

DoD Environmental Data Quality Workgroup

Guide for Implementing EPA SW-846 Method 8330B

Introduction:

In November of 2006 the Environmental Protection Agency (EPA) published method 8330B.¹ The method provides instruction for the trace analysis of explosives and propellant residues by high performance liquid chromatography (HPLC). The method includes an appendix (A), which describes sampling methodologies for collecting and processing representative samples for analysis.

Issue:

Method 8330B introduces several concepts that are new or are a change from 8330 and 8330A. The sampling and analytical modifications in 8330B are collectively intended to decrease the effects of sampling and subsampling error caused by the compositional and distributional heterogeneity typically encountered in solid environmental media at military training ranges. Various studies have shown that concentrations of energetic residues at military training ranges that were measured using the procedures in 8330B were statistically more representative relative to traditional sampling and analytical protocols^{2,3,4}. However, it is uncertain as to whether some of the new concepts utilized in 8330B represent viable sampling and analytical procedures that can be adopted within other SW-846 methodologies or if all of these concepts have practical application to environmental investigations other than military training ranges. Therefore, the application of these sampling and sample preparation techniques to constituents other than those listed in 8330B should be applied with great caution. Like most SW-846 methods, 8330B is a guidance method that provides for flexibility in the choice of apparatus, materials, reagents, and supplies. The objectives of this paper are to highlight those steps that represent a change from historical sampling and analytical methodologies, to provide recommendations as to the appropriate use of the concepts presented in Method 8330B, and to provide recommended minimum method QC requirements for laboratories performing Method 8330B.

Scope:

This paper addresses all aspects of Method 8330B. For simplicity, Method 8330B has been separated into three phases: sampling, preparation/extraction, and analysis. The methodologies that represent changes in each phase, and key issues associated with those

changes are summarized. This paper is intended for DoD personnel and DoD contract support entities to assist in making informed decisions regarding Method 8330B and the sampling/analytical concepts introduced in that method that could be applied to other contaminants and applications.

Precautionary notes:

The most significant note regarding Method 8330B is that the method has been designed to meet very specific data quality objectives of characterizing the mean concentrations of specific energetic compounds within a specified decision unit at active military ranges. Method 8330B is based upon research that involved highly refined conceptual site models (CSM) and included specific knowledge of the physical characteristics of the contaminants, their deposition, and behavior at firing and target points. This highlights the importance of developing a CSM and focusing the sampling and analytical strategies using the systematic planning process. Potential users of 8330B and the sampling/analytical procedures therein are cautioned that the key assumptions and specific CSM details from which Method 8330B were developed may also represent limitations to site investigations where those assumptions are unknown or inconsistent with those established in 8330B. For example, Method 8330B addresses only those energetic material residues of secondary explosives and propellants that fall within the size classification of soil (< 2 mm). Further, it is assumed that most of the energetic material residue deposition on DoD training ranges occurs as pure particles or fibers. The sampling and analytical procedures used in Method 8330B may not be applicable to sites where there is little information about contaminant releases, site history, and the physical and distributional characteristics of the contaminants of concern (COCs).

Sampling

Appendix A of EPA Method 8330B specifically addresses field sampling. The appendix provides guidance for explosive residue sample collection, handling, and laboratory processing techniques. Method 8330B recommends the use of multi-increment (MI) sampling, which involves the extraction of a representative portion of material from within a single decision unit. In MI sampling, several increments from the same decision unit are combined to form one sample that is submitted for laboratory analysis. The procedures for MI sampling are specifically designed to minimize sampling error and provide a more scientifically-representative mean concentration of the contaminant(s) present in the decision unit.

MI sampling uses the advantages of more spatial coverage and an increased sample mass to overcome the problems associated with sample heterogeneity. The tradeoff is that information about the variability in spatial concentrations within the decision unit is lost. Each decision unit is represented by one MI sample which yields one data point. MI sampling therefore does not allow for the calculation of the 95% upper confidence limit (UCL) of the mean concentration unless multiple replicate samples are taken within the decision unit. The 95% UCL of the mean is often the exposure point concentration used

in the refinement stages of a risk assessment.⁵ Variability in spatial concentrations between multiple decision units can be evaluated, provided the project team initially defines the spatial size and number of decision units needed.

