



DoD Training – Environmental Laboratory Accreditation Program Requirements for 8330B

*Environmental Data Quality
Workgroup*

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8330B Training Topics

- Purpose of the training and target audience
- Differences in 8330A versus 8330B
- Quality Systems Manual (QSM)- Implementation of 8330B
 - Soil Drying
 - Laboratory Control Sample (LCS) Drying Study
 - Soil Sieving, Grinding, Subsampling
 - Soil Extraction
 - Aqueous Samples
 - Analytical Requirements
 - Quality Control (QC) Criteria
 - QSM LCS Data (Appendix C Tables)

8330B Training Objectives

- Implementation of Department of Defense (DoD) Environmental Laboratory Accreditation Program (ELAP) requirements of QSM Version 5 (July 2013) for Environmental Protection Agency (EPA) Method 8330B.
 - **Appendix B Table 3**
- Remedial Project Managers (RPM's), contractors, labs, accrediting bodies, and end users.

Evolution of 8330

- EPA 8330- Published 1994
- EPA 8330A- Revision 1, Published February 2007
- EPA 8330B- Revision 2, Published October 2006
 - Appendix A- Collecting and Processing of Representative Samples For Energetic Residues In Solid Matrices From Military Training Ranges (Multi-Increment Sampling)
- **DoD Environmental Data Quality Workgroup (EDQW) Guide for Implementing 8330B - July 2008**
- **QSM Version 5 (July 2013)**
- **Frequently Asked Questions (FAQ's) November 2014**

Analytical Differences- 8330A to 8330B

➤ Differences:

- Additional analytes (Nitroglycerin, PETN, and 3,5-Dinitroaniline)
- Appendix A- Incremental Sampling Methodology (ISM)
- Subsample particle size and weight
- Final volume of extract
- Addition of shaker platform option
- Eliminate the addition of calcium chloride solution

EPA SW-846 METHOD 8330B

Additional Requirements

➤ Sample Preparation

- Drying
- Sieving
- Grinding
- Subsampling
- Extraction

This presentation will focus on the implementation of these 8330B changes

DoD QSM Version 5.0 Method Specific Requirements

- Appendix B, Table 3
- Appendix C, Tables 33, 34, 35, 36, and 37

EPA Method 8330B released in 2006
calls for drying and sieving
(10 mesh or 2 mm) entire sample →

**Drying and sieving should be performed
In the laboratory. NOT IN THE FIELD.**



← Entire portion < 2 mm subjected
to grinding, then subsampling is
conducted using ISM techniques in
the laboratory

Care for cross contamination

Soil Drying

- The Method Blank (MB) and samples
- The LCS is not required to be dried if the vendor of the solid matrix reference material used specifies for it not to be dried
- The matrix of the LCS and MB can be Ottawa sand, soil, or vendor supplied clean matrix

Soil Drying

- Procedure to determine when the sample is dry to constant mass
- Record the date, time, and ambient temperature on a daily basis while drying samples
- **Identification of chunk material greater than 2 mm in size**

Soil Drying

What bias can be introduced during this step?

- Negative bias due to temperature exceeding required range (room temperature or less) or the sample being exposed to direct sunlight during drying
- Negative bias due to incomplete drying of samples prior to grinding
- Negative bias due to volatilization of analytes (e.g., nitrobenzene, nitrotoluene isomers)

2008 EDQW Implementation Guide

- An LCS consisting of a purchased solid reference material, containing all reported analytes, must go through the grinding process and be analyzed with each batch

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.

