State Of Connecticut
Department of Environmental Protection

Recommended Reasonable Confidence Protocols

Quality Assurance and Quality Control Requirements

Chlorinated Herbicides by SW-846 Method 8151

Version 2.0
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Written by the Connecticut DEP QA/QC Workgroup

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1.0	First version for publication	7/05/2005
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1.0 QA/QC Requirements for Method 8151

1.1 Method Overview

Method 8151 is gas chromatography procedure used to determine chlorinated herbicides in a variety of matrices including waters, soils, sediments, wastes, etc. This procedure requires an experienced GC analyst familiar with the QA/QC requirements of the method. The sample introduction procedure requires the use of a solvent extraction followed by a derivitization procedure.

All method references are to the latest promulgated version of the method found in Test Methods for Evaluating Solid Waste, SW-846.

Because these compounds are produced and used in various forms (i.e., acid, salt, ester, etc.), Method 8151 utilizes a hydrolysis step to convert herbicide esters into the acid form prior to derivatization. This hydrolysis step is required to produce data of Reasonable Confidence. Herbicide esters generally have a half-life of less than one week in soil.

Open-tubular, capillary columns are employed with electron capture detectors (ECD). The target analytes may be determined with either a single- or dual-column chromatographic system. Second column confirmation is required for all herbicide analyses.

1.1.1 Reporting Limits for Method 8151

The reporting limit (RL) for a compound is dependent on the concentration of the lowest standard in the initial calibration, sample weight/volume, extraction procedure, and moisture content. The following table lists approximate reporting limits for various matrices utilizing a gas chromatograph with an electron capture detector (GC/ECD). Solid matrices in this table assume 100% solids.

Table 1.0 Typical Reporting Limits

Matrix	Typical Reporting Limit
Water	0.5 to 2.0 ug/L
Soil	5 to 80 ug/Kg

Moisture content of soils and sediments will raise the RL, as all results must be reported on a dry weight basis for these two matrices. Sample dilution or lower sample weight/volume will also cause the RL's to be raised.

Sample container type, preservation requirements, and holding times for waters, soils, and sediments are presented in Table 2A of this document.

1.1.2 General Quality Control Requirements

Each laboratory is required to operate a formal quality assurance program and be certified by the Connecticut Department of Public Health for the analysis performed. The minimum requirements include initial demonstration of laboratory proficiency, ongoing analysis of standards and blanks to confirm acceptable continuing performance, and analysis of laboratory control samples (LCS) to assess precision and accuracy. The use of site specific matrix spikes and matrix spike duplicates is highly recommended. Evaluation of sample matrix effects on compound recovery is key to making good decisions.

Laboratories must document and have on file an Initial Demonstration of Proficiency for each combination of sample preparation and determinative method being used. These data must meet or exceed the performance standards as presented in Section 1.5 and Table 1A. See Section 8.4 of Method 8000 in SW-846 for the procedure. The Initial Demonstration of Proficiency must include the following elements:

Table 1.1 IDOC Requirements

QC Element	Performance Criteria
Initial Calibration	Table 1A
Continuing Calibration	Table 1A
Method Blanks	Table 1A
Average Recovery	Table 1A
% Relative Standard Deviation	Table 1A
Surrogate Recovery	Table 1A
Internal Standards (Optional)	Table 1A

Note: Because of the extensive analyte list and number of QC elements associated with the Initial Demonstration of Proficiency, it should be expected that one or more analytes may not meet the performance standards for one or more QC elements. The laboratory should make every effort to find and correct the problem, and repeat the analysis. All non-conforming analytes along with the laboratory acceptance criteria should be noted in the Initial Demonstration of Proficiency data.

Laboratories are required to generate laboratory specific performance criteria for LCS compound recovery limits, matrix spike/matrix spike duplicate compound recovery and precision (RPD) limits, and surrogate recovery limits. These limits must meet or exceed the limits specified in Table 1A.

1.2 Summary of Method 8151

1.2.1 Sample Extraction and Cleanup

Samples for analysis by Method 8151 require extraction by one of the following methods. Laboratories must use the solvents listed in Method 8151 for extraction.