Hot Spots: If the results of the sampling event will be used for a human health or ecological risk assessment, users should consult a risk assessor during the initial phases of project scoping in order to determine the appropriate minimal size of contaminant spatial resolution (e.g., to characterize “hotspots”). Compositing methods should be limited to decision units that best represent the average exposure of the receptor over time. The Alaska Department of Environmental Conservation has guidance on utilizing MI sampling and emphasizes the importance of this limitation:

“There is a critical item to keep in mind when identifying decision units and developing the MI work plan: MI may not be used to “dilute” contamination and therefore underestimate the need for cleanup. This may occur if the decision unit inappropriately incorporates large, uncontaminated areas in addition to real source areas.”⁶

The size of the decision unit selected should be dependent upon several factors, for example: the area influenced by a single event, the area influenced by an activity, or the area of concern for human health or ecological exposure (habitat). The Hawaii State Department of Health has adopted the use of MI sampling for specific applications and suggests that the size and shape of a decision unit is primarily controlled by the environmental concerns posed by the contaminants present and the intended use of the site.⁷ As an example, for residential human health exposures the EPA recommends that the site be divided into areas or strata depending upon the likelihood of contamination and that each DU should be 0.5 acres or less.⁸ Risk assessments for ecological receptors may require much smaller decision units. MI sampling can be adapted to establish gradients, boundaries, and locations with elevated concentrations if the location and size of decision units are predetermined using systematic planning. However, if the objective of the sampling event is to assess the spatial variability of concentrations, then the sampling design (using appropriately sized decision units to capture the spatial variability) needs to address this objective. The number of samples required to evaluate spatial changes would typically be rather large. Therefore, users must evaluate the costs and practicability of each sampling design prior to use. Of paramount importance, users are encouraged to use the critical elements of the systematic planning process to develop a conceptual site model and then formulate project quality objectives (PQO’s) that can appropriately meet the needs of the project.

Sample Mass: Appendix A of Method 8330B states, “A collection of a 1 kg or larger sample comprised of 30 or more evenly spaced soil aliquots (i.e. increments) of the top 2.5 to 5.0 cm of the ground surface is recommended.” Collection of such a large aliquot of sample represents a change from typical sampling protocols. Increased sample mass is recommended in order to decrease the effects of compositional heterogeneity. This inverse relationship between an increase in sample mass and a decrease in fundamental error is described in the particulate sampling theory described by Gy.⁹ There are, however, some practical considerations that project teams and laboratories must assess with this increased sample mass:

- Large samples will have to be transported and shipped to the laboratory.
- Laboratories must be able to accommodate these large samples with increased storage facilities, large trays and holding racks, and large grinding equipment.
- Laboratory disposal costs will increase due to the large sample sizes. These costs will likely be passed to the client.
- Most commercial, environmental laboratories do not have the equipment and facilities to accommodate the requirements of Method 8330B so project teams should confirm the availability of environmental laboratories to perform Method 8330B.
- The sample preparation time is significantly increased from the previous method 8330 preparation procedure.

Sample Depth: The soil depth horizon of the top 2.5 to 5 cm of the surface soil as prescribed in Method 8330B may not be appropriate for all site investigations. Selection of soil depth in the method was made based upon research studies on fate and transport of munitions residuals at operational ranges. These assumptions may not be appropriate for all range investigations or other types of contaminants.

Sampling media: The appendix in Method 8330B suggests that all organic material that has historically been excluded from soil samples (e.g., moss, grass, roots) be retained and that the entire sample will be processed. The intended purpose of this change in the sampling procedure is to account for the small fibrous particles that have been shown to be deposited or adsorbed on vegetation at firing points or impact areas of active ranges. Historically, vegetation is not included in soil samples because it does not represent the actual soil being evaluated. This is of particular concern relative to data that will be utilized for ecological or human health risk assessments. This decision is mainly dependent upon the exposure assumptions of the receptors being evaluated. As part of the systematic planning process, the project team should first consult a risk assessor and then specifically define the types of media that will be included or excluded from the sample collected (inclusion/exclusion of vegetation, etc.).

