MAINTAINING CONTROL AT A RAPID RESPONSE FIELD ANALYTICAL SUPPORT PROJECT - A CASE STUDY OF PERFORMANCE-BASED MEASUREMENT SYSTEMS

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ABSTRACT

The Lockheed Martin Field Analytical Support Project (FASP) Team routinely uses performance-based analytical methods to provide rapid results at environmental field sites using mobile laboratories. This work is performed under the Environmental Services Assistance Team (ESAT) contract to the U.S. Environmental Protection Agency (EPA) Region 10. This paper describes a case study for the development, validation, and application of a performance-based analytical field method. An EPA Region 10 removal action project required quick turnaround data to determine the extent of contamination and confirm removal action. Drinking-water wells in an agricultural area were contaminated with high concentrations of the herbicide dinoseb. The source of the dinoseb was adjacent to an agricultural irrigation canal, prompting quick action to avoid additional groundwater contamination. A performance based analytical procedure for the herbicide dinoseb in soil was developed using gas chromatography with electron capture detection. Available EPA methods for dinoseb did not meet the data quality objectives for the project, or were not practical for use in a mobile laboratory. The primary objective was to provide reliable analytical data for two action levels of dinoseb in soil (1.6 µg/Kg and 80 µg/Kg). The FASP team developed a procedure two weeks prior to field deployment. The method used a small quantity of extraction solvent with direct injection of the extract into a gas chromatograph with an electron capture detector. The method was validated prior to field deployment, and quality assurance protocols were developed to assure project data quality objectives were met. Field chemists analyzed a total of 820 soil samples at the field site. Quality control included analyzing extraction blanks, extraction spikes, and matrix spikes. In addition, investigators shipped 10% of the samples to a fixed laboratory for comparison analysis. The results of the quality control show the field method produced reliable data. Overall, performance-based analytical methods for field screening allow for quicker, more cost effective site investigations and remedial actions. This paper provides guidelines for establishing quality control procedures to assure generation of data within project data quality objectives.

INTRODUCTION

On October 19, 1998, the FASP Team was tasked by the EPA to determine the feasibility of providing on-site support for the analysis of the herbicide dinoseb (2-sec-butyl-4,6-dinitrophenol) in soil. The project was to support an emergency removal project starting on November 2, 1998 in central Washington. The Region 10 FASP Team's approach to field analysis is to use laboratory-grade instruments in a well-equipped mobile laboratory to provide data of documented quality. If possible, the FASP Team follows standard operating procedures (SOPs) developed for compounds most likely to be encountered in Region 10. These SOPs contain generalized quality assurance procedures, which may be modified depending upon site-specific data quality requirements. However, no field SOP existed for dinoseb. A performance-based method for dinoseb was quickly developed, with site-specific quality control procedures incorporated into an SOP before field deployment. This paper describes the analytical method developed, the method validation procedures, quality control procedures, problems encountered, and corrective actions employed during the project.

METHOD DEVELOPMENT

The first step in preparing the analytical protocol was to obtain the data quality objectives for the removal project. The objectives were well defined. Two action levels were defined for dinoseb. All soil having dinoseb concentrations above 1.6 mg/Kg had to be removed. To track potential "hot spots," the investigators wanted detection limits at least ten times lower than the action level, or at 0.16 mg/Kg. The other action level was at 80 mg/Kg. Soil above this limit had to be segregated from lower level contaminated soil for efficient remediation. A quick analytical data turnaround was an important objective, with an analytical capacity of at least 30 samples per day. Although false positive results were not desired, a higher priority was assuring a minimum of false negative results.

Present EPA methods did not meet the data quality objectives of the project, or were not practical for field laboratory use. Dinoseb is listed as an analyte for EPA methods 8041 and 8151. Method 8041 is a gas chromatographic method using a flame ionization detector for soil extracts. However, flame ionization would not meet the detection levels required for the project. Method 8151 uses a derivatization procedure followed by electron capture gas chromatography. Although this procedure produces low detection limits, the derivatization method is not practical for field laboratory use. In addition, fixed-laboratory extraction procedures were not practical for a mobile laboratory. A method was developed to determine dinoseb by analyzing soil extracts without derivatization using electron capture gas chromatography. The extraction procedure selected was the same as used previously for FASP soil extractions using methyl-tert-butyl ether as an extraction solvent. The extraction method had been validated for pentachlorophenol but not for dinoseb, so further validation studies were required for this project.

The gas chromatograph was a Hewlett Packard Model 5890 Series II equipped with an electron capture detector. The column was a 30-meter J&W™ DB5-MS with a 0.53 mm ID and a 1.5 micron film. Helium was used for the carrier gas at a constant flow of 7.0 milliliters per minute. The initial oven temperature was 100°C for three minutes, ramped at 12°C per minute to 300°C, then held for 5.0 minutes. The injector temperature was 200°C and two microliter injections were made in the splitless mode. The detector temperature was 340°C with 5% methane/argon used as the make-up gas. Soil was extracted in disposable glass culture tubes with PTFE-lined screw caps. Five grams of soil were extracted twice with five milliliters of methyl tert-butyl ether. Before adding the solvent, the soil was spiked with a surrogate compound, and acidified with phosphoric acid. The extraction was performed using a multi-tube vortexer followed by centrifuging to separate the phases.

METHOD VALIDATION

The FASP team follows a set of guidelines for method validation before field deployment, although the specific validation steps depend upon project goals and historical method performance. As a minimum, method validation includes verifying instrument response and linearity over the concentration range of interest for the target compounds. In addition, method extraction blanks must show no interfering compounds and spiked matrix extracts must demonstrate good recovery of target compounds.