Matrix	Method
Aqueous	Separatory Funnel liquid-Liquid Extraction. See Section 7.3 of Method 8151.
Soil/Sediment	Sonication, Pressurized Fluid (Method 3545) or Shaker extraction, see Section 7.2 of Method 8151.
Waste	Method 3580, Waste Dilution, see Section 7.1 of Method 8151.
Extract Concentration	See Section 7.4 of Method 8151
Derivatization	See Section 7.5 of Method 8151

1.2.2 GC Analysis

The herbicides are extracted from the sample using the appropriate method. Water samples are extracted with diethyl ether and then esterified with either diazomethane or pentafluorobenzyl bromide. The derivatives are determined by gas chromatography with an electron capture detector (GC/ECD). The results are reported as acid equivalents.

Soil and waste samples are extracted and esterified with either diazomethane or pentafluorobenzyl bromide. The derivatives are determined by gas chromatography with an electron capture detector (GC/ECD). The results are reported as acid equivalents. Herbicide esters are required to be determined using this method, and hydrolysis conditions for the esters in water and soil extracts must be employed.

Preliminary identification of target analytes is accomplished by comparing the retention time of the chromatographic peaks of the sample to known herbicides analyzed under the exact same conditions. Confirmation is accomplished either by analysis of the same extract on a dissimiliar column, again comparing the retention times of the chromatographic peaks of the sample to known pesticides analyzed under the exact same conditions, or by using at least one other independent qualitative technique such as GC/MS. Quantitation is accomplished by constructing a calibration curve of herbicide concentration vs. peak area. Confirmation is not required in the case where herbicides are not detected above their specific reporting limit.

1.3 Method Interferences

1.3.1 Refer to SW-846 Methods 3500 (Sec. 3.0, in particular), 3600, and 8000 for a detailed discussion of interferences. Interferences co-extracted from the samples will vary considerably from matrix to matrix. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation.

1.3.2 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts or elevated baselines in gas chromatograms. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis, by analyzing reagent blanks.

1.3.2 Glassware must be scrupulously cleaned. Clean each piece of glassware as soon as possible after use by rinsing it with the last solvent used in it. This should be followed by detergent washing with hot water and rinses with tap water, then with organic-free reagent water. Glassware should be solvent-rinsed with acetone and pesticide-quality hexane. After rinsing and drying, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store glassware inverted or capped with aluminum foil. Immediately prior to use, glassware should be rinsed with the next solvent to be used.

1.3.3 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

1.3.4 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from waste to waste, depending upon the nature and diversity of the waste being sampled.

1.3.5 Organic acids, especially chlorinated acids, cause the most direct interference with the determination by methylation. Phenols, including chlorophenols, may also interfere with this procedure. The determination using pentafluorobenzylation is more sensitive, and more prone to interferences from the presence of organic acids or phenols than by methylation.

1.3.6 Alkaline hydrolysis and subsequent extraction of the basic solution removes many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis. However, hydrolysis may result in the loss of dinoseb and the formation of aldol condensation products if any residual acetone remains from the extraction of solids.

1.3.7 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware must be acid-rinsed and then rinsed to constant pH with organic-free reagent water. Sodium sulfate must be acidified.

1.3.8 Sample extracts should be dry prior to methylation or else poor recoveries will be obtained.

1.4 Quality Control Requirements for SW-846 Method 8151

1.4.1 General Quality Control Requirements for Determinative Chromatography Methods

Refer to SW-846 Method 8000 for general quality control requirements for all chromatographic methods, including SW-846 Method 8151. These requirements insure that each laboratory maintain a formal quality assurance program and records to document the quality of all chromatographic data. Quality Control procedures necessary to evaluate the GC system operation may be found in SW-846 Method 8000, Section 7.0, and include evaluation of retention time windows, initial and verification of instrument calibrations and chromatographic performance of sample analyses. Instrument quality control and method performance requirements for the GC system may be found in SW-846 Method 8151, Sections 8.0 and 9.0, respectively.

1.4.2 Specific QA/QC Requirements and Performance Standards for SW-846 Method 8151

Specific QA/QC requirements and performance standards for SW-846 Method 8151 are presented in Table 1A. Strict compliance with the QA/QC requirements and performance standards for this method, as well as satisfying other analytical and reporting requirements will provide the environmental professional ("EP") with "Reasonable Confidence" regarding the usability of analytical data to support DEP decisions.