Note: The sampling procedures described in Appendix A of Method 8330B were developed specifically from studies of energetic compounds and propellant residues at active firing ranges. Nonetheless, the fundamental concepts underlying MI sampling and sub-sampling procedures can be adapted to address a wide variety of sampling objectives, analytes, and settings other than those for which the appendix was developed. When adapting MI sampling for a specific site, the project team, using the systematic planning process and including all relevant technical personnel and decision makers, needs to ensure that all aspects of the strategy employed are well defined (decision units, sample homogenization procedures, quality control criteria, etc.) and will meet all the project goals for each contaminate of concern.

Preparation/Extraction

Grinding: Method 8330B incorporates a very aggressive grinding procedure that represents a change from typical preparation methods. To ensure that representative subsamples can be collected from the portion of the sample that is consistent with the classification of soil (< 2 mm), a particle size reduction step is necessary.¹⁰ Method 8330B suggests grinding of samples to a particle size of <75 µm. This is a change from the previous Method 8330 which directs particle size reduction to 30 mesh (595 µm). The Method 8330B appendix states the importance of obtaining a representative mean concentration for the area selected. The grinding of samples is designed specifically to reduce the uncertainty caused by compositional heterogeneity thereby increasing the statistical representativeness of the original sample. “If evidence for representativeness is not presented, then the data cannot be characterized as effective for project decision making.”¹¹ However, changing the physical characteristics of particle size/shape by grinding may incorporate a bias in the resulting data as the sample is no longer in its original state as it exists in nature. Particle size reduction represents a potential bias when the resulting data are used for risk assessment because it changes the bioavailability and exposure characteristics of the media. Grinding may also create a positive bias when the resulting data are used in fate and transport modeling. Project teams are encouraged to solicit the technical advice of a chemist and risk assessor during planning to evaluate the effects of particle size reduction on uncertainty relative to exposure assumptions and uncertainty associated with sampling error to ensure that the appropriate sampling criteria are used to meet the project goals.

There are additional practical considerations that project teams and laboratories must evaluate relative to grinding:

- The sample preparatory procedure in Method 8330B is significantly more labor intensive than that for Method 8330 or 8330A. Most commercial laboratories do not possess the equipment or facilities to prepare the samples.
- The method appendix gives specific instructions regarding grinding: “For samples containing NC (nitro-cellulose) based propellant residues, five 60-second grinding intervals are needed to adequately pulverize the same quantities of soil. Furthermore, to prevent the ring mill from warming to temperatures where more volatile energetic compounds may be lost, a 2-minute or longer cool down period is recommended between the grind cycles.” Therefore, for any environmental investigations involving thermally labile constituents, it is highly recommended that appropriate data quality indicator(s) be used to evaluate the potential losses of analytes during the grinding step.
- Proficiency testing (PT) samples must go through the grinding process.
- A laboratory control sample (LCS) consisting of a solid reference material containing all reported analytes, must go through the grinding process and be analyzed with each batch.
- Grinding equipment must be thoroughly cleaned between the processing of separate samples and grinding blanks must be processed and analyzed to ensure cross-contamination is not occurring.

- Grinding to such a small particle size will create a dust which can easily result in contamination problems throughout the laboratory performing the test.
- The ball mill is not capable of reducing the size of polymeric materials (nitrocellulose). For this reason it should not be used without project-specific approval for samples from firing points, around direct - line - of sight targets, or other targets used for training with rockets and demolition ranges.