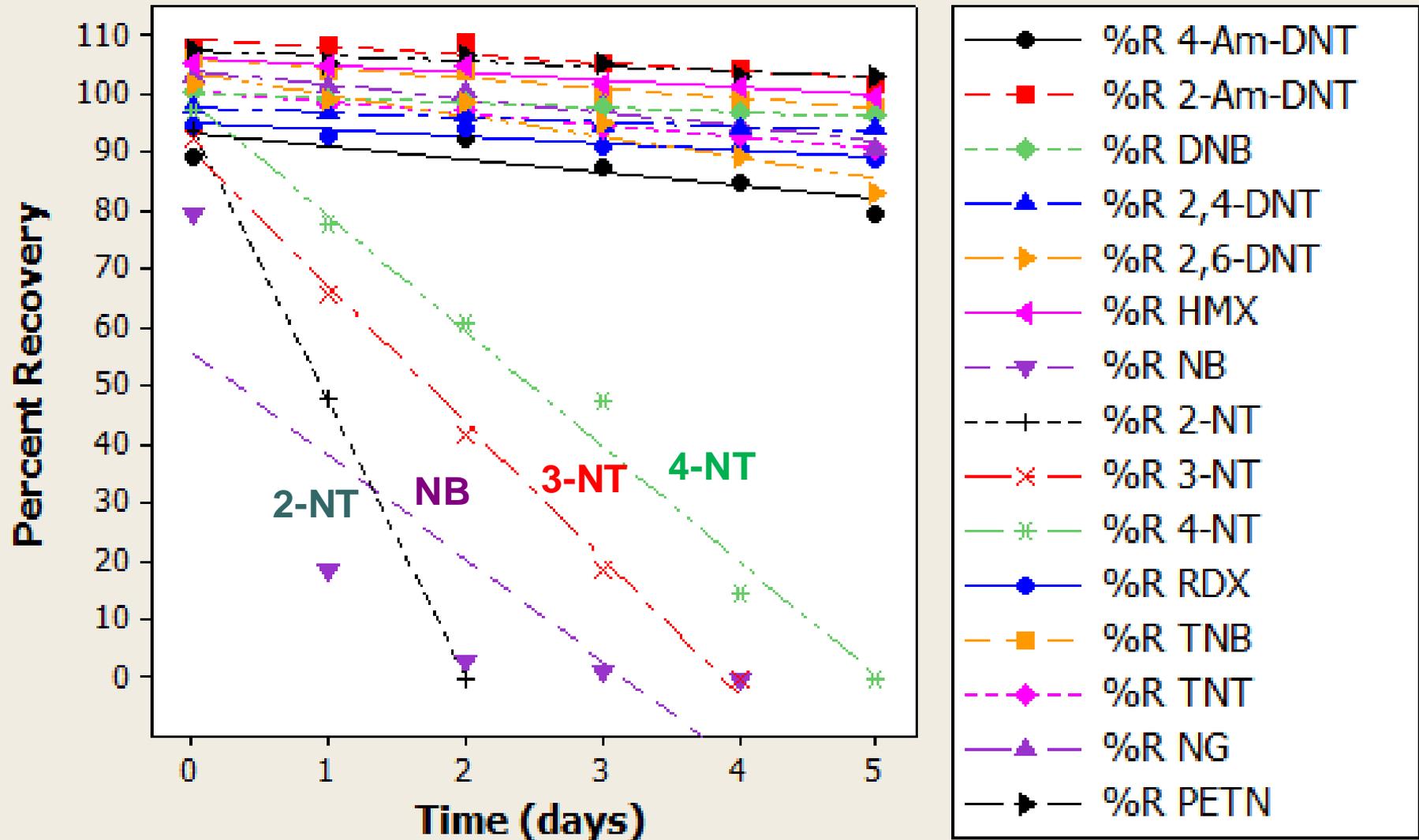
Scope:

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

Drying and Grinding Studies

- After 5 days of drying at room temperature, nitrobenzene and the nitrotoluene isomers volatilized producing 0% recoveries; the 11 remaining explosives were negatively biased by an average of $\approx 10\%$
- Concentrations of the unground LCS decreased about 2% on the average after only 30 min of drying.
- Increasing the grinding time from 90 sec to 240 sec. (4 60-sec cycles) decreased the recoveries of the 15 compounds by an average of 4% - 5%.
- The Purchased Reference Material that is used as an LCS should not be air dried but processed (e.g., ground) with the environmental samples that have been air dried
- Excessive grinding of the LCS should be avoided as this will negatively bias the results