While optional, parties electing to utilize these protocols will be assured that agency reviewers will generally accept "Reasonable Confidence" data. In order to achieve "Reasonable Confidence" parties must:

1. Comply with the applicable QC analytical requirements prescribed in Table 1A for this test procedure;

2. Evaluate and narrate, as necessary, compliance with performance standards prescribed in Table 1A for this test method; and

3. Adopt the reporting formats and elements specified in Section 1.7 of this method.

1.4.3 Site Specific Matrix Spike (MS), Matrix Spike Duplicate (MSD) Samples

It is strongly recommended that site specific MS/MSD samples be analyzed from each site, and each matrix type sampled. Percent recovery data from site specific samples allow the EP to make informed decisions regarding contamination levels at the site. Batch MS/MSD results do not give any indication of site specific matrix interferences or analytical problems related to the specific site matrices and are in general discouraged. Non-site specific MS/MSD's should not be reported for the RCP's. Additionally trip blanks, field blanks, rinsate blanks, etc. should not be used for MS/MSD's.

1.4.4 Special Analytical Considerations for Herbicides

Because of the variable solubility, extraction efficiency and analytical sensitivity of the different compounds that are potentially analyzable by SW-846 Method 8151, the recovery ranges presented in Table 1A for laboratory control samples, matrix spikes, and surrogates should be considered general upper/lower acceptance limits. It is essential that laboratory-specific performance criteria for LCS and surrogate recoveries also be calculated and documented as described in SW-846 Method 8000B, Section 8.7. When experience indicates that the criteria recommended in specific methods are frequently not met for some analytes and/or matrices, the in-house performance criteria will be a means of documenting these repeated exceedances. Laboratories are encouraged to actively monitor pertinent quality control performance standards described in Table 1A to assess analytical trends (i.e., systematic bias, etc) and improve overall method performance by preempting potential non-conformances.

Table 1A Specific QA/QC Requirements and Performance Standards for Method 8151*

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Retention Time Windows	Accurate identification of Herbicides	1) Prior to or during the initial calibration when a new column is installed. 2) Calculate according to Method 8000, Section 7.6.	NO	N/A	N/A
Initial Calibration	Laboratory Analytical Accuracy	1) Minimum of 5 standards. (Note 1) 2) Low std at or below reporting limit 3) % RSD must be ≤20% or if linear regression used "r" ≥ 0.990 4) If curves are used, curve must NOT be forced through origin. 5) Curves must be verified with independent ICV prior to sample analysis. 6) All stds must be derivatized using the same procedure used for samples, whether prepared in laboratory or purchased from a vendor.	NO	Recalibrate as required by the method.	Sample analysis cannot proceed without a valid initial calibration. Report non-conforming compounds in narrative. If avg RF/CF or linear regression not used (e.g. quadratic equation), must note list of affected compounds in narrative
Continuing Calibration (CCAL)	Laboratory Analytical Accuracy	1) Prior to samples, every 12-hours or 10 samples, whichever is more frequent, and at the end of the analytical sequence. 2) Concentration near mid-point of curve. 3) Percent difference or drift ≤15%. 4) Verify all analytes fall in retention time windows. 5) All stds must be derivatized using the same procedure used for samples, whether prepared in laboratory or purchased from a vendor.	NO	1)Perform instrument maintenance, reanalyze CCAL and/or recalibrate. 2) Reanalyze associated samples if beginning or closing CCAL exhibited low response and associated herbicides not detected in samples. 3) Reanalyze associated samples if beginning or closing CCAL high and associated herbicides were detected in samples.	Report exceedances in narrative. Note: Associated samples means all samples analyzed since the last acceptable CCAL.

Table 1A Specific QA/QC Requirements and Performance Standards for Method 8151* (continued)

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Method Blanks	Laboratory Contamination Evaluation	1) Extracted every 20 samples or every batch, whichever is greater. 2) Matrix specific 3) Target analytes must be <RL	YES	Locate source of contamination and correct problem. Reanalyze method blank. Re-extract samples if method blank contaminated	1) Report non-conformances in case narrative. 2) All results for compounds present in method blank above RL must be "B" flagged if detected in samples associated with the method blank. 3) If re-extraction performed within holding time, report only compliant data. If re-extraction performed outside holding time report all data.