Sample Drying: Sample preparation in Method 8330B involves air drying the entire sample prior to sieving. Following sieving (<2mm) the entire sample is spread out and dried at room temperature to constant weight. For such a large sample, hydric soils and sediments will likely require several days to dry at room temperature to constant weight. Drying time can be significantly increased if there is a high concentration of vegetation included as well. Turnaround times could be an issue and the potential for analyte degradation to occur is likely.¹² Although Method 8330B is scoped to include soils and sediments, there is evidence that drying samples with high moisture content (e.g., sediment) can significantly affect extraction efficiencies.¹²

Extraction: Method 8330B recommends a change in the amount of sample extracted prior to analysis. Methods 8330 and 8095 directs that 2 grams of sample be extracted with 10 mLs of solvent while Method 8330B directs that 10 grams of sample be initially extracted with 20 mLs of solvent. This change will theoretically increase the sensitivity of the method but the increased sample mass may also increase the relative contributions of matrix interferences as well. Inclusion of organic material, such as grass and roots, may cause interferences with energetic compounds. The advantages/disadvantages of increased sample mass are specific to each method and each matrix. Therefore, a project chemist should be consulted to ensure that specific measurement performance criteria for the project will be met.

Analysis:

Section 11.4.3 of Method 8330B describes initial calibration verification using a second source QC standard: “Quantitative sample analyses should not proceed for those analytes that fail the second source standard initial calibration verification. However, analyses may continue for those analytes that fail the criteria with an understanding that these results could be used for screening purposes and would be considered estimated values.” While this allowance is acceptable for screening or making qualitative decisions, it would not be appropriate for use in final risk determinations or clean up actions.

Similarly, Section 11.4.4 of Method 8330B describes mid-point calibration factor verification relative to the initial calibration curve: “Should the reanalysis fail for the majority of target analytes, a new initial calibration should be performed. In instances where only a few target analytes fail the verification criteria, sample analyses may proceed with an understanding the sample data associated with these compounds needs to be qualified as estimated.” For the same reasons stated above, this allowance may be acceptable for screening or non-specific uses.

Method 8330B calls for the use of either a dual or multi-wavelength UV detector. Due to the non-specific nature of the UV detector, it is critical that appropriate confirmatory steps are utilized. Method 8330B allows for confirmation by an alternate detector. Due to the potential increase in matrix interference resulting from the Method 8330B sample preparation protocol and the need for definitive data, project teams should consider using mass spectrometry as the primary detector when using Method 8330B. Mass spectrometry provides both selectivity and sensitivity and is best suited to handle these analytical issues. Currently however, there is no analytical method in SW-846 using a mass spectrometric detector for explosives. Therefore, negotiation with regulatory agencies for acceptance of this technology is strongly recommended.

Table 1 contains minimum laboratory quality control criteria developed to improve the reliability of the data when using Method 8330B. These criteria are recommended for the routine use of the procedure and will be incorporated into the next update to the DoD Quality Systems Manual for Environmental Laboratories (DoD QSM).¹³

Table 1 - Quality Control Criteria for Method 8330B

QC Element	Minimum Frequency	Criteria/Requirements	Corrective Action/Flagging Criteria
Batch Quality Control Samples	Every batch	<p>Laboratory Control Sample (LCS) – A solid reference material containing all reported analytes, must be prepared (e.g., ground and subsampled) and analyzed in exactly the same manner as a field sample. In-house laboratory control limits for the LCS must demonstrate the laboratory’s ability to meet the project’s MQOs.</p> <p>Matrix Spike (MS) – For matrix evaluation only, therefore is taken post grinding from same ground sample as parent subsample is taken. Percent recovery must meet LCS limits.</p> <p>Matrix Spike Duplicate (MSD) or Sample Duplicate (SD) - For matrix evaluation only, therefore is taken post grinding from same ground sample as parent subsample is taken. Percent recovery must meet LCS limits and relative percent difference (RPD) < 20%.</p>	Take corrective actions or flag data as prescribed in the DoD QSM.
Soil Drying Procedure	Each sample and batch LCS	<p>Laboratory must have a procedure to determine when the sample is dry to constant weight.</p> <p>Record date, time, and ambient temperature on a daily basis while drying samples.</p>	
Soil Sieving Procedure	Each sample and batch LCS	<p>Weigh entire sample.</p> <p>Sieve entire sample with a 10 mesh sieve. Breakup pieces of soil (especially clay) with gloved hands. Do not intentionally include vegetation in the portion of the sample that passes through the sieve unless this is a project-specific requirement.</p> <p>Collect and weigh any portion unable to pass through the sieve.</p>	n/a

