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SUMMARY DATA VERIFICATION AND VALIDATION REPORT

Site: Colorado Smelter
Project/Task: Demonstration of Method Applicability
Report Date: July 2, 2015
Data Reviewer: Ruth Siegmund, E2 Consulting Engineers, Inc.

This verification and validation report is provided as a summary of the analytical results of soil and field quality control (QC) samples (equipment rinsate blank [ERB] samples) collected in support of the Demonstration of Method Applicability (DMA) for Colorado Smelter. All soil and water QC samples were analyzed for Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) metals (16 target analytes) by the *US Environmental Protection Agency (USEPA) Contract Laboratory Program (CLP) Statement of Work for Multi-Media Multi-Concentration Inorganics Analysis (ISM02.2; USEPA 2014a)*. Data were examined referencing *USEPA Contract Laboratory Program National Functional Guidelines (NFG) for Inorganic Superfund Data Review (USEPA, 2014b)*. All data generated for the soil and ERB samples were labeled as electronically verified via Stage 3 criteria (S3VE) by the laboratory, as defined in *USEPA Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use (USEPA, 2009)*. E2 verified the S3VE flags electronically using NFG-rules, and all discrepancies are discussed below. Manual Stage 3 verification and validation (S3VM) was performed on data submitted in each of six sample delivery groups (SDGs) containing soil samples. Calibration standards and batch QC samples were processed correctly by the laboratory, and the example calculations for sample result, initial calibration verification (ICV) recovery, interference check sample (ICS) recoveries, and laboratory control sample (LCS) recoveries were confirmed.

DMA Sampling Event

A total of 40 primary soil samples collected in bags, 26 primary soil samples collected in jars that were split and analyzed in triplicate by the laboratory, and 14 ERB samples were collected during 12 days between May 4 and 31, 2015. Samples were shipped to the CLP laboratory, and the CLP laboratory generated six SDGs for the soil samples and one SDG for the ERB samples.

General:

All sample data were electronically verified via Stage 3 criteria (S3VE) by the CLP laboratory. The CLP laboratory applied U/UJ flags in cases where the validator is prompted in NFG to use professional judgment. During the manual Stage 3 verification and validation, E2 used professional judgment to remove all U/UJ flags applied in these cases, specifically:

- Code EXES-478: “The following samples have analyte results greater than CRQLs. The associated ICB analyte results are greater than or equal to MDLs but less than or equal to CRQLs. Use professional judgment to qualified detected and nondetected analytes.”
- Code EXES-479: “The following samples have analyte results greater than CRQLs. The associated CCB analyte results are greater than or equal to MDLs but less than or equal to CRQLs. Use professional judgment to qualified detected and nondetected analytes.”

- Code EXES-508: “The following samples have analyte results greater than CRQLs. The associated preparation blank analyte results are greater than or equal to MDLs but less than or equal to CRQLs. Use professional judgment to qualify detected and nondetected analytes.”

The laboratory reported data using laboratory-established reporting limits (RLs), as opposed to reporting to the CLP Contract Required Quantitation Limits (CRQLs). For all metals, for undiluted analyses, the laboratory RL was less than the CRQL.

Evaluation of ERB Samples:

- There were no detections in ERB samples that exceeded detections in any associated soil sample. No field contamination was observed, so flagging of soil samples because of potential field contamination was not required.

Soil SDGs MH0AB1, MH0AB2, MH0AE3, MH0AH9, MH0AJ1, and MH0AM6:

All of the following QC results were within NFG acceptance criteria, so qualification of field samples was not required:

- Preservation and holding times.
- Initial calibration, ICV, and continuing calibration standards.
- LCSs.
- ICSs.

Due to insufficient sample mass, the following laboratory QC samples were not analyzed:

- Laboratory duplicate samples.
- Matrix spike samples.
- Post-digestion spike samples.
- Serial dilution samples.

Sample results were qualified per NFG for the following:

- Calibration and preparation blanks: antimony, selenium, silver, and thallium were detected in calibration and preparation blanks, and associated results were flagged per NFG.

There were no rejected results in the DMA dataset.

Summary of Verification/Validation Criteria

The data generated by samples collected in support of the MDA are verified and validated. Samples were analyzed for metals by CLP Scope of Work ISM02.2 (USEPA, 2014a), and data were verified per USEPA NFG (USEPA, 2014b). The verification and validation were based on completeness and compliance checks of sample-related and instrument-related QC results tabulated by the laboratory, and the direct inspection of the raw data. Validation was classified as S3VE as defined in *Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use* (USEPA, 2009). E2’s electronic verification confirmed that the S3VE-flagged data were accurate compared to NFG rules, with the exception of the application of U/UJ flags in cases where professional judgment is directed. Additionally, the CLP laboratory reported data using laboratory-established RLs instead of CRQLs. There were no other discrepancies discovered during the manual Stage 3 review (S3VM). Since all data were electronically and manually verified and validated, all data for this monitoring event are considered verified and validated and are labeled S3VEM.