Table 1A Specific QA/QC Requirements and Performance Standards for Method 8151* (continued)

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Laboratory Control Sample (LCS)	Laboratory Method Accuracy	1) Every 20 samples or each batch, whichever is more frequent. 2) Standard source different from initial calibration source. 3) Concentration level should be near or at the mid-point of the initial calibration. 4) Matrix specific. 5) Laboratory determined percent recovery limits must be between 40-140% . 6) Labs expected to develop own in-house control limits that meet or exceed limits listed above.	YES	Recalculate the percent recoveries Reanalyze the LCS If MS/MSD in same batch compare to determine if problem isolated to LCS Re-extract LCS and samples if compounds outside acceptance criteria and no MS/MSD with acceptable criteria Locate & correct problem, reanalyze associated samples	1) Report non-conformances in case narrative. 2) Individual laboratories must identify and document problem analytes that routinely fall outside the limits. Any exceedances must be noted in narrative. Data to support laboratory problem compounds kept on file at lab for review during audit 3) If re-extraction performed within holding time, report only compliant data. If re-extraction performed outside holding time report all data.

Table 1A Specific QA/QC Requirements and Performance Standards for Method 8151* (continued)

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Site Specific Matrix Spike/Matrix Spike Duplicate	Precision and Accuracy in Sample Matrix	1) Every 20 samples per matrix* 2) Spike concentration in lower half of calibration curve. 3) Must contain all analytes. 4) Laboratory determined percent recovery limits must be between 30-150% 5) RPD's ≤ 30%	Yes* (*If analyzed)	If compounds out compare to LCS; if LCS recoveries in note in narrative; if LCS compounds out note in narrative probable lab error	Note outliers in narrative
Surrogates	Accuracy in Sample Matrix	1) Minimum 1 compound across retention times of GC run and does not interfere with target analytes. Recommended compound DCAA. 2) Recovery limits lab generated and within 30-150% for both compounds on both columns. 3) Labs must develop own in-house limits that fall within 30-150% limits. 4) If surrogate exceeds limits on one column and greater then RL herbicide concentrations are not comparable (RPD>40%), re-extract and reanalyze samples.	Yes	If the surrogate outside limits on both columns, re-extract sample. If surrogates outside limits on one column only, and sample herbicide conc. Are <RL, note in narrative. If surrogate diluted out below lowest calibration std, no recovery criteria. If surrogate recovery outside on one column only, and RPD comparable (<40%), note in narrative.	1) Note exceedances in narrative. 2) If re-extraction or reanalysis confirms matrix interference or if re-extraction outside holding times report all results. 3) If re-extraction or reanalysis results in criteria and in holding time, report only compliant data.

Table 1A Specific QA/QC Requirements and Performance Standards for Method 8151* (continued)

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Identification and Quantitation	Inter-laboratory Consistency	1) Laboratory should use the average calibration factor of analyte for quantitation. 2) Second column analysis: Laboratory must utilize a second dissimiliar column to confirm all positive results above the RL. Report the higher of the two analyses unless obvious interference, in which case report lower result.. The QA/QC parameters in this document must be met for both columns. 3) If calibration stds are prepared using methyl esters, the calculation of concentration must include a correction for the weight of the methyl ester vs. the acid herbicide.	N/A	N/A	1) If the RPD between the results for the two columns exceeds 40%, the laboratory must flag the results with a "P" suffix and note in narrative. 2) If avg Rf or linear regression not used (e.g. quadratic equation), must note list of affected compounds in narrative. Note: If a high RPD between the two columns can be definitely attributed to a matrix interference, report the lower value and note in the narrative with an explanation.

Table 1A Specific QA/QC Requirements and Performance Standards for Method 8151* (continued)

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
General Reporting Issues	N/A	1) The laboratory should report only concentrations detected above the sample specific RL. 2) Concentrations below the reporting limit (RL) should be reported as "ND" with the sample specific RL also reported 3) Dilutions: If diluted and undiluted analyses are performed, the laboratory should report results for both sets of data. Compounds that exceed the linear range should be flagged ("E" flag). Do not report more than 2 sets of data per sample. 4) If a dilution is performed, the highest detected analyte must be in the upper 60% of the calibration curve, unless there are non-target analytes whose concentrations are so high as to cause damage to the instrumentation	N/A	N/A	Performance of dilutions must be documented in the case narrative

Notes for Table 1A

* Refers to latest published version of SW-846 Method 8151.
GC/MS = Gas Chromatography/Mass Spectrometry
CCC = Calibration Check Compound
%RSD = Relative Percent Standard Deviation
RF = Response Factor
r = Correlation Coefficient
RPD = Relative Percent Difference
CF = Calibration Factor
N/A = Not Applicable

Note 1: Six standards are required for a quadratic equation calibration curve, and seven are required for a polynomial fit. In either case the correlation coefficient must be ≥ 0.990.