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QC Element	Minimum Frequency	Criteria/Requirements	Corrective Action/Flagging Criteria
Soil Grinding Procedure	Initial demonstration	The laboratory must initially demonstrate that the grinding procedure is capable of reducing the particle size to <75um by passing representative portions of ground sample through a 200 mesh sieve (ASTM E11).	
Soil Grinding Blank	Between each sample	A grinding blank using clean solid matrix (such as Ottawa sand) must be prepared (e.g., ground and subsampled) and analyzed in the same manner as a field sample. Grinding blanks can be analyzed individually or composited. No target analytes detected greater than 1/2 Reporting Limit (RL).	If the composite grinding blank exceeds the acceptance criteria, all samples associated with the grinding composite shall be qualified with a "B" qualifier. If any individual grinding blank is found to exceed the acceptance criteria, then the sample following that blank shall be "B" qualified. All blank results must be reported and the affected samples must be flagged accordingly.
Soil Subsampling Process	Each sample, duplicate, and batch LCS	Entire ground sample is mixed, spread out on a large flat surface (e.g., baking tray), and 30 or more randomly located increments are removed from the entire depth to sum a ~10 g subsample.	n/a
Soil Sample Triplicate	At the subsampling step, one sample per batch. Cannot be performed on any type of blank sample.	Three 10 g subsamples are taken from a sample expected to contain the highest levels of explosives within the Quantitation Range of the method. The % RSD (percent relative standard deviation) for results above the RL must not be more than 20%.	Corrective actions must be taken if this criterion is not met (e.g., the grinding process should be investigated to ensure that the samples are being reduced to a sufficiently small particle sizes).
Aqueous Sample Preparation	Each sample	Solid phase extraction (SPE) using resin-based solid phase disks or cartridges, is required. The salting-out procedure is not permitted.	n/a

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QC Element	Minimum Frequency	Criteria/Requirements	Corrective Action/Flagging Criteria
Primary Analysis		<p>Detection by HPLC UV, LC/MS, or LC/MS/MS is allowed.</p> <p>Initial Calibration (ICAL) - Minimum of 5 calibration standards with the lowest standard concentration at or below the RL. The apparent signal-to-noise ratio at the RL must be at least 5:1. Once the calibration curve or line is generated, the lowest calibration standard must be re-analyzed. All target analytes must recover within $\pm 20\%$ of the true value (initial source).</p> <p>Second source Initial Calibration Verification (ICV) – Prior to analysis of any samples, immediately following the ICAL. All target analytes must recover within $\pm 20\%$ of the true value (initial source).</p> <p>Continuing Calibration Verification (CCV) – Beginning of sequence, every ten samples, and at the end of the sequence. All target analytes and surrogates recover within $\pm 20\%$ of the true value (initial source).</p>	n/a
Confirmation Analysis	When target analytes are detected on the primary column using the UV Detector (HPLC) at concentrations exceeding the Limit of Detection (LOD).	<p>Confirmation analysis is not needed if LC/MS or LC/MS/MS was used for the primary analysis</p> <p>Secondary column – Must be capable of resolving (separating) all of the analytes of interest and must have a different retention time order relative to the primary column.</p> <p>Any HPLC column used for confirmation analysis must be able to resolve and quantify all project analytes. Detection by HPLC UV, LC/MS or LC/MS/MS.</p> <p>Calibration and calibration verification acceptance criteria is the same as for the primary analysis.</p>	Report from both columns. If there is a > 40% RPD between the two column results data must be flagged accordingly.

References:

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