Percent Recoveries of 15 Explosives vs. Time



Soil Sieving

➤ Each Sample, LCS, MB

- Weigh entire sample post drying
- Sieve entire sample with a 2-mm nominal opening (US Standard 10) mesh sieve
 - Break up pieces of soil with gloved hands
 - Do not intentionally include vegetation unless project specifies
 - Collect and weigh the portion that does not pass through the sieve

Soil Sieving

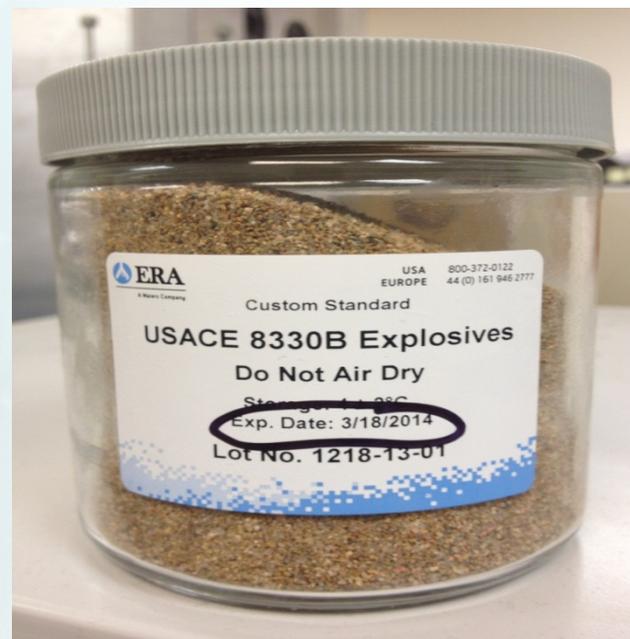
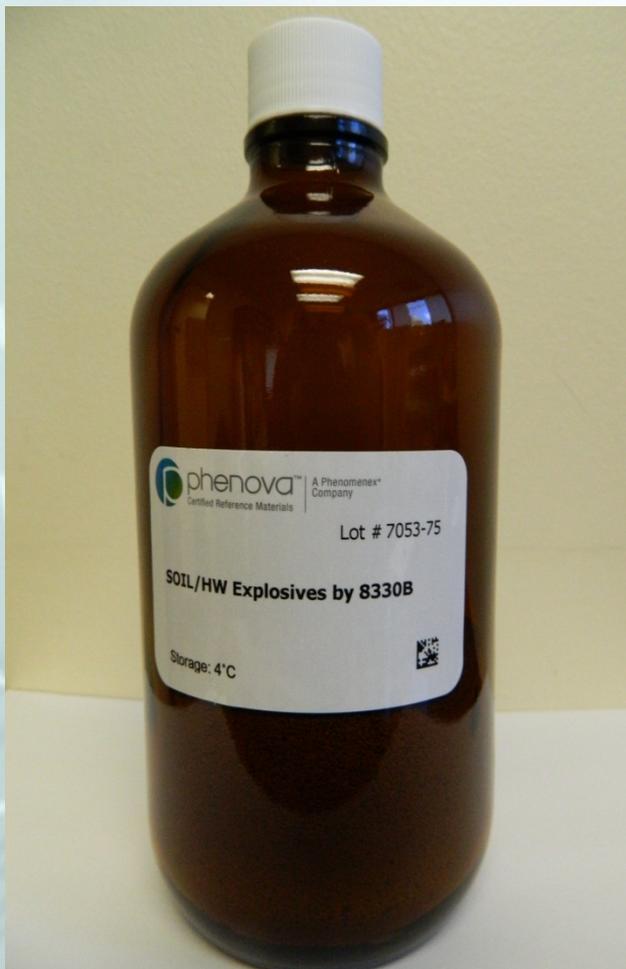
What bias can be introduced during this step?