1.5 Analyte List for SW-846 Method 8151

The Connecticut DEP (DEP) analyte list for SW-846 Method 8151 is presented in Table 1B. The compounds listed are readily determined by Method 8151.

1.5.1 Additional Reporting Requirements for SW-846 Method 8151

While it is not necessary to request and report all the analytes listed in Table 1B to obtain Reasonable Confidence status, it is necessary to document such a limitation, for site characterization and data representativeness considerations. DEP strongly recommends that full list of analytes be reported during the initial stages of a site investigation and/or at sites with an unknown or complicated history of chemical usage or storage.

In cases where a shortened list of analytes is selected, the laboratory must still meet the method specific quality control requirements and performance standards associated with the requested analytes list to obtain Reasonable Confidence.

The Reporting Limit (RL) is based upon the lowest standard in the initial calibration. It is the responsibility of the EP to specify to the laboratory the detection limits required for the samples. In order to meet the detection limits it may be necessary to modify the analytical method by using increased sample volume or mass or other techniques. In such cases the modifications must be noted in the narrative.

1.6 Routine Reporting Deliverables for Method 8151

The following table (Table 1.2) lists the routine report deliverables. Note that while laboratories are not required to report certain items, they must keep the data on file and may be required to report all items in special circumstances.

1.6.1 Reporting and Flagging of Results

The following rules apply to reporting results:

Non-Detects: Report all non-detects and results below the reporting limit as “ND” (Not Detected at the specified Reporting Limit). The reporting limit for each compound in each sample must be listed on the report and take into account the exact sample mass, any dilution factors, percent moisture, etc.

Compounds detected above the reporting limit in blanks and found in samples, also above the reporting limit, shall be flagged with a "B" suffix (e.g. 25B).

All soil/sediment results shall be reported on a dry weight basis.

Table 1.2 Report Deliverables

PARAMETER	DELIVERABLE	COMMENTS
Retention Time Windows	NO	
Initial Calibration	NO	Note non-conformances in narrative
Continuing Calibration	NO	Note non-conformances in narrative
Method Blanks	YES	Note non-conformances in narrative. Flag all positive sample results above RL with "B" flag.
Lab Control Sample (LCS)	YES	Note non-conformances in narrative
Site Specific Matrix Spike/ Matrix Spike Duplicate	YES (If requested)	Note non-conformances in narrative
Surrogate Recoveries	YES	Note non-conformances in narrative
General Reporting Issues	YES	Note non-conformances in narrative
QA/QC Certification Form	YES	Signed by laboratory director or his/her designee.

Table 1B Analyte List For SW-846 Method 8151

ANALYTE	CAS NUMBER	NOTES
2,4-D	94757	
2,4,5-TP (Silvex)	93721	
2,4,5-T	93765	
Dicamba	1918009	
Dalapon	75990	

Table 2A Sample Containers, Preservation, and Holding Times

MATRIX	CONTAINER	PRESERVATIVE	HOLDING TIME
Aqueous with no chlorine present	1-liter amber glass bottle with Teflon line cap	Store at 4 ± 2º C.	7 days to extraction. 40 days from extraction to analysis.
Aqueous with chlorine present	(1-liter amber glass bottle with Teflon line cap	Neutralize chlorine with sodium thiosulfate. Store at 4 ± 2º C.	7 days to extraction. 40 days from extraction to analysis.
Soil/Sediment samples.	250 mL amber glass jar with Teflon lined cap.	Cool to 4 ± 2º C	14 days to extraction. 40 days from extraction to analysis. Up to one year for samples frozen within 48 hours of collection. (Note 1)
High Concentration Waste Samples	Collect in amber glass jar with Teflon lined cap.	Cool 4 ± 2º C.	14 days to extraction. 40 days from extraction to analysis.

Notes:
The number of containers is optional. Additional containers may be collected in case of breakage or if reanalysis necessary.

Note 1: If the freezing option is selected, the sample must be frozen within 48 hours of collection. The holding time recommences when thawing begins. The total holding time is calculated from the time of collection to freezing plus the time allowed for thawing. The total elapsed time must be less than 14 days.