Since the method developed for dinoseb was a new procedure, additional quality assurance validation was performed. The precision of the method near the detection limit was found by analyzing a series of spiked soils. These results were compared with a precision study using the EPA method 8151 laboratory procedure. Although a thorough check for possible interfering compounds could not be done because of time limitations, several chlorinated pesticides and herbicides were found not to interfere. The definitive validation procedure was analyzing samples collected from the site using the developed method. These samples were also analyzed by a commercial laboratory. The results of the split samples had to agree before the mobile laboratory deployment.

FIELD QUALITY CONTROL

Quality control protocols used in the field laboratory are generally the same as those used in fixed laboratories, with the difference that criteria used in the field are not as strict as those used in fixed laboratories. This greater flexibility allows sample analyses to continue thus avoiding project slowdowns without adversely affecting data quality objectives.

The initial instrument calibration was performed with a minimum of five calibration levels. The calibration was successful if concentrations were found within ± 25% of the expected value and with a regression correlation coefficient (r^2) greater than 0.995. A calibration verification standard was analyzed once every 12 hours at a level near the lower action value for dinoseb. The acceptance criterion was the result being within ± 35% of expected value, or a new calibration curve was prepared. Retention time windows for dinoseb standards and spikes were established to be within ± 0.4% of the initial calibration retention time. Matrix spike and matrix spike duplicates were analyzed once per 20 samples. The acceptance criterion was recovery between 50% and 150% and the relative percent difference (RPD) less than or equal to 30%. Surrogate spike control limits were set at a recovery between 50% and 150%. Reagent extraction blanks and spikes were analyzed once per day.

In addition, a minimum of 10% of the samples analyzed on site were shipped to a commercial laboratory for confirmation analysis by EPA Method 8151. Duplicate field samples were submitted blindly to the field laboratory. Quality assurance included a peer review of all documentation, chromatograms, and results before reporting to the site investigator.

RESULTS AND DISCUSSION

Method validation experiments before field deployment displayed to site investigators that the performance-based method would meet the data quality objectives of the project. A method detection limit and precision study was performed by spiking a soil sample with dinoseb at a level near the desired lower detection limit. A series of seven replicate soil samples spiked at 0.2 mg/Kg was analyzed. The results showed a mean concentration of 0.24 mg/Kg with a standard deviation of 0.018 mg/Kg, or a percent relative standard deviation of 7.3%. The minimum detection limit was set at 0.10 mg/Kg, which was below the objective of 0.16 mg/Kg. The field method was compared with EPA method 8151 by extracting a series of seven soil samples spiked at 0.2 mg/Kg, then methylating the extract as specified in the EPA method. Although the methylated dinoseb has a greater response with sharper peaks, the precision was poorer using Method 8151 (a resulting mean concentration of 0.195 mg/Kg with a standard deviation of 0.97 mg/Kg). The primary method validation was the comparison of 40 samples from the site analyzed by the field method compared to split samples sent to a commercial laboratory for quick-turnaround analysis by Method 8151. Of the 40 samples, 33 samples showed non-detects for dinoseb in each methods. The seven samples with dinoseb showed good comparison, with an average percent difference of nine percent between the two methods.

The only problem encountered during the method validation was poor recovery of the surrogate compound. The surrogate selected for the method was 2,4,6-tribromophenol. This surrogate had successfully been used in previous projects as a surrogate for pentachlorophenol analyses. However, for the analysis of the 40 soil samples from the site, nearly all recoveries were less than 50%. It was felt that the problem was due to a matrix effect specific to the surrogate but not the dinoseb. The dinoseb recoveries from spiked site samples were good, and the confirmation results for the dinoseb agreed with dinoseb results from the field method. Another compound (2,4,5,6-tetrachloro-m-xylene) was selected as the surrogate, with this surrogate showing good recoveries from the on-site samples.

After validation results verified the performance-based method would meet the project objectives, the mobile laboratory was immediately moved to the site location, where 820 samples were analyzed over a six-week period. Nearly all of the quality control samples were within the acceptance criteria established for the project; however, one problem developed during the project. Four days into sample analyses, two batches of samples had many surrogate recoveries below the target value of 50%, 24 of the 62 samples. The problem was believed to be due to a high concentration of carbonates in the soil matrix. The extraction procedure called for adding acid to the soil prior to extraction, to assure the dinoseb analyte (a weak acid) was extracted with the organic solvent. Upon adding acid to some of the soil samples, a vigorous reaction was observed, producing excessive foaming suggesting a high concentration of lime in the matrix. The first step of corrective action was to discuss the problem with the project managers. The decision was made to continue with the sampling and analyses, with low surrogate results flagged to assist with selection of samples for confirmation analyses. The other corrective action was to modify the method, using a weaker buffering solution. The modified method was tested by analyzing six samples containing high carbonate levels in duplicate, one set analyzed with the original buffer and the second set analyzed with the weaker buffer. All six samples showed good surrogate recoveries using the modified procedure. The new buffer solution was incorporated into the procedure, with acceptable surrogate recoveries found afterwards.

CONCLUSION

Performance-based analytical methods are practical and useful means to analyze environmental samples in the field. Analytical methods can be optimized for the analytes of interest with quality control protocols specific for project data quality objectives. For this project, quality control included continuing calibration levels and matrix spike levels near the removal action defined for the cleanup, providing on-site investigators estimates of analytical precision and accuracy. Verification of performance-based method results with laboratory-based methods is an important component of quality assurance. Typically, 10 percent of the field samples are shipped to an off-site laboratory for analysis. Confirmation results not only verify the results of the field project, but can be used to direct method improvement.