- Positive bias due to inadequate sieve cleaning procedure or poorly ventilated/cleaned work area

There are standard reference materials available.

The material MUST be ground prior to extraction and analysis.

May not contain all project analytes which will have to be spiked.



Soil Grinding

➤ Initial Demonstration

- Demonstrate the grinding process used is capable of reducing the particle size to <75 μm by passing ground sample through a 200 mesh sieve

Note: This is a change from the previous Method 8330 which directs particle size reduction to 30 mesh (595 μm) and Grinding Blanks were not required

Soil Grinding

What kind of grinder is required?

- Any mode of grinding that reduces the particle size to <75 μm consistently over the range of types of samples received (gravel, sand, peat, soil) while meeting QSM Version 5.0 QC criteria
 - **Puck Mill is preferred as it allows reference material sub-sampling options for the LCS**

Soil Grinding

➤ Grinding Blank

- Clean solid matrix
- Frequency is prior to grinding samples, after every 10 samples, and at the end of the batch
- The order in which the samples and QC are ground must be documented

Soil Grinding

➤ Grinding Blank

- Prepared and analyzed in exactly the same way as samples (such as same grinding intervals)
- No analytes detected $> \frac{1}{2}$ Limit of Quantitation (LOQ)

Soil Grinding Blank

➤ Grinding Blank

- Can be prepared and analyzed individually or as a composite, however there are factors to consider if composited during subsampling:
 - Multiply the result by the number of individual grinding blanks combined to create the composited blank

Soil Grinding Blank

- If a composited blank fails criteria, the laboratory must re-subsample and analyze the grinding blanks individually, along with the MB and LCS to determine which samples could have been affected

Soil Grinding Blank

- If analysis of individual grinding blanks confirms the presence of contamination:
 - In the associated samples, apply B-Flag to the analytes which failed criteria in the grinding blank

Soil Grinding

What bias can be introduced during this step?

- Negative bias due to sample overheating during the grinding process
- Positive bias due to inadequate cleaning procedure for grinding apparatus

Soil Subsampling

- All samples and QC samples must be subsampled in same manner
 - Entire ground sample is mixed, spread out, and 30 or more randomly located increments are taken to total approximately 10 grams for each subsample
 - Added QC samples in this step are MS, MSD, and subsample triplicates

Soil Subsampling

How can you tell if the ground sample is homogenous?

➤ Subsampling Triplicate

- One per batch
- Cannot be done on any type of blank
- 3 separate 10 gram subsamples of one field sample

Soil Subsampling

- Client should identify to the laboratory the sample thought to have the highest analyte concentrations. If identified, the laboratory should use this sample for the triplicate
- Homogeneous if RSD of triplicate is $\leq 20\%$ for results $>LOQ$

Soil Subsampling

What does a triplicate failure indicate with regard to precision?

- If the RSD of the triplicate fails to meet criteria, the uncertainty of the results of the batch is greater than the method allows, per QSM Version 5.0

Soil Subsampling

- Client decides what corrective actions are needed for the batch when triplicate results fail:
 - Report with narration and flagging
 - Regrind, re-prepare, and reanalyze

Soil Extraction

- 10 gram subsamples are spiked with surrogate and matrix spikes are spiked prior to addition of acetonitrile (ACN)
- Samples should dry after addition of spikes and prior to addition of 20mL of ACN
- Vortex for 1 minute

Soil Extraction

- Place on platform shaker or in a cooled (<30°C) ultrasonic bath for 18 hours.
- Allow to settle for 30 minutes, at a minimum
- Remove 8.0 mL of supernatant and filter thorough a 0.45 um PTFE filter, discarding the first mL

Soil Extraction

What bias can be introduced during this step?

- Negative bias if the platform shaker is in a room where the temperature exceeds 30°C or the ultrasonic bath temperature exceeds 30°C.