References

US Environmental Protection Agency (USEPA), 2009. *Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use*. EPA 540-R-08-005. USEPA Office of Solid Waste and Emergency Response. Washington, DC. January.

USEPA, 2014a. *Contract Laboratory Program (CLP) Statement of Work for Multi-Media Multi-Concentration Inorganics Analysis ISM02.2*. August.

USEPA, 2014b. *Contract Laboratory Program National Functional Guidelines (NFG) for Inorganic Superfund Data Review*. USEPA-540-R-13-001. USEPA Office of Superfund Remediation and Technology Innovation. Washington, DC. August.

Review and Verification of XRF Sampling Colorado Smelter - 2015 Demonstration of Method Applicability Project

Introduction

This review and verification addresses the procedures set forth in the Standard Operating Procedure (SOP) for X-ray fluorescence (XRF) sample analysis during the 2015 Demonstration of Method Applicability (DMA) project completed at the Colorado Smelter Superfund Site (Site). The objectives of the 2015 DMA project are described in more detail in the DMA Quality Assurance Project Plan (QAPP).

The SOP was used to analyze all soil samples collected during the 2015 DMA by XRF. The SOP follows the standard template for SOPs produced by Pacific Western Technologies, Ltd. (PWT) for environmental support operations.

Purpose and Scope

The quality control procedures for XRF soil sampling was reviewed for completeness and general quality and quantification for the final data set. The quality control guidelines followed the projects SOP - *XRF Sample Analysis for 2015 DMA - Procedure No. PWT-COS_DMA-303 Rev 1* and the EPA XRF method 6200 - *Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment*.

The procedures that are addressed are as follows:

- Initial control charting
- Interference Checks
- Blank Analysis
- Laboratory Control Sample (LCS) analysis
- Instrument Duplicates
- Calibration of XRF
- XRF Sample Precision Measurements

The review and verification utilized, whenever possible, the raw data output files from the XRF instrument to recreate and recalculate control charts, calibrations, and %RSD's. The original raw data files were also used to verify the daily quality controls and frequencies of the standards and blanks.

It is also noted that only data pertaining to arsenic and lead were reviewed and utilized for any verification and recalculations.

Instrumentation

Two portable Niton GOLDD+ Ultra XRF instruments were used for the analysis of metals. One was from the EPA and is identified in the raw data files as instrument 92959 (which is the instruments serial number). The other was rented and identified as 82347. The instruments, although portable, were set up in separate lab rooms and fixed to a stationary bench during analyses.

Routine Quality Control Procedures

Initial Control Charting

Initial control charting refers to a graphical representation of the acceptable limits for concentration results from an SRM of known concentration. The purpose of a control chart is monitoring the performance of an XRF before and after batches of samples are analyzed. Markings on a number line (the y-axis) display the range of acceptable results. When an LCS is read, the result is plotted to show

where it falls in relation to the acceptable limits which are derived from the mean and standard deviation of evaluation data. Results that fall outside of the limits indicate there is an analytical problem that needs to be resolved before sample results can be finalized and reported.

Control charts for several metal analytes were generated using Standard Reference Material (*SRM - refers to a commercially prepared soil certified to have known (a mean plus/minus variability) concentrations for various elements or compounds*) samples for each of the two XRF instruments used in the DMA study. Each instrument had initial charts created from running standards over a period of several days, generating at least 25 readings. Then the control charts were updated later in the project with data from all the SRM's that were run on a daily basis and was dependent on the batch size of each day.

The reviewer verified four (two for each instrument) of the control charts created for lead and arsenic and verified the calculations for the mean value for the analyte, values for the mean +/- two standard deviations, and the mean +/- three standard deviations. The daily SRM's were plotted on the control charts and the reviewer spot checked 10 percent or more of these, and verified that corrective actions were completed and documented when necessary.

Interference checks

Each lot number of plastic bags was checked for interference by taking a reading with and without the plastic bags using all the SRM samples. Lot numbers for the bags were PO262009, PO26010, and PO257439. The SRM samples were run at low, medium, and high concentrations with 4 readings (NIST2709a – Low, RCRApp – Medium, and USGS sdAR-M2 – High). The SOW stated that 7 to 10 readings be conducted but the information given the reviewer only consisted of 4 readings.

Only t-tests were run to confirm that the bags did not interfere significantly with the results. Once a particular lot number had been cleared as free from interference, no other bags needed to be checked from that lot.

The bags from lot numbers PO262009, PO26010 passed the interference check with the exception of lot number PO262009 at the higher concentration levels (NIST2710a) for Lead and Arsenic. The conclusions were:

For arsenic;

It is ok to use this bag if these concentrations are not relevant to decision-making

For Lead;

Don't use this bag lot unless concentrations are not relevant to decision-making

The SRM concentrations levels for arsenic (~1650 ppm) and lead (~5500 ppm) and the readings of any samples with the bags are several times higher than the action levels of the project and could still be considered relevant to the project due to any sample concentrations exceeding the action levels.

