, completeness, comparability, and sensitivity were assessed for the reference method, based on project-specific QA objectives. Key demonstration findings are summarized below for the prim ary objectives.
***Sensitivity*:** The two primary sensitivity evaluations performed for this demonstration were the MDL and PQL. Both will vary dependent upon whether the matrix is a soil, waste, or aqueous solution. Only soils/sediments were tested during this demonstration, and therefore, MDL calculations and PQL determinations for this evaluation are limited to those matrices. By definition, values measured below the PQL should not be considered accurate or precise and those below the MDL are not distinguishable from background noise.

Method Detection Limit - The evaluation of an MDL requires seven different measurements of a low concentration standard or sample following the procedures established in the 40 Code of Federal Regulations (CFR) Part 136. The evaluation of MDL requires seven different measurements of a low concentration standard or sample. Several standards were evaluated for calculation of the MDL. The range for the calculated MDL is between 16.5 and 26.9

mg/kg. This MDL is very close to the PRG action limit noted above and therefore this should be considered carefully by potential users of this technology for detection of mercury in soils and sediments. Mercury concentrations close to this action limit may not be detected by this technology. The equivalent MDL for the referee laboratory is 0.0026 mg/kg.

Practical Quantitation Limit - The low standard calculations suggest that a PQL for the Metorex field instrument is approximately 64 m g/kg. Given that the definition of a PQL is associated with a defined accuracy and precision, an actual PQL for the Metorex field instrument is difficult to estimate due to the accuracy discrepancy between the X-MET 2000 and the referee laboratory results. The referee laboratory PQL confirmed during the demonstration is 0.005 mg/kg, with a %D <10%.

Accuracy: The results from the X-MET 2000 were compared to the 95% prediction interval for the SRM materials and to the referee laboratory results (Method 7471B). The percentage of Metorex analyses within the 95% prediction interval for SRM materials was only 19% with n = 63. The statistical comparison between the Metorex field data and the referee laboratory results suggests that the two data sets are, in fact, different. Metorex data was found to be both above and below referee laboratory concentrations, and therefore there is no implied or suggested bias. In determining the number of results significantly above or below the value reported by the referee laboratory, 22 of 32 average results are greater than 50% different. Overall, the accuracy evaluations suggest that the Metorex field instrument provides results that are not comparable to the referee laboratory, and not within predicted accuracy specifications as determined by SRM reference materials. Metorex did not bring and utilize calibration standards to the demonstration. The reason for the low accuracy is unknown, and is beyond the scope of this demonstration.

Precision: The precision of the Metorex field analyzer is better than the referee laboratory. The overall average RSD is 20.6% for the referee laboratory, compared to the Metorex average RSD of 9.34%. Both of these RSDs are within the predicted 25% RSD objective for precision; expected from both analytical and sampling variance.

Measurement Time: From the time of sample receipt, Metorex required 18 hours (36 man hours) to prepare a draft data package containing mercury results for 197 samples. Two technicians performed all setup, sample preparation and analysis, and equipment demobilization. However, it was estimated that the second technician worked approximately 25 percent of the tim e. Individual measurements took 3 or 4 minutes each (after sample preparation), but the total time per analysis averaged 6.9 minutes when all field activities and data package preparation were included, and one-one/fourth technician is included in the calculation.

Measurement Costs: The cost per analysis, based upon 197 samples, when renting the X-MET 2000, is $33.28 per sample. The cost per analysis for the 197 samples, excluding rental fees, is $16.02 per sample. Based on the 2-day field demonstration, the total cost for equipment rental and necessary supplies is estimated at $6,556. The cost breakout by category is: capital costs, 51.9%; supplies, 3.7%; support equipment, 4.2%; labor, 18.3%; and IDW, 22.0%.
Key demonstration findings are summarized below for the secondary objectives.

Ease of Use: Based on observations made during the demonstration, the X-MET 2000 is very easy to operate, requiring one field technician with a high school education and brief training on the analyzer. A training course on instrument operation is included in the purchase price and training is available for $1000 a day for anyone renting the instrument. The user's manual is easy to follow and the software is menu-driven.

Potential Health and Safety Concerns: No significant health and safety concerns were noted during the demonstration. Potential exposure to radiation from the excitation sources (Cd-109 and Am-241) was the only health and safety concern during the demonstration. The analyzer should never be pointed at anyone while the sources are exposed. No solvents or acids are used for sample preparation.

Portability: The X-MET 2000 is a field-portable, hand-held instrument, consisting of a m ain unit, external keyboard, battery and a probe. The system is supported with auxiliary devices including a spare battery, battery charger and a water repellent backpack for field transport between sampling locations. The analyzer operates on 110 or 220 volt AC or battery. During the demonstration, the analyzer, operating on 1 NiCd battery, lasted for 4 hours and 10 minutes.

Durability: Based on observations during the demonstration, the main unit and probe were well constructed, field rugged and durable. They are constructed of aluminum and stainless steel. During the two days in which the instrument was observed there was no downtime, maintenance or repairs. The equipment was not apparently effected by the two days of almost continuous rain.

Availability of the Device: The X-MET 2000 is readily available for lease or purchase. The X-MET 2000 rental is available on a limited basis (total of 2 or 3 units). Supplies not provided by Metorex are readily available from supply firm s. According to Metorex, no standards are required to analyze samples.

PERFORMANCE SUMMARY
In summary, during the demonstration, the X-MET 2000 exhibited the following desirable characteristics of a field mercury measurement device: (1) good precision, (2) high sample throughput, (3) low measurement costs, and (4) ease of use. During the demonstration the X-MET 2000 was found to have the following limitations: (1) poor accuracy and (2) an MDL that m ay exceed the residential soil PRG action limit and a PQL that was difficult to define due to poor accuracy. It is recommended that the X-MET 2000 be used only with a strong quality control program in place, utilizing

similar matrix standards (i.e., soil) in the field to enable the operator to know when results, with project specific accuracy requirements, are being m et. Nonetheless, the X-MET 2000 is a rapid, field rugged measurement device for mercury in soil and sediment.