QC Requirements

- Total QC requirements for soils (from drying to extraction):
 - One LCS
 - One Grinding Blank/Method Blank (if composited); three if grinding blanks analyzed separately
 - One subsample triplicate
 - One MS/ MSD pair

Aqueous Samples

- Solid phase extraction is the only extraction procedure allowed
- Uses a resin-based solid phase disk or cartridge
- All QC samples must go through the entire process in exactly the same manner as samples

Aqueous Sample

- Surrogates and matrix spikes are added to the original sample container, capped, and shaken or the sample is transferred to a graduated cylinder and spiked. This is done prior to the sample being introduced onto the disk or cartridge.
- Let stand for several minutes.

Aqueous Sample

- If sample contains a lot of particulates, the sample can be filtered after spikes are added.
- Refer to EPA SW-846 Method 3535 for specifics

QC Requirements

Total QC for aqueous samples:

- One MB
- One LCS
- One MS/MSD pair

Analytical Instrument Options

- High Performance Liquid Chromatograph (HPLC)
 - Requires confirmation analysis
 - UV detection using a column with different retention time order from the primary column
 - UV diode array detector not permitted for primary or confirmation analysis
- Liquid Chromatograph/Mass Spectrometer (LC/MS) or LC/MS/MS
 - No confirmation analysis required

Initial Calibration

- All target analytes and surrogates
- Minimum of 5 levels for linear and 6 for non-linear
- RSD for each analyte and surrogate $\leq 15\%$ or,
- Linear or non-linear least squares regression for each analyte and surrogate $r^2 \geq 0.99$

Note: If confirmation analysis is required, the same criteria applies to confirmation column

Initial Calibration Verification

- After each ICAL
- Second source standard used
- Prior to analysis of any batch QC or samples
- All target analytes and surrogates must be within $\pm 20\%$ of their true value
- Flagging is not an option

Note: If confirmation analysis is required, the same criteria applies to confirmation column

Continuing Calibration Verification

- Before sample analysis, after every 10 field samples, and at the end of the sequence
- All reported analytes and surrogates must be within $\pm 20\%$ of their true value

Note: If confirmation analysis is required, the same criteria applies to confirmation column

Continuing Calibration Verification

- Corrective actions
 - Recalibrate and reanalyze all affected samples, or
 - Immediately analyze two additional consecutive CCVs. If both pass, samples can be reported without flagging

Note: If confirmation analysis is required, the same criteria applies to confirmation analysis

Confirmation Analysis

- Confirm all positive results (greater than DL) in samples and QC
- Results between primary and secondary column RPD must be $\leq 40\%$. If not met, report in case narrative, flag and report from both columns
- Project defines which column to report from (e.g., lowest, highest, primary)

QC Criteria

➤ Method Blank (MB)

- One per preparation batch
- No analyte $> \frac{1}{2} \text{LOQ}$ or $> 1/10$ the amount measured in any sample or $1/10$ the regulatory limit, whichever is greater.
- Corrective action must be taken
- Narrate failure and flag data appropriately

QC Criteria

➤ LCS

- One per preparation batch
- Must use QSM Appendix C appropriate tables for batch control if project limits are not specified
 - Tables 33 and 34 for analysis by LC/MS or LC/MS/MS
 - Tables 36 and 37 for analysis by HPLC

QC Criteria

➤ MS/MSD

- One per preparation batch
- Use LCS Appendix C control limits as a basis for comparison
- MS/MSD RPD of all analytes $\leq 20\%$
 - Contact client if fails to determine next step
 - If required to report, flag failing analytes in the parent sample

Neutralization of Alkaline Hydrolysis Treated Soils for SW-8330B Analysis

Presenters

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Resources

- Please see the DENIX website where all of the FAQs regarding 8330B are located

http://www.denix.osd.mil/edqw/upload/FAQS-2014_final.docx

- Any questions generated by this training session can be sent through DENIX for a response

<http://www.denix.osd.mil/tools/page-mgt.cfm?reqID=contactUs&pageid=34754>