As stated with the Bag Checker Tool provided by the EPA:

If the bag passes at the low concentration level, but fails at high concentrations that are not relevant to project decisions, use a medium concentration SRM or fine-grained sample to check the bag. If the bag passes at elevated, but relevant concentrations, then the bag is acceptable.

Data for the bags from lot number PO057439 at the time of review were not available and verbal and email discussions with the XRF operators have verified that an interference check was not conducted for the small bag lot.

Blank Analysis

An instrument blank consists of silicon dioxide or sand in the same type of analysis bag as the samples. Instrument blanks were run at the start, middle and end of every batch and were verified by the reviewer.

As stated in the SOW, if arsenic or lead is detected in the blank, the instrument should be considered to be out of control, and corrective actions should be taken.

Only six incidents of the sand blanks having arsenic readings exceeding >10ppm were identified and all corrective actions or subsequent readings were non-detect and the instrument was considered to be in check.

Only one incident of the sand blanks having lead readings exceeding >10ppm were identified and all corrective actions or subsequent readings were non-detect and the instrument was considered to be in check.

SRM Analysis

Before and after each batch of samples, SRM samples were run to confirm that the instrument remained in control. Many of the batches had SRM's conducted after 10 samples in the least. The reviewer confirmed the frequency of the SRM runs per batch and found that the analyses per day and per batch were conducted according to the SOW even if the number of runs were left to the discretion of the analyst.

Most of the SRM samples run at each frequency consisted of at least two or three SRM samples with low, medium, and high concentrations of the target analytes. Spot checks where the results of any SRM was outside 2 standard deviations of the initial control charts values for the analyte (Arsenic or Lead) were verified to have corrective actions as required in Section 4.5.2 or Section 4.5.3 of the SOW. All corrective actions for the spot checks were conducted and completed indicating the instrument was in check.

Instrument Duplicate Analysis

Duplicate Analysis it used as a tool to build an instrument history to assess the drift. It is not data critical and could be removed as a procedure if deemed necessary because other instrument checks with the SRMs and blanks account for such drifts and are required. The reviewer did verify some instances where a duplicate was run or was coincidental. There is no indication that any troubles were determined.

Calibration of XRF Instruments and Performance Analysis

Along with the initial control charts, a set of standard calibration curves were completed for each analyte using an specified set of data run in the earliest days and then augmented through the project with more data from the SRM samples. The EPA provided an overview document discussing the performance of each instrument. The data presented in the overview write up was evaluated and spot checked for mean, standard deviation, and mean ratio's calculations. In general, the data presented in the overview was verified from the raw data files and log books. The reviewer agrees with the stated performance evaluation as presented by the EPA for the XRF instruments used in the DMA study.

XRF Sample Precision Measurements

Spot checks were completed to verify the statistical confidence goals for a given sample were met. They included as stated in the projects SOP:

- a. If the mean is lower than the decision limit for the metal being examined, compare the 95% upper confidence limit (95% UCL) of the mean to the decision limit. If the UCL is also below the decision limit, then no further analysis of the bag is necessary.
- b. If the mean is greater than the decision limit, compare the 95% lower confidence limit (95% LCL) of the mean to the decision limit. If the LCL is also below the decision limit, then no further analysis of the bag is necessary.

If further analysis is necessary as noted in steps above, continue making additional measurements in pairs (one on each side of the bag) until one of the following occurs:

- c. The mean and UCL are both below the decision limit, or the mean and LCL are both above the decision limit.
- d. 10 measurements have been made, and the mean and UCL (or LCL) are still on opposite sides of the decision limit. If this occurs, remix the bag following Section 4.1.3, and reanalyze the sample following Section 4.2. See step 10 below for how to handle the results from the initial analysis.

If a second 10 measurements still does not provide a clear decision, the following steps may be taken to try to resolve the problem:

- e. Check whether the readings from the two sides of the bag demonstrate a consistent bias relative to each other. If a consistent bias is demonstrated and it appears that this bias may be introducing artificial variability, remix the bag by rotating it as described in Section 4.1.3. See step 10 below for how to handle the results from the initial analysis.
- f. Double the scan time of the instrument, and repeat the analysis, which will provide more signal averaging. See step 10 below for how to handle the results from the initial analysis.

A review of ten percent of the individual sample sets found that all but one result of four XRF readings failed to satisfy the statistical confidence goals. However, corrective actions were completed for the sample with results needing further XRF readings. No other anomalies were observed in the individual assessment of the sample sets to indicate that the average results for all the final samples did not meet the statistical confidence goals of the project.

Summary

The review and verification of the XRF analyses for the DMA project are complete and followed the guidelines set forth in the SOP and EPA Method 6200. Initial control charts, performance evaluations, and interference checks were completed and indicated that the instruments were in check for the duration of the project. Frequency of blanks and other SRM standards were documented and complete. Statistical goals for individual sample sets were met.